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**Modyfikacja właściwości fizycznych chiralnej matrycy
ciekłokrystalicznej poprzez domieszkowanie nanocząstkami**

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Rozprawa napisana pod kierunkiem **prof. dr hab. Moniki Marzec**

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Oświadczenie

Ja niżej podpisany Sebastian Lalik (nr indeksu: 1053193) doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. „*Modyfikacja właściwości fizycznych chiralnej matrycy ciekłokrystalicznej poprzez domieszkowanie nanocząstkami*” jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem prof. dr hab. Moniki Marzec. Pracę napisałem samodzielnie.

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Jestem świadomy, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

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Podziękowania

Serdeczne podziękowania składam wszystkim Osobom, które w mniejszym lub większym stopniu przyczyniły się do powstania niniejszej rozprawy.

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Artykuł II. S. Lalik, A. Deptuch, T. Jaworska-Gołąb, P. Fryń, D. Dardas, O. Stefańczyk, M. Urbańska, M. Marzec, Modification of AFLC Physical Properties by Doping with BaTiO₃ Particles, *Journal of Physical Chemistry B* 124(28), 6055-6073, 2020. DOI: 10.1021/acs.jpcc.0c02401.

Artykuł III. S. Lalik, O. Stefańczyk, D. Dardas, N. Górską, S. Ohkoshi, M. Marzec, Modifications of FLC Physical Properties through Doping with Fe₂O₃ Nanoparticles (Part I), *Materials* 14(16), 2021. DOI:10.3390/ma14164722.

Artykuł IV. S. Lalik, O. Stefańczyk, N. Górską, K. Kumar, S. Ohkoshi, M. Marzec, Modifications of EHPDB Physical Properties through Doping with Fe₂O₃ Nanoparticles (Part II), *International Journal of Molecular Sciences* 23(1), 2022. DOI: 10.3390/ijms23010050.

Artykuł V. S. Lalik, O. Stefańczyk, D. Dardas, A. Deptuch, T. Yevchenko, S. Ohkoshi, M. Marzec, Nanocomposites Based on Antiferroelectric Liquid Crystal (S)-MHPOBC Doping with Au Nanoparticles, *Molecules* 27(12), 2022. DOI: 10.3390/molecules27123663.

Osobisty wkład autora do publikacji

Artykuł I: Autor wykonał pomiary metodami POM, DSC, FDDS, EOM; brał czynny udział przy przeprowadzaniu pomiarów XRD; opracował wszystkie dane eksperymentalne, dokonał ich analizy i interpretacji; przeprowadził studium literaturowe; napisał pełny manuskrypt oraz brał czynny udział w odpowiedziach na pytania recenzentów. Wkład autora został określony przez współautorów na 70%.

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3. P. Fryń, **S. Lalik**, N. Górską, A. Iwan, M. Marzec, Comparison of the Dielectric Properties of Ecoflex® with L,D-Poly(Lactic Acid) or Polycaprolactone in the Presence of SWCN or 5CB, *Materials* 14(7), 2021. DOI: 10.3390/ma14071719.
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1. Streszczenie/Abstract

W niniejszej pracy określono wpływ małych koncentracji (do 1% wag.) wybranych submikrocząstek oraz nanocząstek na właściwości fizyczne organicznych związków małocząsteczkowych, wykazujących ciekłokrystaliczne chiralne fazy smektyczne. Po raz pierwszy zaprezentowano wpływ domieszkowania na właściwości antyferroelektrycznej fazy SmC^*_A , stosując dwa typy materiałów: ferroelektryczne submikrocząstki i nanocząstki tytanianu baru (45 i 280nm) oraz nanocząstki złota (2-4nm) o właściwościach plazmonicznych. Pokazano także wpływ kilku koncentracji ferromagnetycznych nanocząstek maghemitu (< 50nm) oraz wpływ kwasu oleinowego (czynnik dekorującego) na właściwości ferroelektrycznej fazy SmC^* . Jako matryce organiczne zastosowano zarówno materiały komercyjnie dostępne jak i nowo zsyntezowane. Przygotowano oraz przebadano cztery matryce ciekłokrystaliczne (w tym jedna mieszanina dwuskładnikowa), osiem kompozytów dwuskładnikowych oraz jeden kompozyt trójskładnikowy. W celu sprawdzenia wpływu domieszkowania na właściwości związków wykazujących fazy SmC^* i/lub SmC^*_A wykonano porównawcze badania kompozytów i matryc metodami komplementarnymi, do których należą metody elektro-optyczne, magnetyczne, mikroskopowe, spektroskopowe, strukturalne oraz termo-optyczne. Motywacją do realizacji badań było wypełnienie luki badawczej w zakresie szczegółowej analizy wpływu nanocząstek na właściwości ciekłokrystalicznej antyferroelektrycznej fazy SmC^*_A . Otrzymane wyniki badań poszerzają znacząco zakres wiedzy w obszarze wpływu domieszkowania na właściwości ciekłokrystalicznych chiralnych faz smektycznych.

In the frame of thesis, the influence of small concentrations (up to 1%wt.) of selected submicroparticles and nanoparticles on the physical properties of low molecular weight organic compounds exhibiting chiral liquid crystalline smectic phases was determined. For the first time, the effect of doping on the properties of the antiferroelectric SmC^*_A phase was presented, by using two type of materials: ferroelectric submicroparticles and nanoparticles of barium titanate (45 and 280nm) and gold nanoparticles (2-4nm) with plasmonic properties. The influence of several concentrations of ferromagnetic maghemite nanoparticles (<50nm) and the influence of oleic acid (decorating factor) on the properties of the ferroelectric SmC^* phase were also shown. Both commercially available and newly synthesized materials were used as organic matrices. Four liquid crystalline matrices (including one two-component mixture), eight two-component composites and one three-component composite were prepared and studied. In order to verify the effect of doping on the properties of compounds exhibiting SmC^* and/or SmC^*_A phases, comparative studies of composites and matrices were performed using complementary methods, including electro-optic, magnetic, microscopic, spectroscopic, structural and thermo-optical methods. The motivation for the research was to fill the research gap in the field of detailed analysis of the nanoparticles influence on the properties of the liquid crystalline antiferroelectric SmC^*_A phase. The obtained research results significantly broaden the scope of knowledge in the area of the influence of doping on the properties of chiral liquid crystalline smectic phases.

2. Wstęp

Nieprzerwalny rozwój różnych gałęzi przemysłu stanowi siłę napędową do poszukiwania nowych materiałów, które wykazywałyby określone/dobrze sprecyzowane właściwości dla danego typu zastosowania. Taki wymóg dotyczy różnych klas materiałów, wliczając w to także materiały organiczne, w tym ciekłe kryształy. Chociaż od odkrycia stanu ciekłokrystalicznego (mezofazy) upłynęło prawie 140 lat i materiały te znalazły wiele zastosowań, to chemicy po dziś dzień projektują nowe związki, coraz bardziej złożone, podstawiając niektóre atomy lub ich ugrupowania innymi oraz łącząc związki w wieloskładnikowe mieszaniny. Ma to na celu wytworzenie materiału o ściśle określonych właściwościach. Jednak taki sposób jest zwykle wieloetapowy, kosztowny oraz czasochłonny, wymagający specjalistycznych laboratoriów do syntezy oraz bardzo szczegółowej wiedzy z zakresu chemii organicznej.

Alternatywnym podejściem do projektowania nowych materiałów, dostosowanych do potrzeb danego zastosowania jest proces domieszkowania związków/mieszanin wykazujących fazy ciekłokrystaliczne, które są komercyjnie dostępne. W zdecydowanej większości przypadków w zastosowaniach przemysłowych materiały wykazujące mezofazy są stosowane w postaci cienkich warstw (rzędu kilku, kilkunastu mikrometrów). Dlatego do procesu domieszkowania ciekłych kryształów używa się małe koncentracje materiałów o rozmiarach podobnych do molekuł organicznych. Zastosowanie domieszki o rozmiarach znacznie większych od molekuly ciekłokrystalicznej (w postaci dużych ziaren) utrudni wytworzenie cienkiej warstwy (np. przez dużą chropowatość powierzchni) a dla domieszki o dużym przewodnictwie elektrycznym może dojść do uformowania ścieżek perkolacji. Z kolei duża koncentracja domieszki skutkować będzie silnym procesem aglomeracji, zaburzeniem porządku orientacyjnego i pozycyjnego molekuł matrycy ciekłokrystalicznej i finalnie spowoduje degradację właściwości ciekłokrystalicznych. Dlatego do procesu domieszkowania najlepszymi kandydatami są nanomateriały (nanocząstki, nanodruły, kropki kwantowe) o koncentracjach do 1-2% wag.. Ważna jest także czystość chemiczna wytwarzanego kompozytu, gdyż wszelkie zanieczyszczenia, w postaci nieprzereagowanych półproduktów czy obcych wtrąceń, mogą w niekontrolowany sposób wpływać na parametry wyjściowego kompozytu. Szybki rozwój nanotechnologii na przestrzeni ostatnich kilku lat otwiera bardzo duże możliwości dla wyboru domieszki nie tylko w postaci pierwiastków, ale także związków chemicznych w skali nanometrycznej. Dobrze opanowane syntezy nanomaterialów dają także możliwość doboru domieszki różnych rozmiarów i kształtów. Z ekonomicznego punktu widzenia nanomateriały są powszechnie dostępne oraz wyraźnie tańsze niż związki ciekłokrystaliczne.

Zainteresowanie zagadnieniem domieszkowania ciekłych kryształów trwa od około 15 lat, ale głównie jest ukierunkowane na modyfikację parametrów fazy nematycznej, ponieważ to właśnie nematyki znalazły, jak na razie, największe zastosowanie na rynku (dobrze znane wszystkim wyświetlacze ciekłokrystaliczne, z ang. LCD). Z punktu widzenia molekularnego nematyki wykazują jedynie porządek orientacyjny bez samoorganizacji w układy warstwowe, jak ma to miejsce w fazach smektycznych. Do chwili obecnej ukazała się bardzo ograniczona liczba artykułów naukowych, gdzie podejmowano próby domieszkowania prętopodobnych związków wykazujących fazy inne niż nematyczna, jednakże ograniczając się zasadniczo do paraelektrycznej ortogonalnej fazy SmA^* oraz ferroelektrycznej pochylonej fazy SmC^* . Faza antyferroelektryczna SmC_A^* oraz fazy cechujące się większym uporządkowaniem (np. porządkiem pozycyjnym krótkiego/długiego zasięgu środków ciężkości molekuł w obszarze warstw, np. SmB , SmI , SmF , SmJ , SmG), wedle mojej wiedzy, nie były przedmiotem badań w kontekście domieszek nanomaterialami.

Bazując na powyższym, postanowiłem w ramach rozprawy doktorskiej zsyntezować kilka nanokompozytów na bazie materiałów wykazujących antyferroelektryczną fazę SmC_A^* i/lub ferroelektryczną fazę SmC^* . Jako domieszki wybrałem trzy rodzaje nanomaterialów: ferroelektryczne

nanocząstki oraz submikrocząstki tytanianu baru BaTiO_3 , ferromagnetyczne nanocząstki maghemitu $\gamma\text{-Fe}_2\text{O}_3$ oraz dekorowane nanocząstki złota Au o właściwościach plazmonicznych. Nanocząstkami $\gamma\text{-Fe}_2\text{O}_3$ i Au domieszkowano komercyjnie dostępne związki, odpowiednio EHPDB¹ wykazujący ferroelektryczną fazę SmC^* i (S)-MHPOBC² wykazujący antyferroelektryczną fazę SmC^*_A . W obu związkach fazy helikoidalne (SmC^* oraz SmC^*_A) występują w szerokim zakresie temperatur, ponadto cechują się one bogatym polimorfizmem, obejmującym m.in. fazy N^* , SmA^* , SmC^*_α , SmC^*_γ czy SmI^* . Z tego względu badania modyfikacji właściwości matrycy ciekłokrystalicznej po domieszkowaniu rozszerzono na wszystkie wymienione fazy. Z kolei domieszkę BaTiO_3 zastosowano do matrycy będącej mieszaniną dwuskładnikową niekomercyjnych, nowo zsyntezowanych związków z szeregu homologicznego $\text{nFmX}_1\text{PhX}_2$ ^{3,4}. Wyniki przeprowadzonych badań są zebrane w formie pięciu artykułów naukowych (trzy z nich zawierają informacje uzupełniające, tzw. *Supplementary Information*) opublikowanych w recenzowanych czasopismach z listy JCR i wysoko punktowanych na Liście Czasopism Ministerialnych. Artykuły prezentują wyniki z szerokiego spektrum badań podstawowych, obejmującego pomiary elektro-optyczne, magnetyczne, mikroskopowe, spektroskopowe, strukturalne, termiczne oraz termo-optyczne.

Niniejsza dysertacja została podzielona na następujące sekcje: streszczenie, wstęp, charakterystyka wybranych faz ciekłokrystalicznych, metody badawcze, omówienie wyników badań, podsumowanie, literatura i kopie artykułów będących podstawą rozprawy.

¹ 4-[(S,S)-2,3-epoksyheksyloksy]fenyl 4-(decyloksy)benzoetan.

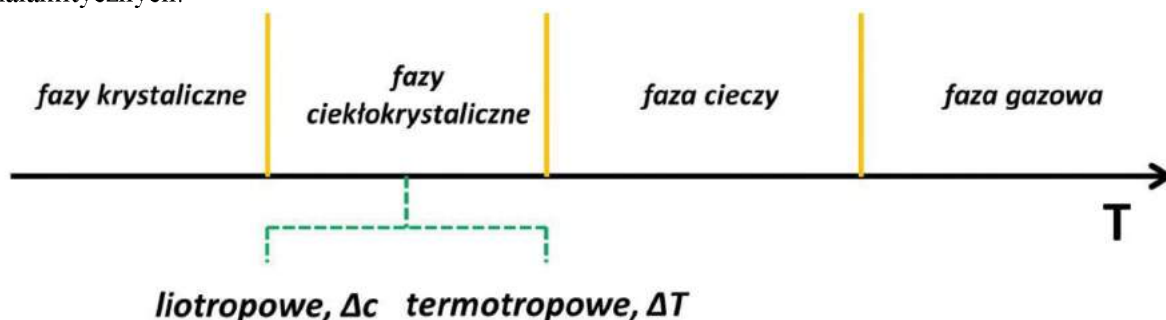
² (S)-4-[(1-metyloheptyloksy)karbonylo]fenyl 4'-oktyloksy-4-bifenylkarboksylan.

³ (S)-4'-(1-metyloheptyloksykarbonylo)bifenyl-4-ilu 4-[5-(2,2,3,3,4,4,4-heptafluorobutoksy)pentyl-1-oksy]-2-fluorobenzoetan.

⁴ (S)-4'-(1-metyloheptyloksykarbonylo)bifenyl-4-ilu 4-[7-(2,2,3,3,4,4,4-heptafluorobutoksy)heptyl-1-oksy]-1-fluorobenzoetan.

3. Charakterystyka wybranych faz ciekłokrystalicznych

Stan ciekłokrystaliczny jest ułożony między fazą kryształu (uporządkowanie 3D) i cieczą izotropową (Rys. 1). Ciekłe kryształy wykazują częściowe uporządkowanie i są podzielone na dwie kategorie: termotropowe i liotropowe [1]. Pierwsza grupa jest obserwowana pod wpływem zmian temperatury, z kolei druga jest formowana w obecności rozpuszczalnika (dodatkową zmienną jest koncentracja). Ze względu na kształt molekuł, termotropowa kategoria dzieli się na następujące grupy: kalamityczne (molekuły prętopodobne), dyskotyczne (molekuły w kształcie dysku), sanidyczne (molekuły kształtem przypominające cegielki) i banano-podobne. Ze względu na przedmiot rozprawy, w dalszej części omawiane są tylko właściwości termotropowych ciekłych kryształów o molekułach kalamitycznych.



Rys. 1 Umieszczenie faz ciekłokrystalicznych w obrębie ogólnego schematu powszechnie znanych stanów materii. Wyróżnia się dwie podstawowe grupy ciekłych kryształów: liotropowe (które formują się, jako funkcja koncentracji w obecności rozpuszczalnika) i termotropowe (które formują się w wyniku zmiany temperatury).

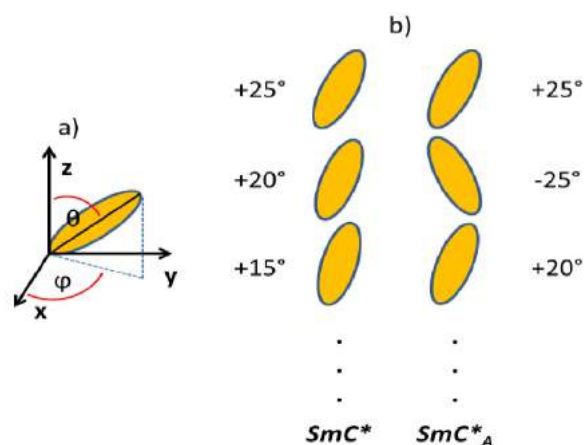
Wspólną cechą strukturalną molekuł prętopodobnych jest względnie sztywny rdzeń (często zawierający grupy fenyłowe i bifenylowe) oraz dwie elastyczne grupy końcowe (często alkilowe lub alkoksylowe łańcuchy). Ogólny podział faz ciekłokrystalicznych dla molekuł prętopodobnych, pochodzi od Friedel'a, ale został na przestrzeni lat rozwinięty (zwłaszcza rodzina faz smektycznych). Zasadniczo fazy smektyczne były nazywane w porządku alfabetycznym w miarę odkrywania kolejnych faz, a wraz z odkrywaniem pod-faz np. fazy SmC^* , zaczęto dodawać indeks dolny na ich rozróżnienie np. SmC^*_{α} , SmC^*_{β} , SmC^*_{γ} . Jeżeli molekuły organiczne są chiralne to do oznaczenia fazy stosuje się gwiazdkę, np. SmA^* . Ponieważ obiektem rozprawy są materiały chiralne wykazujące fazy warstwowe (SmC^* , SmC^*_A), dalsza część poświęcona jest przedstawieniu cech charakterystycznych tylko takich materiałów/faz [1]. Według powszechnie obowiązującej nomenklatury, w materiałach ciekłokrystalicznych zbudowanych z molekuł chiralnych, mogą pojawić się, wraz ze wzrostem temperatury, następujące fazy:

- ✓ Fazy krystaliczne (Cr_1 , Cr_2 ...),
- ✓ Fazy „miękkich kryształów” (SmE^* , SmG^* , SmH^* , SmJ^* , SmK^*),
- ✓ Fazy smektyczne (SmA^* , SmB^* , SmC^* , SmC^*_A , SmI^* , SmF^*),
- ✓ Pod-fazy typu SmC^* (SmC^*_{α} , $SmC^*_{1/3}$, $SmC^*_{1/4}$),
- ✓ Fazy typu „twist grain boundary” ($TGBA^*$, $TGBC^*$),
- ✓ Faza chiralnego nematyka (N^*),
- ✓ Fazy niebieskie (BPI^* , $BPII^*$, $BPIII^*$),
- ✓ Faza cieczy izotropowej (Iso).

Wraz z obniżaniem temperatury związki chiralne wykazujące fazy ciekłokrystaliczne poniżej fazy cieczy izotropowej mogą wykazywać fazę nematyczną chiralną (tzw. cholesteryk), a z dalszym obniżaniem temperatury pojawiają się fazy smektyczne wykazujące dodatkowe cechy uporządkowania, np. porządek pozycyjny środków ciężkości molekuł w fazie SmA^* czy SmC^* , co ostatecznie prowadzi do porządku w dwóch wymiarach. Takie fazy mogą być rozpatrywane, jako dwu

wymiarowe ciecze. W fazach smektycznych środki ciężkości molekuł są ułożone na tzw. płaszczyznach smektycznych, tworząc warstwy (stąd nazwa fazy warstwowe), w obrębie których występuje uporządkowanie orientacyjne molekuł. Rozróżnia się smektyki ortogonalne i pochylone. W tych pierwszych (np. w fazie SmA^*) średni kierunek długich osi molekuł opisywany przez jednostkowy wektor (direktor) jest prostopadły do płaszczyzny smektycznej, wyznaczonej przez środki ciężkości molekuł. Z kolei w smektykach pochylonych (np. w fazie SmC^*) direktor tworzy niezerowy kąt z normalną do płaszczyzny smektycznej (tzw. kąt pochylenia molekuł). W każdej kolejnej warstwie fazy SmC^* kąt pochylenia pozostaje stały, ale zmienia się nieznacznie jego orientacja w przestrzeni w stosunku do poprzedniej warstwy, co powoduje, że direktor zakreśla helisę o pewnym skoku. Natomiast w fazie SmC^*_A w sąsiadujących warstwach smektycznych kąt pochylenia molekuł ma przeciwną orientację w przestrzeni i faza ta cechuje się obecnością dwóch naprzemiennych helis przesuniętych o jedną warstwę. Występują również fazy smektyczne wykazujące różny stopień porządku pozycyjnego molekuł w warstwie. Dla faz SmA^* , SmC^* , SmC^*_A występuje jedynie porządek bliskiego zasięgu. Natomiast dla faz smektycznych takich jak np. SmB^* , SmG^* , SmJ^* występuje heksagonalne uporządkowanie dalekiego zasięgu środków ciężkości molekuł.

Z punktu widzenia symetrii, chiralna faza SmC^* różni się od achiralnej fazy SmC niższą grupą punktową symetrii, odpowiednio C_2 i C_{2h} . Obecność centrum chiralnego powoduje, że molekula chiralna nie ma środka symetrii ani płaszczyzny zwierciadlanej. Takie obniżenie symetrii między SmC i SmC^* z grupy punktowej C_{2h} na C_2 powoduje, że faza SmC^* jest ferroelektryczna. Elementy symetrii zaliczane do grupy punktowej C_2 to: obrót o 180° wokół osi prostopadłej do płaszczyzny zawierającej pochyloną molekułę oraz operacja identyczności. Składowe wektora polaryzacji muszą być niezmiennicze względem wszystkich operacji symetrii zaliczanych do danej grupy punktowej. W przypadku fazy SmC^* , zarówno wartość polaryzacji w kierunku prostopadłym do warstw smektycznych (kierunek z) i w kierunku pochylenia molekuł (kierunek y) są zerowe pod wpływem operacji symetrii z grupy C_2 . Natomiast niezerowa wartość polaryzacji jest w kierunku prostopadłym do płaszczyzny pochylenia (płaszczyzna yz) (Rys. 2). Dodatkowe elementy symetrii fazy SmC (odbicie zwierciadlane względem płaszczyzny pochylenia i inwersja) powodują, że wszystkie składowe wektora polaryzacji muszą być równe zero, zatem ferroelektryczność nie jest dopuszczona. Spontaniczna polaryzacja w fazie SmC^* jest proporcjonalna do składowej wektora momentu dipolowego molekuly równoległej do płaszczyzny smektycznej. Zatem niezerowa musi być ta składowa momentu dipolowego molekuly, aby dana faza wykazywała właściwości ferroelektryczne.



Rys. 2 Reprezentacja molekuly w smektycznych pochylonych fazach ciekłokrystalicznych w kartezjańskim układzie współrzędnych (a). Pochylenie molekuł w sąsiadujących warstwach smektycznych w fazie SmC^* i SmC^*_A wraz z przykładowymi wartościami zmian kątów pochylenia (b). W rzeczywistości pochylenie molekuł względem normalnej do warstwy smektycznej między sąsiadującymi warstwami jest niewielkie, natomiast zamierzeniem tego rysunku jest jedynie przedstawienie idei.

Dla ferroelektrycznej fazy SmC^* obserwuje się typową dla ferroelektryka pętlę histerezy $P(E)$, natomiast dla antyferroelektrycznej fazy SmC^*_A dwie pętle histerezy. Ponieważ każda warstwa smektyczna jest scharakteryzowana przez wypadkowy wektor polaryzacji, to ze względu na helikoidalną strukturę direktora, podczas przejścia z warstwy do warstwy kierunek wypadkowego wektora polaryzacji ulega zmianie i wypadkowa spontaniczna polaryzacja makroskopowej próbki w fazach SmC^* i SmC^*_A jest równa zero. Dopiero zastosowanie zewnętrznego, wystarczająco silnego pola elektrycznego równoległego do warstw smektycznych, powoduje rozwinięcie helisy (wypadkowe wektory polaryzacji wszystkich warstw mają ten sam kierunek i zwrot) i obserwuje się niezerową wartość spontanicznej polaryzacji. Podobna jest dla fazy SmC^*_A , gdzie pod wpływem zewnętrznego pola elektrycznego obie helisy ulegają rozwinięciu.

Molekuły w fazach ciekłokrystalicznych mają możliwość wykonywania pewnych ruchów, dlatego pojawiają się procesy relaksacyjne z nimi związane. We wszystkich fazach występują molekularne procesy relaksacyjne – reorientacja wokół osi krótkiej i długiej molekuly. Dodatkowo, w chiralnych fazach smektycznych pojawiają się tzw. procesy kolektywne (amplitudony i fazony). W paraelektrycznej fazie SmA^* (i w pobliżu przejścia fazowego $\text{SmA}^*-\text{SmC}^*$) występuje jeden proces kolektywny (amplitudon zwany procesem miękkim, związany z niewielkimi zmianami kąta pochylenia molekuł), natomiast w ferroelektrycznej fazie SmC^* dwa procesy kolektywne – proces miękkie i fazon (proces Goldstone'a, związany z niewielkimi zmianami fazy direktora). Z kolei dla antyferroelektrycznej fazy SmC^*_A mogą pojawić się 4 procesy kolektywne – dwa amplitudony (zmiana kąta pochylenia molekuł w fazie i przeciw fazie w sąsiednich warstwach) i dwa fazony (zmiana fazy direktora w fazie i przeciw fazie w sąsiednich warstwach).

W przejściu z fazy o wyższej symetrii (wysokotemperaturowej, np. paraelektrycznej) do fazy o niższej symetrii (niskotemperaturowej, np. ferroelektrycznej) następuje spontaniczne łamanie symetrii, które powoduje, że faza o niższej symetrii nie ma pewnych elementów symetrii charakterystycznych dla fazy o wyższej symetrii. Do charakterystyki takiego przejścia wybiera się wielkość fizyczną (tzw. parametr porządku), której niewielka zmiana doprowadza do zmiany symetrii. W przypadku przejścia pomiędzy ciekłokrystaliczną fazą paraelektryczną SmA^* a ferroelektryczną SmC^* takim parametrem porządku jest kąt pochylenia molekuł, którego wartość w fazie SmA^* jest równa 0, a w fazie SmC^* różna od zera. Do opisu przejścia fazowego $\text{SmA}^*-\text{SmC}^*$ (paraelektryk-ferroelektryk) stosuje się teorię przejść fazowych Landau'a [2].

W teorii Landau'a której dokonuje się rozwinięcia w szereg potęgowy względem parametru porządku η energii swobodnej $G(T, \eta)$. Ten potencjał termodynamiczny powinien być niezmienniczy względem grupy symetrii fazy o wyższej symetrii, co oznacza m.in. że przy zamianie $+\eta$ na $-\eta$, funkcja $G(T, \eta)$ ma być funkcją parzystą. Stąd rozwinięcie przyjmuje postać [2,3]:

$$G(T, \eta) = G_0(T) + G_2(T)\eta^2 + G_4(T)\eta^4 + \dots \quad (1)$$

W pobliżu temperatury przejścia fazowego T_c parametr porządku przyjmuje małe wartości, natomiast dla stanu równowagi termodynamicznej potencjał $G(T, \eta)$ przyjmuje minimum.

W przypadku rozwinięcia potencjału $G(T, \eta)$ w szereg dla przejścia pomiędzy ciekłokrystalicznymi fazami $\text{SmA}^*-\text{SmC}^*$, przyjmuje ono postać ($\eta \rightarrow \theta$):

$$G(T, \theta) = G_0(T) + \frac{1}{2}A(T - T_c)\theta^2 + \frac{1}{4}B\theta^4 + \dots \quad (2)$$

W celu określenia zależności parametru porządku od temperatury, wyznacza się ekstremum potencjału:

$$\frac{\partial G(T, \theta)}{\partial \theta} = A(T - T_c)\theta + B\theta^3 = 0 \quad \Leftrightarrow \quad \theta(T) = \sqrt{\frac{A}{B}(T_c - T)} = \theta_0(T_c - T)^\beta, \quad (3)$$

gdzie A i B , stałe rozwinięcia w szereg potęgowy, β – wykładnik krytyczny, dla przejścia drugiego rodzaju równy $\frac{1}{2}$. Ponieważ dla małych kątów θ spontaniczna polaryzacja jest proporcjonalna do kąta

pochylenia molekuł ($P_s \sim \sin(\theta) \sim \theta$) to jej zależność od temperatury jest taka sama jak dla kąta pochylenia, i nazywana jest ona wtórnym parametrem porządku.

Ze względu na naturalną samoorganizację molekuł w warstwy smektyczne oraz wprowadzanie nanomateriałów w takie układy warstwowe, oprócz parametrów porządku (P_s , θ) charakterystycznych dla ciekłych kryształów, ważne i ciekawe jest badanie m.in.: czasu przełączania, procesów relaksacji, dwójłomności, morfologii powierzchni, defektów strukturalnych, fluorescencji, absorpcji światła w zakresie widzialnym i podczerwieni czy zwilżalności powierzchni.

4. Metody badawcze

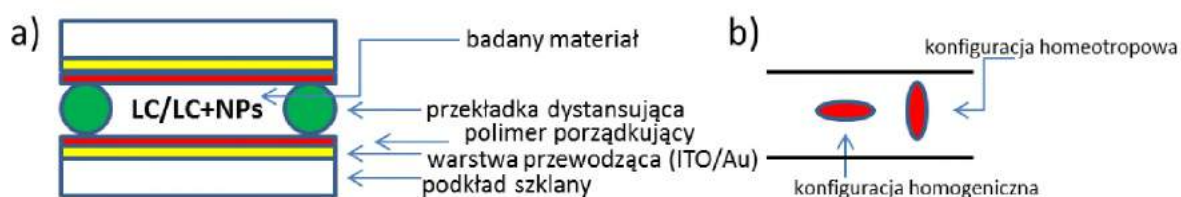
Metody badania materiałów ciekłokrystalicznych (CK) stanowią różnorodny zbiór. Zasadniczo wszystkie narzędzia badawcze używane w chemii i fizyce ciała stałego są stosowane do badania materiałów CK, począwszy od szeroko rozwiniętych metod mikroskopowych, przez metody termiczne, elektryczne, optyczne, strukturalne a kończąc na metodach spektroskopowych i magnetycznych. Jedynym ograniczeniem jest zwykle bardzo mała ilość materiału badawczego. Podobnie jak czyste związki ciekłokrystaliczne i ich mieszaniny, tak i bardziej wyrafinowane układy np. nanokompozyty, blendy czy wieloskładnikowe materiały hybrydowe mogą być badane tymi samymi metodami. W niniejszym rozdziale opisano metody pomiarowe, które zastosowano do badania materiałów będących przedmiotem niniejszej rozprawy.

Tabela 1. Spis metod pomiarowych używanych do badań.

Techniki pomiarowe	Metoda
Elektro-Optyczne	Pomiar dwójłomności (OB , ang. Optical Birefringence), Pomiar parametrów elektryczno-optycznych (EOM , ang. Electro-Optical Methods),
Magnetyczne	Magnetometria kwantowa (SQUID , ang. Superconducting Quantum Interference Device),
Mikroskopowe	Skaningowa mikroskopia elektronowa (SEM , ang. Scanning Electron Microscopy), Mikroskopia optyczna (OM , ang. Optical Microscopy), Mikroskopia optyczna ze światłem spolaryzowanym (POM , ang. Polarizing Optical Microscopy), Mikroskopia konfokalna (FCPM , ang. Fluorescence Confocal Polarizing Microscopy),
Spektroskopowe	Spektroskopia dielektryczna (FDDS , ang. Frequency Domain Dielectric Spectroscopy), Spektroskopia w zakresie ultrafioletowym i widzialnym (UV-Vis , ang. Ultra Violet-Visible), Spektroskopia Ramana (RS , ang. Raman Spectroscopy), Spektroskopia w zakresie podczerwieni (FT-IR , ang. Fourier Transform Infrared Spectroscopy),
Strukturalne	Dyfrakcja rentgenowska (XRD , ang. X-Ray Diffraction),
Termiczne	Różnicowa kalorymetria skaningowa (DSC , ang. Differential Scanning Calorimetry),
Termo-Optyczne	Pomiar intensywności światła transmitowanego (TLI , ang. Transmitted Light Intensity), Pomiar kąta zwilżania (CA , ang. Contact Angle),

4.1. Metody elektro-optyczne

Do metod elektro-optycznych zalicza się metody, w których stosuje się zarówno pole elektryczne jak i promieniowanie w zakresie widzialnym. Za pomocą tych metod można wyznaczyć takie parametry badanych materiałów jak spontaniczna polaryzacja P_s , czas przełączania τ , kąt pochylenia molekul θ , skok helisy p czy odpowiedź elektrooptyczna i . Dla wszystkich próbek zastosowano do badań takie same, typowe homogeniczne komórki elektro-optyczne typu kanapka (Rys. 3) z elektrodami ITO (z ang. Indium Tin Oxide) oraz poliimidowymi warstwami orientującymi (AWAT Sp. z o.o.). Powierzchnia elektrod wynosiła 25mm^2 , a grubość w granicach ok. $5\text{-}8\mu\text{m}$. Komórki napelniano materiałem badawczym dzięki efektowi kapilarnemu (niewielką ilość materiału umieszczano przy szczelinie komórki oraz podgrzewano do temperatury powyżej temperatury przejścia do fazy cieczy izotropowej tego materiału. Po całkowitym napelnieniu, komórkę wypełnioną próbką powoli ochładzano do temperatury pokojowej.



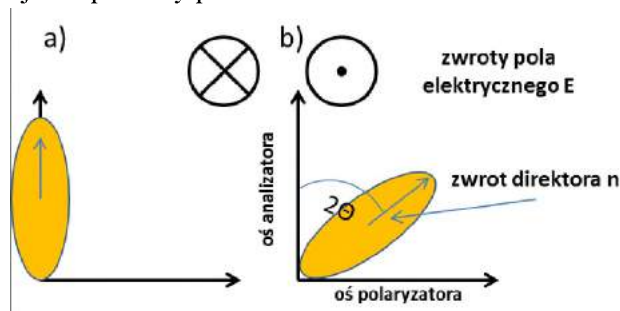
Rys. 3 Schemat komórki do pomiarów elektro-optycznych (a) oraz ułożenie molekul organicznych w komórce w konfiguracji hometropowej i homogenicznej (b).

Badania elektro-optyczne prowadzi się na tzw. monodomenie, czyli próbce, w której molekuly są idealnie uporządkowane (długie osie molekul są równoległe do siebie i elektrod, uporządkowanie homogeniczne). Samo stosowanie warstwy polimeru porządkującego molekuly ciekłego kryształu zwykle nie jest wystarczające i orientację planarną (homogeniczną) uzyskuje się przez przyłożenie zewnętrznego zmiennego pola elektrycznego o parametrach (kształt, amplituda, częstotliwość) indywidualnie dobieranych do badanego materiału.

W ramach niniejszej pracy, ze względu na rodzaje badanych materiałów, parametry elektro-optyczne wyznaczano dla różnych faz, m.in. ferroelektrycznej SmC^* , antyferroelektrycznej SmC^*_A i pod-fazy SmC^*_a . Badania zarówno kąta pochylenia molekul, jaki i czasu przełączania wykonano dla sygnału prostokątnego, a spontanicznej polaryzacji dla sygnału trójkątnego.

4.1.1. Metoda pomiaru kąta pochylenia molekul

Metoda pomiaru kąta pochylenia molekul jest oparta o zjawisko Clarka-Lagerwalla, czyli przełączania molekul w monodomenie przy zmianie polaryzacji sygnału wejściowego (przełączanie zachodzi w płaszczyźnie komórki i możliwa jest detekcja położenia minimów kątowych transmisji). Do próbki przykładano sygnał prostokątny i rejestrowano optyczną odpowiedź próbki przez fotodetektor. Dla obu polaryzacji sygnału wejściowego szukano minimum odpowiedzi optycznej poprzez obrót stolika mikroskopowego, notując położenia kątowe dla pełnego zaciemnienia, stan „off” (Rys. 4). W celu dokładnego wyznaczenia kąta pochylenia molekul, rejestrowano odpowiedź fotodetektora w kilku punktach kątowych wokół stanu „off”, a do otrzymanych punktów dopasowywano funkcję kwadratową. W trakcie zmiany polaryzacji sygnału, molekuly wykonują ruch po poboczniczy stożka o kącie rozwarcia 2θ , zatem odległość kątowna pomiędzy najbliższymi położeniami pełnego wygaszenia obrazu jest równa podwojonej wartości kąta pochylenia molekul $2\theta = |\phi_1 - \phi_2|$ [4]. Pomiary prowadzone były w funkcji temperatury podczas ochładzania.



Rys. 4 Wyznaczanie kąta pochylenia molekul metodą Clarka-Lagerwalla. Dla uproszczenia zaprezentowano jedną molekulę w warstwie smektycznej homogenicznie uporządkowanej próbki: (a) oś optyczna (direktor n) jest równoległa do osi analizatora (położenie kątowe ϕ_1 , stan „off”) przy jednym zwrocie zewnętrznego pola elektrycznego, (b) położenie molekul przy przeciwnym zwrocie E (położenie kątowe ϕ_2 , stan „off”).

4.1.2. Metoda pomiaru czasu przełączania molekul

Metoda wyznaczania czasu przełączania, tj. czasu potrzebnego na przeorientowanie wszystkich molekul pod wpływem zewnętrznego pola elektrycznego także opiera się na zjawisku Clarka-Lagerwalla. W tym przypadku na próbkę w komórce elektrooptycznej połączonej szeregowo z opornikiem ($R_{zew} = 100k\Omega$) podaje się sygnał prostokątny i rejestruje się spadek napięcia na tym oporze, czyli sygnał odpowiedzi próbki. Czas liczony od momentu zmiany polaryzacji sygnału wejściowego do pojawienia się maksimum w sygnale odpowiedzi próbki, jest czasem przełączania. Badania prowadzono w funkcji temperatury podczas ochładzania [6,7].

4.1.3. Metoda pomiaru spontanicznej polaryzacji

Spontaniczna polaryzacja P_s w ciekłych kryształach smektycznych jest tzw. niewłaściwą spontaniczną polaryzacją, ponieważ pod nieobecność zewnętrznego pola elektrycznego jest równa

zero ze względu na spiralne ułożenie wypadkowych momentów dipolowych od poszczególnych warstw smektycznych. Dopiero przyłożenie wystarczającego silnego pola elektrycznego prostopadle do warstw smektycznych powoduje rozwinięcie spirali smektycznej i uporządkowanie momentów dipolowych warstw w jednym kierunku, a w efekcie pojawia się niezerowa spontaniczna polaryzacja. Konfiguracja do pomiaru spontanicznej polaryzacji jest taka sama jak dla czasu przełączania, z tym, że na komórkę połączoną szeregowo z opornikiem podaje się sygnał trójkątny i rejestruje się odpowiedź próbki (tzw. metoda rejestracji prądu odwrócenia polaryzacji, ang. Reversal Current Method) [7]. Wtedy próbka umieszczona w komórce elektrooptycznej jest traktowana, jako układ trzech elementów połączonych równolegle: opornika o oporze R , kondensatora o pojemności C i źródła ładunków P (wynik polaryzacji próbki), a prąd płynący przez próbkę jest sumą prądu związanego ze skończonym oporem próbki $I_R(t)$, który jest proporcjonalny do przyłożonego napięcia, prądu związanego z ładowaniem kondensatora $I_C(t)$, gdyż komórka pomiarowa jest kondensatorem oraz prądu związanego z polaryzacją badanego materiału $I_P(t)$:

$$I(t) = I_R(t) + I_C(t) + I_P(t) = \frac{U(t)}{R} + C \frac{dU(t)}{dt} + \frac{dQ(t)}{dt}, \quad (4)$$

gdzie R – opór, C – pojemność, Q – wielkość ładunku elektrycznego, jaki został wyindukowany w procesie porządkowania próbki. W celu obliczenia wartości $P_s(T)$ z powyższej sumy natężeń należy wyodrębnić ostatni człon. Wkład pochodzący od pierwszych dwóch członów $I_R(t) + I_C(t)$ jest liniowy dla sygnału trójkątnego i po odjęciu tego wkładu oblicza się pole powierzchni pod pikiem odpowiedzi, które jest proporcjonalne do wartości spontanicznej polaryzacji:

$$P_s(T) = \frac{1}{2S_{kom}} \int dQ(T, t) = \frac{1}{2S_{kom}} \int I_P(T, t) dt = \frac{1}{2S_{kom} R_{zew}} \int U(T, t) dt, \quad (5)$$

gdzie S_{kom} – pole powierzchni elektrod komórki pomiarowej, R_{zew} – opór zewnętrzny połączony szeregowo z komórką, $I_P(T, t)$, $U(T, t)$ odpowiedź prądowa i napięciowa próbki po odjęciu tła. Należy tak dobrać częstotliwość przykładanego zmiennego pola elektrycznego, aby polaryzacja orientacyjna (związana z przełączaniem molekul) nadążała za zmianami tego pola.

4.1.4. Metoda pomiaru odpowiedzi elektrooptycznej

Metodą, która pozwala na wykazanie istnienia faz występujących w bardzo wąskim zakresie temperatur jest badanie transmisji światła przez próbkę poddaną działaniu zmiennego pola elektrycznego, podczas bardzo wolnego ochładzania. Natężenie światła przechodzącego przez cienką warstwę ciekłego kryształu (dla konfiguracji skrzyżowanych polaryzatorów) jest opisane wzorem Fresnela [8]:

$$I(\alpha, \Delta n, d, \lambda) = I_0 \sin^2(2\alpha) \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right), \quad (6)$$

gdzie I_0 – natężenie światła padającego na próbkę, α – kąt pomiędzy osią optyczną (oś helisy w chiralnych fazach pochyłonych) a płaszczyzną polaryzacji polaryzatora, Δn – dwójłomność optyczna, d – grubość próbki, λ – długość fali światła padającego. Przyłożone zmienne pole elektryczne powoduje zmianę położenia osi optycznej $\Delta\alpha$ względem polaryzatora oraz zmianę polaryzacji próbki, a w konsekwencji zmianę dwójłomności Δn :

$$\alpha = \alpha_0 + \Delta\alpha, \quad (7)$$

$$\Delta n(E) = \Delta n_0 + \Delta n, \quad (8)$$

gdzie α_0 , Δn_0 – kąt pomiędzy osią optyczną a płaszczyzną polaryzacji polaryzatora i wartość dwójłomności dla $E = 0$. $\Delta\alpha$ jest zmianą położenia osi optycznej względem płaszczyzny polaryzatora pod wpływem przyłożonego pola E . Zmiana położenia osi optycznej jest liniową funkcją ΔE , natomiast zmiana dwójłomności jest funkcją kwadratową ΔE :

$$\Delta\alpha \propto \Delta E, \quad \Delta n \propto \Delta E^2. \quad (9)$$

Przekształcając równanie (3) i uwzględniając wpływ pola elektrycznego można zapisać:

$$\frac{I}{I_0} = \sin^2(2\alpha(E)) \sin^2\left(\frac{\pi \Delta n(E) d}{\lambda}\right). \quad (10)$$

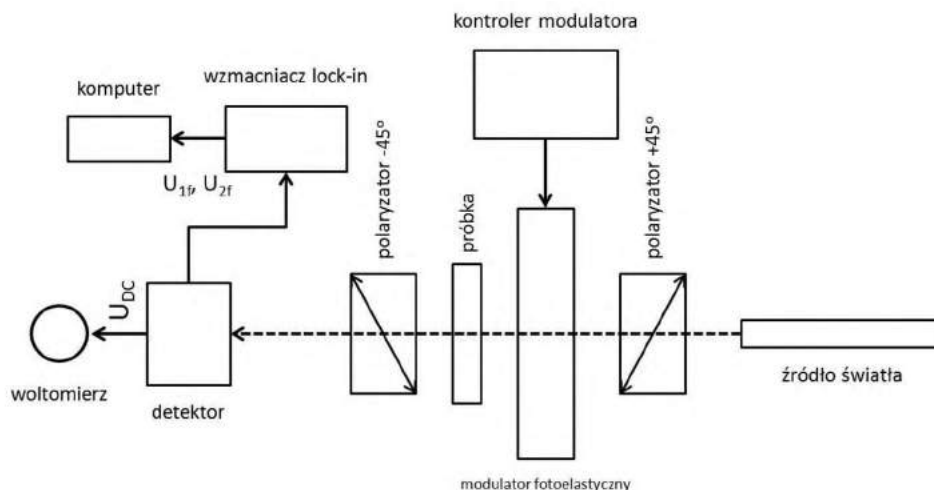
Odpowiedź elektrooptyczna i jest zdefiniowana, jako względna zmiana intensywności światła transmitowanego $\Delta I = I_0 - I$ przypadająca na jednostkę zmiany pola elektrycznego ΔE :

$$i = \frac{\Delta I}{I_0} \frac{1}{\Delta E}. \quad (11)$$

W przypadku fazy SmA* odpowiedź elektro-optyczna jest zdefiniowana, jako $\Delta \Theta_{ind} / \Delta E$, gdzie Θ_{ind} jest kątem pochylenia molekuł indukowanym polem elektrycznym (efekt elektroklinczny). Zatem w celu wyznaczenia odpowiedzi elektrooptycznej wystarczy zmierzyć tylko wyindukowany kąt pochylenia. W fazach pochylnych odpowiedź zależy od zmiany osi optycznej próbki $\Delta \alpha$ i zmiany dwójłomności Δn , dlatego odpowiedź elektrooptyczna musi być zmierzona fotometrycznie zgodnie ze wzorem (11). Nawet subtelne zmiany natężenia światła ΔI w strukturalnie podobnych fazach np. SmC*_a i SmC* (I_0 oraz ΔE takie same) oraz wolne ogrzewanie/ochładzanie próbki pozwalają na rozróżnienie tych faz. Badania prowadzono w konfiguracji skrzyżowanych polaryzatorów dla kąta $\alpha_0 = 22,5^\circ$ w fazie SmA* w celu uzyskania maksimum zmodulowanej odpowiedzi elektrooptycznej.

4.1.5. Metoda pomiaru dwójłomności

Badania dwójłomności wykonano z zastosowaniem modulatora fotoelastycznego, który moduluje polaryzację źródła światła. Metoda działania modulatora jest oparta na zjawisku fotoelastycznym, które polega na zmianie dwójłomności elementu optycznego (poprzez mechaniczne ściskanie albo rozprężanie) proporcjonalnie do odkształcenia. Jeżeli do elementu optycznego nie jest przyłożone naprężenie, światło przechodzi bez zmiany polaryzacji przez modulator, w przeciwnym przypadku następuje wyprzedzanie jednej składowej polaryzacji względem drugiej. Ta różnica fazowa składowych równoległej i prostopadłej polaryzacji nazywana jest opóźnieniem lub retardacją. W szczególnych przypadkach, gdy opóźnienie generowane przez modulator osiąga $\frac{1}{4}$ długości fali światła padającego, modulator fotoelastyczny działa jak płytka ćwierćfalowa. Schemat układu zastosowanego do pomiaru dwójłomności jest zaprezentowany na Rys. 5.



Rys. 5 Schemat blokowy układu do pomiaru dwójłomności.

Źródłem światła jest laser He-Ne (632,8nm). Za laserem znajduje się polaryzator o osi zorientowanej pod kątem $+45^\circ$ względem osi modulatora oraz modulator z osią opóźnienia ustawioną na 0° . Światło zmodulowane przez modulator przechodzi następnie przez badaną próbkę umieszczoną w komórce pomiarowej w systemie grzewczym i kolejny polaryzator o osi zorientowanej pod kątem -45° względem osi modulatora. Następnie pada na detektor, którego wyjście jest rozdzielone: jedna gałąź na wzmacniacz typu lock-in do detekcji sygnałów $1f$ i $2f$, a druga do woltomierza. Zmienne napięcie przykładane do modulatora powoduje powstanie okresowych zmian dwójłomności elementu

optycznego modulatora (tu płytki krzemionkowej), natomiast wynikowa retardacja δ jest sumą opóźnień wprowadzonego przez modulator $\delta_{modulator}$ i badaną próbkę $\delta_{próbka}$ [9,10]:

$$\delta = \delta_{modulator} + \delta_{próbka} = A \cos(2\pi f t) + B, \quad (12)$$

gdzie f – częstotliwość sygnału podawanego na element optyczny modulatora, A – amplituda sygnału podawanego, B – retardacja próbki. Wzmacniacz lock-in mierzy napięcie przy pierwszej harmonicznej częstotliwości (U_{1f}) z modulatora, które odpowiada wyjściu układu przy tej częstotliwości. Dla małych A i B , wyjście wzmacniacza lock-in można przekształcić do postaci:

$$I = I_0 \left(\frac{1}{2} (1 - J_0 \cos(B)) + J_1 \sin(B) \cos(2\pi f t) + J_2 \cos(B) \cos(4\pi f t) \right), \quad (13)$$

gdzie I_0 , I – natężenie światła padającego na próbkę i po przejściu przez układ, J_0 , J_1 , J_2 – funkcje Bessela związane z retardacją modulatora. Wykrywane są trzy sygnały: wzmacniacz lock-in wykrywa napięcie skuteczne U_{1f} sygnału detektora przy częstotliwości modulatora $1f$ oraz napięcie skuteczne U_{2f} sygnału detektora przy częstotliwości modulatora $2f$ oraz średnie napięcie U_{DC} sygnału. Następnie oblicza się stosunki R_{1f} oraz R_{2f} według wzorów:

$$R_{1f} = \frac{U_{1f}}{U_{DC}} \quad \text{oraz} \quad R_{2f} = \frac{U_{2f}}{U_{DC}}. \quad (14)$$

Zgodnie z teorią fotoelastycznej modulacji, opóźnienie wprowadzone przez badaną próbkę można obliczyć według wzoru:

$$\tan(B) = \frac{R_{1f} J_2(A)}{R_{2f} J_1(A)} = \frac{U_{1f} J_2(A)}{U_{2f} J_1(A)}, \quad (15)$$

a dwójłomność próbki (w danej temperaturze) jako:

$$\Delta n(T) = \frac{B(T)}{2\pi d} = \frac{1}{2\pi d} \arctan \left(\frac{U_{1f} J_2(A)}{U_{2f} J_1(A)} \right), \quad (16)$$

gdzie d – grubość próbki.

4.2. Metoda magnetometrii z interferencją kwantową

Do określenia wpływu nanocząstek (i dekorującego surfaktanta) na magnetyzację i parametry charakteryzujące ferromagnetyczną pętlę histerezy zastosowano metodę magnetometrii w trybie nadprzewodzącej interferometrii kwantowej. Zgodnie z mechaniką kwantową każda cząstka elementarna oprócz orbitalnego momentu pędu posiada także spinowy moment pędu. Orbitalny moment magnetyczny elektronu m_o jest antyrównoległy do orbitalnego momentu pędu elektronu l i jest równy [11]:

$$\vec{m}_o = -\mu_B \vec{l} = -\frac{eh}{4\pi m_e} \vec{l}, \quad (17)$$

gdzie μ_B – magneton Bohra, e – ładunek elementarny elektronu, h – stała Plancka, m_e – masa elektronu. Spinowy moment magnetyczny elektronu m_s jest antyrównoległy do spinowego momentu pędu (spinu) s i jest równy:

$$\vec{m}_s = -g\mu_B \vec{s} = -g \frac{eh}{4\pi m_e} \vec{s}, \quad (18)$$

gdzie g – czynnik Landégo. Ze względu na fakt, że badane próbki są makroskopowe (złożone z wielu atomów), możliwe jest tylko zmierzenie wypadkowego momentu magnetycznego i ewentualne jego odniesienie do masy lub ilości moli próbki. Zatem wypadkowy moment magnetyczny atomu m_w to suma wektorowa orbitalnego i spinowego momentu magnetycznego:

$$\vec{m}_w = -\mu_B (\vec{l} + g\vec{s}), \quad (19)$$

Wektory L i S opisują wypadkowy orbitalny i spinowy moment pędu elektronów na niezapełnionych powłokach.

Do podstawowych wielkości charakteryzujących własności magnetyczne należy podatność magnetyczna χ , która opisuje reakcję układu na zmianę natężenia pola magnetycznego, czyli mówi

o łatwości namagnesowania oraz magnetyzacja M , będąca momentem magnetycznym zwykle wyrażanym na jednostkę objętości. Obie wielkości są powiązane wzorem:

$$M(H) = \chi H, \quad (20)$$

gdzie H – natężenie pola magnetycznego. Zależność liniowa między M i H jest prawdziwa dla materiałów będących diamagnetykami, paramagnetykami lub antyferromagnetykami (co jest prawdziwe tylko dla niskich wartości H).

W przypadku pomiarów stałoprądowych, moment magnetyczny badanej próbki jest mierzony poprzez odczyt napięcia wyjściowego detektora SQUID, kiedy próbka w rurce kaptonowej zamontowana na pręcie magnetometru wykonuje ruch w górę, przechodząc przez cewki odbiorcze. Taki ruch przez cewki z punktu A do B stanowi jeden pełny pionowy skan. Wynikiem pomiaru są wartości napięć odczytane na wyjściu w funkcji położenia próbki pomiędzy cewkami odbiorczymi. W celu poprawy rozdzielczości próbka poddana jest wielu skanom, które są uśredniane. Typowa dokładność pomiarów wynosi 0.1%. Przed rozpoczęciem pomiarów próbka jest centrowana pomiędzy cewkami odbiorczymi.

Badania wykonano na próbkach unieruchomionych klejem (varnish) w żelatynowych kapsułkach. Kapsułki umieszczano w rurkach kaptonowych i mocowano na pręcie pomiarowym magnetometru. Podczas obróbki danych pomiarowych odejmowano diamagnetyczne tło pochodzące od kapsułki żelatynowej, natomiast wkład diamagnetyczny od rurki kaptonowej, jako zanedbywalnie mały, nie był uwzględniany. Zaobserwowane pętle histerezy dla próbek kompozytowych pochodzą od nanocząstek w stanie zblokowania (stan ferromagnetyczny) poniżej temperatury blokowania T_B . Powyżej T_B nanocząstki wykazują zachowanie paramagnetyczne, jednak ich podatność magnetyczna χ jest większa od typowych paramagnetyków, dlatego stan powyżej T_B jest nazywany superparamagnetycznym. Nanocząstkę można traktować, jako jedną domenę magnetyczną – jeden duży moment magnetyczny, będący sumą wszystkich pojedynczych momentów magnetycznych niesionych przez składowe atomy nanocząstki.

Przeprowadzone magnetyczne pomiary stałoprądowe, dały informację o zależnościach magnetyzacji M poszczególnych próbek od zewnętrznego pola magnetycznego H . Dzięki nim możliwe było wyznaczenie m.in. pętli histerezy pochodzących od nanocząstek, zależności magnetyzacji remanencji M_R i pola koercji H_c zarówno od temperatury jak i koncentracji nanocząstek. Pomiary wykonano do wartości pola $H = 50\text{kOe}$, co pozwoliło na wyznaczenie magnetyzacji saturacji M_S . Pomiary w zmiennych polach magnetycznych nie były wykonywane, dlatego opis relaksacji magnetycznych zostaje pominięty.

4.3. Metody mikroskopowe

4.3.1. Metoda mikroskopii optycznej i mikroskopii polaryzacyjnej

Mikroskop optyczny składa się ze źródła światła, elementów optycznych (lustra, soczewki, kondensor, pryzmat), stolika obrotowego do umieszczenia próbki, śrub mikro- i makrometrycznych, obiektywu i okularów, przysłon (aperturowej i pola widzenia), kamery cyfrowej, filtra selektywnej długości fali. Obrazy mikroskopowe są pozorne, powiększone i odwrócone. Całkowite powiększenie mikroskopu optycznego p jest iloczynem powiększeń soczewek w obiektywie p_{ob} i okularze p_{ok} [12]:

$$p = p_{ob} p_{ok}. \quad (21)$$

Istotnym parametrem charakteryzującym układ mikroskopu optycznego jest zdolność rozdzielcza d :

$$d(\lambda, n, \zeta) = \frac{\lambda}{2n \sin \zeta}, \quad (22)$$

gdzie λ – długość fali światła padającego na próbkę, n – współczynnik załamania otoczenia, w którym znajduje się próbka (zwykle powietrze), ζ – kąt pomiędzy osią obiektywu a najbardziej brzegowym promieniem wchodzącym do niego (który bierze udział w tworzeniu obrazu). Zdolność rozdzielcza mikroskopu to najmniejszy dystans pomiędzy dwoma miejscami próbki, które mogą być od siebie

odróżnione, a ograniczona jest m.in. przez dyfrakcję: przy odpowiednio dużych powiększeniach informacje o szczegółach próbki zostają utracone, ponieważ światło uginając się na krawędziach małych struktur, powoduje że szczegóły stają się mniej widoczne. Mikroskopię optyczną o wysokiej rozdzielczości zastosowano do określenia wpływu nanocząstek na morfologię powierzchni w skali mikrometrycznej, oceny powstawania aglomeratów oraz obrazowania wpływu kwasu oleinowego na matrycę ciekłego kryształu. Obrazowanie przeprowadzono z różnymi powiększeniami w modzie transmisyjnym. Wysoka zdolność rozdzielcza mikroskopu pozwoliła na poznanie szczegółów na poziomie 1µm.

Mikroskop polaryzacyjny jest mikroskopem optycznym wyposażonym dodatkowo w dwa polaryzatory, których osie polaryzacji są zwykle skrzyżowane pod kątem 90°. Jeden polaryzator jest umieszczony między źródłem światła i próbką, a drugi między próbką a okulem. Gdy materiał dwójłomny umieszczony jest pod mikroskopem to w świetle spolaryzowanym można oglądać obrazy interferencyjne cienkiej warstwy materiału (tzw. tekstury), natomiast intensywność światła transmitowanego przez próbkę jest opisana wzorem:

$$I = \frac{1}{2} I_0 \sin^2 2\varphi \sin^2 \frac{1}{2} \delta, \quad (23)$$

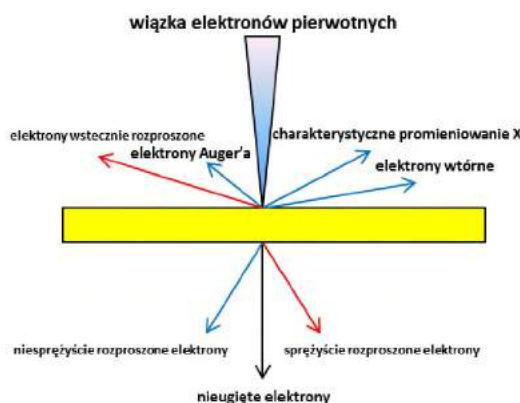
gdzie φ – kąt azymutalny (kąt pomiędzy osią polaryzacji polaryzatora i rzutem osi optycznej na warstwę smektyczną, δ – różnica faz. W równaniu (23) pierwszy czynnik opisuje zmiany natężenia światła transmitowanego względem orientacji dwójłomnej próbki między dwoma polaryzatorami, drugi odpowiada za kolor tekstury. Mikroskopia polaryzacyjna pozwala na identyfikację faz ciekłokrystalicznych i dostarcza informacji o temperaturach przejść fazowych. Należy zaznaczyć, że pomimo subtelnych różnic między niektórymi fazami ciekłokrystalicznymi (np. dla SmC* i SmC*_a) metoda ta pozwala je odróżnić poprzez zmiany koloru, prążkowania czy modyfikacji defektów strukturalnych obrazu. Obrazowanie w kontraście polaryzacyjnym posłużyło także do identyfikacji defektów strukturalnych obecnych w danym materiale oraz określenia miejsc gromadzenia się nanocząstek. Próbkę w komórce elektrooptycznej (homogeniczna, elektrody ITO) umieszcza się w przystawce grzewczej na obrotowym stoliku. Pomiary prowadzono w funkcji temperatury.

4.3.2. Metoda skaningowej mikroskopii elektronowej

Metodą skaningowej mikroskopii elektronowej można badać topografię powierzchni, ocenić obecności aglomeratów nanocząstek czy wpływu surfaktantu (kwas oleinowy) na chropowatość powierzchni. Zaletą tej metody jest wysoka zdolność rozdzielcza, możliwość obrazowania za pomocą elektronów wtórnych lub elektronów wstecznie rozproszonych oraz możliwość wyznaczania składu chemicznego badanej próbki. Obrazowanie jest wykonywane w warunkach wysokiej próżni, aby wiązka padających elektronów nie została zaburzona przez atomy/cząsteczki gazu w komorze pomiarowej. Za pomocą detektorów umieszczonych w komorze z próbką otrzymuje się obraz badanej próbki. Do obrazowania wykorzystuje się wiązkę elektronów emitowanych z katody, przyspieszanych w polu elektrycznym i formowanych przez układ soczewek elektromagnetycznych. Rozdzielczość obrazu jest uzależniona od długości fali elektronów, zależnej od wielkości napięcia przyspieszającego. Typowa zdolność rozdzielcza tego typu mikroskopu jest rzędu 1nm [13].

Uformowana wiązka elektronów padając na powierzchnię badanej próbki może zostać całkowicie zaabsorbowana, przeniknąć przez materiał, ulec odbiciu od jego powierzchni czy spowodować emisję promieniowania. Ilość elektronów odbitych, zaabsorbowanych i przechodzących przez próbkę zależy m.in. od jej grubości i składu pierwiastkowego. W wyniku oddziaływania wiązki elektronów z próbką można zaobserwować emisję elektronów wtórnych, odbitych czy elektronów Auger'a, emisję promieniowania rentgenowskiego (charakterystycznego i hamowania) czy fluorescencję. Ze wzrostem napięcia przyspieszającego rośnie pęd elektronów w wiązce, zatem mogą one penetrować próbkę głębiej i ze wzrostem objętości obszaru emisji.

Otrzymywanie obrazu zachodzi poprzez skanowanie powierzchni badanej próbki punkt po punkcie wiązką elektronów o średnicy nanometrycznej, a sygnał z powierzchni próbki (zwykle w postaci elektronów wtórnych albo odbitych) dociera do układu detekcyjnego. Część elektronów pierwotnych ulega rozproszeniu niesprężystemu przez atomy badanej próbki i traci stopniowo swoją energię kinetyczną, co prowadzi do powstania elektronów wtórnych (Rys. 6). W skaningowej mikroskopii elektronowej najistotniejszy sygnał niskoenergetyczny pochodzi od elektronów wtórnych (o energiach poniżej 50eV) emitowanych blisko powierzchni próbki. Obraz próbki uzyskany przez elektrony wtórne daje informację o topografii powierzchni. Ze względu na wzmocnienie emisji elektronów wtórnych blisko uskoku (krawędzi wzniesień), możliwe jest bardzo dokładne odwzorowanie nie tylko tarasów, ale ich krawędzi. Z kolei część elektronów pierwotnych zostaje rozproszona sprężysto, co jest wynikiem oddziaływania elektrostatycznego między ujemnie naładowanymi elektronami z wiązki padającej i dodatnio naładowanymi jądrami atomów próbki. W wyniku tego dochodzi do zmiany kierunku ich ruchu o ponad 90°. Te elektrony wstecznie rozproszone służą do konstrukcji obrazu próbki, dając informację o różnorodności chemicznej (kontraście chemicznym) próbki (Rys. 6). Ze względu na brak lub stosunkowo małe zmiany energii elektronów wstecznie rozproszonych uzyskana informacja o próbce pochodzi z jej głębszych regionów niż przy obrazowaniu za pomocą elektronów wtórnych.

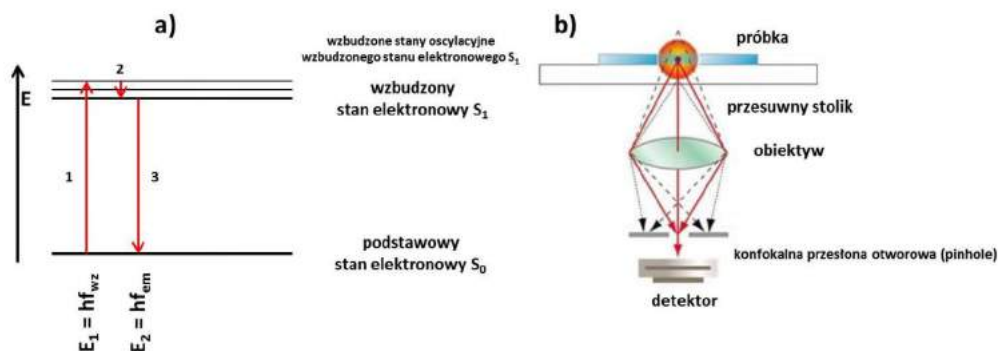


Rys. 6 Oddziaływanie wiązki elektronów z próbką.

Przed obrazowaniem, koliste końcówki na próbki poddawane były procesowi czyszczenia (usuwanie powierzchniowych zanieczyszczeń) w myjce ultradźwiękowej. Następnie czyste szkiełko mikroskopowe zamontowane zostało na końcówce za pomocą dwustronnej taśmy. Na zamontowane szkiełko naniesiono próbkę i w celu zapewnienia kontaktu między końcówką i powierzchnią szkiełka z próbką użyto taśmy miedziovej. Nie nanoszono dodatkowej warstwy metalu, w celu zachowania oryginalnego koloru i morfologii.

4.3.3. Metoda fluorescencyjnej mikroskopii konfokalnej ze światłem spolaryzowanym

W metodzie tej sercem układu jest mikroskop konfokalny pracujący na bazie mikroskopu fluorescencyjnego, który opiera się na zjawisku fluorescencji. Energia fotonu E_1 dostarczanego przez źródło światła jest absorbowana przez elektrony fluoroforu i powoduje ich przejście z podstawowego stanu elektronowego S_0 na wyższy poziom energetyczny (wzbudzony stan oscylacyjny wzbudzonego elektronowego stanu S_1 , proces 1 na Rys. 7a). Następnie zachodzi bardzo szybko relaksacja wibracyjna (proces 2), w której elektron oddaje do otoczenia nadmiar energii osiągając podstawowy stan oscylacyjny we wzbudzonym elektronowym stanie S_1 . Kiedy elektron powraca ze wzbudzonego stanu elektronowego S_1 do podstawowego stanu elektronowego S_0 , emitowany jest foton o energii $E_2 < E_1$ (proces 3). Różnica w energii czy długości fali fotonu wzbudzającego i emitowanego jest określana, jako reguła Stokesa [14,15].



Rys. 7 Schemat poziomów energetycznych oraz przejścia między nimi dla elektronu absorbującego promieniowanie padające (a), bieg promieni emitowanych z próbki wraz z ich przejściem przez przesłoną otworową (b).

W mikroskopie konfokalnym wiązka wzbudzająca i detekcji są ogniskowane w tym samym punkcie na próbce na określonej głębokości, a źródłem światła są lasery diodowe generujące określone długości fal (np. 405nm, 473nm, 559nm i 635nm). Konfokalna przesłona otworowa (Rys. 7b) jest kluczowym elementem, z którego wiązka dociera do detektora, co pozwala rejestrować nawet najsłabsze impulsy światła wzbudzonego i zapewnia poprawę rozdzielczości oraz możliwość otrzymania przekrojów (tzw. skrawków optycznych). Impulsy świetlne zostają przetworzone na impulsy elektryczne i na obraz.

Metodę fluorescencyjnej mikroskopii konfokalnej ze światłem spolaryzowanym zastosowano do określenia fluorescencji w zakresie światła widzialnego w matrycy organicznej, domieszcze oraz kompozytach. Próbkę do obrazowania były w postaci cienkich warstw na szkiełku mikroskopowym.

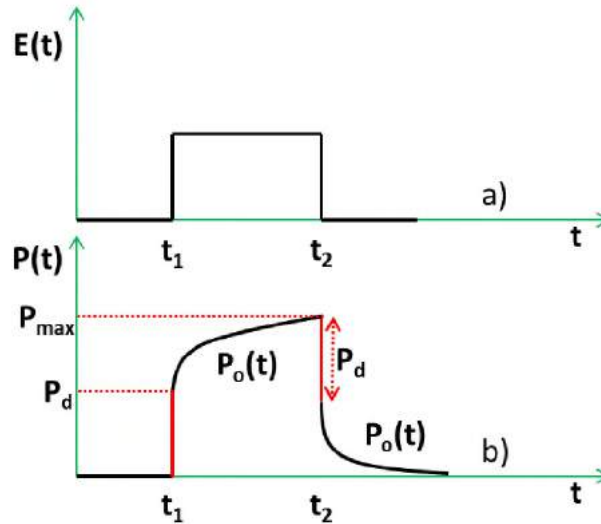
4.4. Metody spektroskopowe

4.4.1. Metoda spektroskopii dielektrycznej w domenie częstotliwości

Metoda spektroskopii dielektrycznej w domenie częstotliwości pozwala na zbadanie dynamiki na poziomie molekularnym związanej m.in. ze stałym lub indukowanym elektrycznym momentem dipolowym w materiałach dielektrycznych (bez ładunków swobodnych). W metodzie tej, do próbki umieszczonej w kondensatorze pomiarowym przykładana się słabe zmienne pole elektryczne, tzw. pole mierzące. Po umieszczeniu dielektryka w zewnętrznym zmiennym polu elektrycznym dochodzi do indukowania momentów dipolowych, które wynikają z polaryzacji elektronowej P_e (przesunięcie chmur elektronowych względem jąder) oraz atomowej P_a (przemieszczenie atomów molekuly o różnych ładunkach – odkształcenie wiązań chemicznych). Dodatkowo, dla dielektryków polarnych, pojawia się polaryzacja orientacyjna P_{or} , związana ze stałym elektrycznym momentem dipolowym. Po przyłożeniu do dielektryka polarnego zmiennego pola elektrycznego polaryzacje P_e i P_a pojawiają się natychmiast (ich suma jest nazywana polaryzacją deformacyjną P_d), natomiast polaryzacja orientacyjna narasta w pewnym interwale czasowym (Rys. 8). Po usunięciu pola elektrycznego natychmiast zanika polaryzacja deformacyjna, podczas gdy polaryzacja orientacyjna maleje w czasie w sposób wykładniczy. Efekt narastania i zaniku polaryzacji orientacyjnej w czasie jest nazwany relaksacją dielektryczną i opisany funkcją [16,17]:

$$P_{or}(t) = (P_{max} - P_d) \left(1 - \exp\left(-\frac{t}{\tau_D}\right) \right), \quad (24)$$

gdzie P_{max} – sumaryczna wartość wszystkich typów polaryzacji, $\exp(-t/\tau_D)$ – funkcja relaksacji, t – czas, τ_D – czas relaksacji dielektrycznej, charakteryzujący określony ruch molekul potrzebny na reorientację jej momentów dipolowych.



Rys. 8 Kształt przykładanego zmiennego pola elektrycznego do próbki badanej (a) oraz narastanie i zanik polaryzacji orientacyjnej, jako efekt przyłożenia do próbki zmiennego pola elektrycznego (b).

Jak wspomniano, w trakcie pomiaru do próbki przykładana się pole mierzące (stała amplituda i zmienna częstotliwość). Po przyłożeniu do próbki zmiennego napięcia elektrycznego $U^*(f)$, przez próbkę popłynie prąd o zmiennym natężeniu $I^*(f)$. Wielkości pozwalają wyznaczyć impedancję $Z^*(f)$:

$$Z^*(f) = \frac{U^*(f)}{I^*(f)} = Z'(f) + iZ''(f), \quad (25)$$

która jest związana z zespoloną przenikalnością dielektryczną

$$\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f), \quad (26)$$

relacją:

$$\epsilon^*(f) = -\frac{i}{2\pi f C_0 Z^*(f)}, \quad (27)$$

gdzie i – jednostka urojona, f – częstotliwość zastosowanego sygnału, $C_0 = \epsilon_0 S/d$ – pojemność pustej komórki (kondensatora), ϵ_0 – przenikalność dielektryczna próżni, d – odległość między okładkami, S – pole powierzchni elektrod. Zatem znając parametry geometryczne kondensatora pomiarowego oraz zmierzone wartości impedancji, można wyznaczyć część rzeczywistą (dyspersję dielektryczną) i urojoną (absorpcję dielektryczną) przenikalności dielektrycznej poprzez rozwiązanie dla każdej częstotliwości układu równań:

$$Z'(f) = \frac{1}{2\pi f C_0} \frac{\epsilon''(f)}{\epsilon'(f)^2 + \epsilon''(f)^2}, \quad Z''(f) = -\frac{1}{2\pi f C_0} \frac{\epsilon'(f)}{\epsilon'(f)^2 + \epsilon''(f)^2}, \quad (28)$$

Stosunek absorpcji do dyspersji dielektrycznej nazywa się tangensem kąta strat dielektrycznych $\tan \delta$:

$$\tan \delta(f) = \frac{\epsilon''(f)}{\epsilon'(f)}. \quad (29)$$

Wartość δ jest przesunięciem fazowym między przyłożonym zewnętrznym polem elektrycznym E a indukcją elektryczną D w próbce:

$$\epsilon^*(f) = \frac{D(t)}{\epsilon_0 E(t)} = \frac{D_0 \exp(i(2\pi f t - \delta))}{\epsilon_0 E_0 \exp(i2\pi f t)}, \quad (30)$$

gdzie E_0 i D_0 są odpowiednio amplitudami zewnętrznego pola elektrycznego i indukcji elektrycznej w próbce.

Istnieje wiele modeli opisujących relaksacje występujące w różnego rodzaju materiałach. Model Debye'a opisuje relaksację wszystkich składowych układu z jednym czasem relaksacji τ_D :

$$\epsilon^*(f) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + 2\pi f i \tau_D} \text{ model Debye'a} \quad (31)$$

$$\epsilon'(f) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (2\pi f \tau_D)^2} \quad \epsilon''(f) = \frac{2\pi f \tau_D (\epsilon_s - \epsilon_\infty)}{1 + (2\pi f \tau_D)^2} + \frac{\sigma_{DC}}{2\pi f \epsilon_0} \quad (32)$$

gdzie ϵ_s i ϵ_∞ są przenikalnościami w granicy niskich i wysokich częstotliwości:

$$\text{jeżeli } f \rightarrow 0 \text{ to } \varepsilon' \rightarrow \varepsilon_s, \quad (33)$$

$$\text{jeżeli } f \rightarrow \infty \text{ to } \varepsilon' \rightarrow \varepsilon_\infty, \quad (34)$$

$$\text{jeżeli } 2\pi f\tau_D = 1 \text{ to } \varepsilon''_{\max} \equiv \varepsilon'' = \frac{1}{2}(\varepsilon_s - \varepsilon_\infty) = \frac{1}{2}\Delta\varepsilon. \quad (35)$$

Wartość częstotliwości $f_{\max}$, w której obserwuje się maksymalną wartość absorpcji jest związana z czasem relaksacji Debye'a τ_D :

$$\tau_D = \frac{1}{2\pi f_{\max}}. \quad (36)$$

Najogólniejszym modelem teoretycznym jest model Havriliak-Negami (HN):

$$\varepsilon^*(f) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (2\pi f i \tau_{HN})^{1-\alpha})^\beta} \text{ model Havriliak - Negami} \quad (37)$$

gdzie τ_{HN} – czas relaksacji Havriliak-Negami, α – parametr opisujący symetryczny rozkład czasów relaksacji, β – parametr opisujący asymetryczny rozkładu czasów relaksacji (współczynnik skośności). Zarówno α i β mogą przyjmować wartości z przedziału $[0,1]$. W zależności od specyfiki badanych materiałów model Havriliak-Negami może zostać uproszczony:

$$\text{gdy } \alpha = 0 \rightarrow \varepsilon^*(f) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + 2\pi f i \tau_{CD})^\beta} \text{ model Cole - Davidson'a,} \quad (38)$$

$$\text{gdy } \beta = 1 \rightarrow \varepsilon^*(f) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi f i \tau_{CC})^{1-\alpha}} \text{ model Cole - Cole'a,} \quad (39)$$

τ_{CD} – czas relaksacji Cole-Davidson'a, τ_{CC} – czas relaksacji Cole-Cole'a. Wartość czasu relaksacji dla powyższych modeli jest powiązana z parametrami rozkładu czasu relaksacji:

$$\tau_{CD} = \frac{1}{2\pi f_{\max}} \operatorname{tg} \frac{\pi}{2\beta + 2}, \quad (40)$$

$$\tau_{CC} = \frac{1}{2\pi f_{\max}}, \quad (41)$$

$$\tau_{HN} = \frac{1}{2\pi f_{\max}} \left(\sin \frac{\alpha\pi}{2\beta + 2} \right)^{1/\alpha} \left(\sin \frac{\alpha\beta\pi}{2\beta + 2} \right)^{-1/\alpha}. \quad (42)$$

Dla materiałów ciekłokrystalicznych pasma absorpcyjne są poszerzone symetrycznie, dlatego stosuje się model Cole-Cole'a do opisu relaksacji w tych materiałach. Poszerzenie pasm na poziomie molekularnym jest efektem różnic w lokalnym otoczeniu poszczególnych molekuł, różnej w czasie reakcji molekuł na pole zewnętrzne, oddziaływania pomiędzy poszczególnymi molekułami i różnego ułożenia ich długich osi względem kierunku linii pola elektrycznego (różne momenty bezwładności). Należy także podkreślić mnogość procesów relaksacyjnych występujących w materiałach ciekłokrystalicznych, dlatego w zależności od liczby obserwowanych relaksacji do zarejestrowanego widma dielektrycznego dopasowywany jest określony model w postaci sumy. W wyniku dopasowania otrzymuje się parametry procesu relaksacyjnego (częstość relaksacji, inkrement dielektryczny, parametr α). Prowadzenie pomiarów w funkcji temperatury pozwala na wyznaczenie temperaturowej zależności parametrów procesu relaksacyjnego i w konsekwencji jego interpretację.

Należy także zaznaczyć, że metoda spektroskopii dielektrycznej jest niezwykle czuła na obecność w badanym materiale swobodnych nośników ładunku, np. jonów, których obecność może wynikać z różnych przyczyn, a objawia się, jako gwałtowny wzrost wartości absorpcji ε'' w obszarze niskich częstotliwości. Taki pasożytniczy proces wpływa na jakość widm dielektrycznych, utrudniając uzyskanie rzeczywistych wartości czasów relaksacji. W takim przypadku, podczas dopasowania, do modelu relaksacji (tu Cole-Cole) dodawany jest człon związany z przewodnością elektryczną właściwą σ_{DC} (drugi człon w równaniu (32)).

W ramach niniejszej pracy pomiary prowadzono w funkcji temperatury w celu zbadania dynamiki molekularnej we wszystkich fazach ciekłokrystalicznych pojawiających się w danej próbce. Zastosowano taki sam typ komórek jak do pomiarów elektro-optycznych, jednak w celu obniżenia oporu warstwy przewodzącej oraz wyeliminowania pasożytniczych relaksacji od elektrod ITO, zastosowano komórki ze złotymi elektrodami o grubości ok. 5µm i powierzchni elektrod 0.25mm².

4.4.2. Metoda spektroskopii w zakresie nadfioletu i światła widzialnego

W metodzie spektroskopii UV-Vis stosuje się spektrofotometr, który wykorzystuje promieniowanie elektromagnetyczne w zakresie bliskiego ultrafioletu i światła widzialnego (od 200nm do 850nm). W wyniku pomiaru otrzymuje się widmo elektronowo-oscylacyjno-rotacyjne (tzw. widmo UV-Vis), które składa się z pasm absorpcyjnych. Kiedy próbka jest wystawiona na działanie promieniowania może dojść do zjawisk: transmisji promieniowania przez materiał, absorpcji, odbicia lub rozproszenia. Jeżeli energia padającego światła jest równa różnicy energii ΔE pomiędzy stanem podstawowym i wzbudzonym dojdzie do absorpcji [18]. Wzbudzenie elektronu ze stanu podstawowego do stanu wzbudzonego stanowi przejście elektronowe. Związek między różnicą energii ΔE i długością fali padającego światła λ jest dany wzorem Planck'a:

$$\Delta E = hf = h \frac{c}{\lambda}, \quad (43)$$

gdzie h – stała Planck'a, c – prędkość światła, f – częstotliwość fali padającego światła. Pasma absorpcyjne są wskaźnikiem struktury molekularnej próbki. W zależności od warunków środowiskowych i oddziaływań molekularnych będą się przesunąć (przesunięcie hipsochromowe/batochromowe). Obserwowane pasma absorpcyjne są szerokie, co wynika ze struktury oscylacyjnej i tak naprawdę przejście między dwoma stanami elektronowymi np. S_0-S_1 obejmuje wiele przejść na poziomie oscylacyjnym. Zatem z powodu dużej ilości podpoziomów i małych odstępów energetycznych między nimi, obserwuje się szerokie pasmo absorpcyjne a nie grzebiń podpoziomów. Zwykle spektrofotometr mierzy transmitancję T lub natężenie światła transmitowanego przez próbkę I_T . Wielkości te są powiązane relacją:

$$T = \frac{I_T}{I_P}, \quad (44)$$

gdzie I_P – natężenie światła padającego na próbkę. Związek między absorbancją A i transmitancją T jest następujący:

$$A = \log_{10} \left(\frac{I_P}{I_T} \right) = \log_{10} \left(\frac{1}{T} \right) = \log_{10}(T^{-1}) = -\log_{10} T. \quad (45)$$

Wraz ze wzrostem grubości próbki d fala świetlna oddziałuje z większą liczbą molekuł i natężenie światła przechodzącego I_T maleje w sposób wykładniczy według prawa Bouguer'a-Lambert'a:

$$I_T(d) = I_P \exp(-kd), \quad (46)$$

gdzie k – współczynnik absorpcji.

Metoda pozwoliła na określenie modyfikacji właściwości optycznych matrycy organicznej przez nanocząstki. Zbadano wpływ koncentracji domieszki i temperatury na pasma absorpcyjne (przesuwanie, zanik/pojawianie się nowych pasm) w zakresie długości fal 200-850nm. Określono zakres przezroczystości materiału, a więc długości nieabsorbowanych przez próbkę. Wszystkie pomiary przeprowadzono w modzie odbiciowym na próbkach stałych naniesionych na płytkach kwarcowych. Zaletą podkładów kwarcowych jest nieabsorbowanie światła w zakresie UV-Vis.

4.4.3. Metoda pomiaru skoku helisy

Skok helisy standardowo mierzy się metodą selektywnego odbicia światła przy użyciu spektrometru UV-Vis. Pomiar polega na rejestracji widma transmisji światła przez badaną próbkę, na którym obserwuje się minimum dla określonej długości fali. W wielu przypadkach układ spektrometru UV-Vis jest systemem tandemowym z mikroskopem polaryzacyjnym, pod którym umieszczona próbka jest zorientowana. W takiej geometrii oś helisy jest prostopadła do powierzchni szklanego podkładu, na którym jest umieszczona próbka i wpływ powierzchni podkładu jest znacznie mniejszy na strukturę helisy, co przekłada się na uzyskanie pomiarów o wyższej dokładności. Ograniczeniem tej metody jest zakres spektrometru.

Poprzez skok helisy p należy rozumieć odległość, w jakiej dyrektor rotuje o 360° . Charakterystyczną właściwością makroskopowej struktury helisy jest selektywne odbicie światła dla

dlugości fali λ_s proporcjonalnej do wartości skoku helisy p . Mając wyznaczone wartości długości fali w minimum transmitancji, wartość skoku helisy jest wyznaczana na podstawie zależności [19]:

$$\text{faza SmC}^* \rightarrow p = \frac{\lambda_s}{2n_{sr}}, \quad (47)$$

$$\text{fazy SmC}_V^*, \text{SmC}_A^*, \text{SmI}^* \rightarrow p = \frac{\lambda_s}{n_{sr}}, \quad (48)$$

gdzie n_{sr} – średni współczynnik załamania światła w pochyłonych fazach smektycznych (przyjmuje się 1,5).

Czasami jednak wartość skoku helisy wykracza poza zakres pomiarowy dostępnego spektrometru, wówczas można wyznaczyć skok helisy na podstawie analizy obrazu otrzymanego bezpośrednio z mikroskopu polaryzacyjnego. Takiego pomiaru dokonuje się dla swobodnej kropli na płycie szklanej. Obrazy interferencyjne rejestruje się zwykle podczas bardzo wolnego ochładzania materiału z fazy izotropowej, z zadaną szybkością zmian temperatury. Po ustabilizowaniu docelowej temperatury obserwuje się tworzenie prążków, których odległość odpowiada długości helisy. Wadą tej metody jest przesunięcie temperatur przejść fazowych ze względu na charakter pomiaru (swobodna kropla umieszczona na szkiełku laboratoryjnym jest ogrzewana tylko od dołu, bez górnej pokrywy) oraz często słaba jakość uzyskanych prążków.

Pomiar skoku helisy wykonano w celu określenia wpływu domieszki na parametry helisy smektycznej matrycy organicznej.

4.4.4. Metoda spektroskopii Ramana

W metodzie spektroskopii Ramana próbka jest oświetlana monochromatycznym promieniowaniem z zakresu Vis lub UV a bada się widmo promieniowania rozproszonego (nieelastycznego rozpraszania fotonów), tzw. widmo Ramana. W widmie tym można zaobserwować trzy rodzaje pasm: Raileghy'a, stokesowskie oraz antystokesowskie. Do słabego oddziaływania promieniowania z molekułami dochodzi nawet, gdy częstotliwość tego promieniowania nie odpowiada odległości pomiędzy poziomami energetycznymi. Składowa elektryczna zmiennego pola elektromagnetycznego o częstotliwości f_0 indukuje w molekułach moment dipolowy ζ , który jest proporcjonalny do natężenia pola elektrycznego E i podatności chmury elektronowej molekuly na odkształcenie, tj. polaryzowalności α :

$$\zeta = \alpha E \rightarrow E = E_0 \cos(2\pi f_0 t), \quad (49)$$

gdzie E_0 – amplituda natężenia pola elektrycznego, t – czas. Łącząc powyższe wzory, otrzymuje się wyrażenie na drgania dipola elektrycznego z częstotliwością f_0 :

$$\zeta = \alpha E_0 \cos(2\pi f_0 t). \quad (50)$$

Taki drgający dipol elektryczny staje się źródłem promieniowania o częstotliwości f_0 , które jest wypromieniowanie z próbki we wszystkich możliwych kierunkach (rozproszenie elastyczne Rayleigha). W trakcie drgania zmiana geometrii molekuly może spowodować okresowe zmiany polaryzowalności:

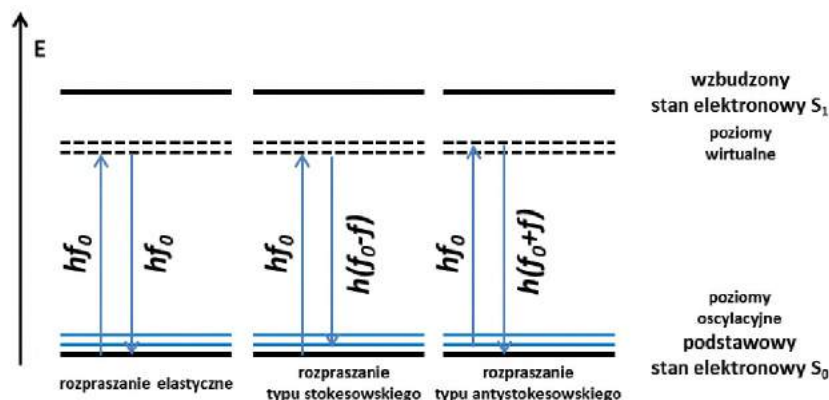
$$\alpha(x) = \alpha_0 + \left(\frac{d\alpha}{dx}\right)x \rightarrow x = x_0 \cos(2\pi f t), \quad (51)$$

gdzie α_0 – polaryzowalność w stanie równowagi, x – wychylenie od stanu równowagi, x_0 – maksymalne wychylenie ze stanu równowagi. Po przekształceniach otrzymuje się relację opisującą zmianę indukowanego momentu dipolowego molekuly w czasie:

$$\zeta = \alpha_0 E_0 \cos(2\pi f_0 t) + \frac{1}{2} x_0 E_0 \left(\frac{d\alpha}{dx}\right) (\cos(2\pi(f_0 - f)t) + \cos(2\pi(f_0 + f)t)). \quad (52)$$

Bazując na powyższej relacji Placzka widać, że jeżeli podczas drgania molekuly pochodna polaryzowalności nie jest równa 0, to zostaną zarejestrowane trzy składowe promieniowania rozproszonego o częstotliwościach f_0 (Rayleigha), $f_0 + f$ (składowa antystokesowska) i $f_0 - f$ (składowa stokesowska) (Rys. 9) [20]. Odnotowana różnica energii kwantu jest zużyta na wzbudzenie

oscylacyjno-rotacyjne molekuly. Odległość składowej stokesowskiej i antystokesowskiej od składowej Rayleigh'a odpowiadają częstotliwościom z zakresu IR.



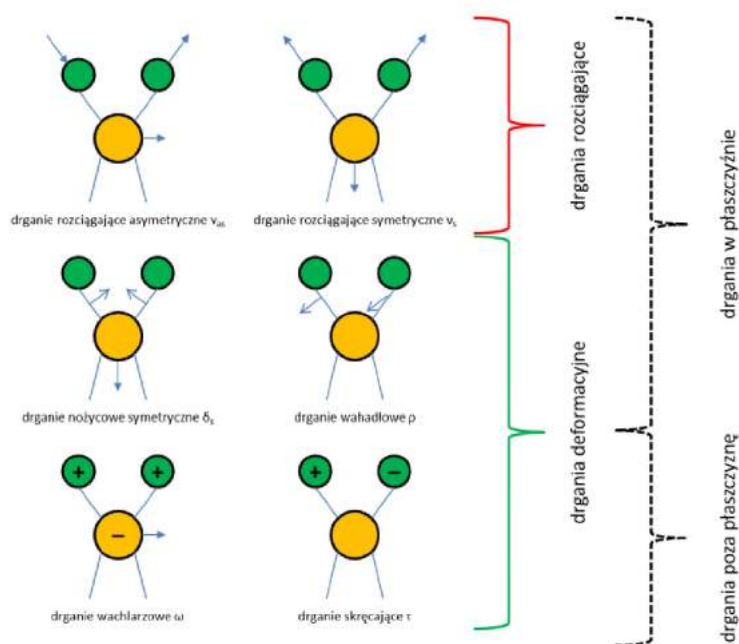
Rys. 9 Schemat poziomów energetycznych i przejść między nimi wraz z podziałem na typy rozpraszania.

Spektroskopię Ramana zastosowano do określenia elektrycznego charakteru domieszki (submikrocząstek i nanocząstek BaTiO₃). Bazując na położeniach pasm antystokesowskich, takiej samej liczbie pasm dla obu typu domieszek i widmach z baz danych stwierdzono, że oba typy domieszek BaTiO₃ krystalizują w układzie tetragonalnym, zatem są ferroelektryczne. Podczas pomiarów rejestrowano promieniowanie rozproszone przez próbkę pod kątem 90° względem wiązki światła padającego i promieniowania przepuszczonego przez próbkę. Próbkę były w postaci proszku, pomiary prowadzono w temperaturze pokojowej.

4.4.5. Metoda spektroskopii w podczerwieni z transformacją Fourier'a

Metoda spektroskopii absorpcyjnej w podczerwieni (IR) jest metodą spektroskopową, w której stosuje się promieniowanie elektromagnetyczne w zakresie podczerwieni właściwej (4000-700cm⁻¹, 2,5-14,3μm). W tym zakresie promieniowania występują drgania cząsteczek tj. przejścia oscylacyjno-rotacyjne. Absorpcja w zakresie IR powoduje zmiany energii rotacyjnej i oscylacyjnej molekuly. Ze względu na duże różnice energetyczne między poziomami oscylacyjnymi w stosunku do rotacyjnych, widmo IR jest zdominowane przez pasma oscylacyjne a wzbudzenia rotacyjne odpowiadają za poszerzenie tych pasm.

Do opisu ruchu każdego z atomów, jakie tworzą molekulę N-atomową, konieczne jest użycie trzech współrzędnych, zatem taka molekuła ma 3N stopni swobody. Molekulę nieliniową można traktować, jako układ 3N-6 oscylatorów anharmonicznych, nie są to proste oscylatory dwuatomowe, ale reguły kwantowania energii i wyboru się do nich stosują. Poszczególne atomy molekuly wykonują złożone ruchy, jako wypadkowa oscylacji wszystkich 3N-6 oscylatorów, które rozkłada się na 3N-6 drgań normalnych. Każde drganie ma charakterystyczną częstotliwość i jest niezależne. Drgania normalne dzieli się na: rozciągające (zmiana długości wiązań chemicznych: ν) i deformacyjne (zmiana kątów między wiązaniami chemicznymi: γ , δ , ρ , ω , τ), a także na drgania w płaszczyźnie i poza płaszczyzną oraz drgania symetryczne i asymetryczne grup atomów (Rys. 10) [20]. Zwykle pasma absorpcyjne dla konkretnego ugrupowania atomów występują w wąskim przedziale częstotliwości, co umożliwia identyfikację grup funkcyjnych w badanym materiale. Jeżeli wiązania oscylują ze zbliżoną częstotliwością i są połączone wspólnym atomem dochodzi do sprzężenia mechanicznego i w widmie podczerwonym otrzymuje się dwa pasma o częstotliwości niższej i wyższej od charakterystycznych częstotliwości grupowych. Obecne w molekulach grupy funkcyjne czy inne charakterystyczne ugrupowania atomów zwykle absorbują promieniowanie podczerwone w wąskim zakresie częstotliwości. Ze względu na mnogość możliwych przejść na poziomie oscylacyjnym i rotacyjnym, otrzymane widma są skomplikowane i są typowym odciskiem palca danego związku chemicznego.



Rys. 10 Podział drgań normalnych.

W spektrometrach z transformacją Fourier'a (FTIR) próbkę oświetla się wiązką o szerokim spektrum częstotliwości i nieodzownym elementem jest interferometr Michelson'a, z którego wiązka po interferencji jest kierowana na kuwetę pomiarową i trafia do detektora. Natężenie wiązki po wyjściu z interferometru $I(x)$ zależy od różnicy długości drogi optycznej x oraz długości fali promieniowania λ :

$$I(x) = \frac{1}{2} I_0 \left(1 + \cos \left(2\pi \frac{x}{\lambda} \right) \right) = \frac{1}{2} I_0 (1 + \cos(2\pi\nu)), \quad (53)$$

gdzie I_0 – natężenie wiązki wchodzącej do interferometru Michelson'a, ν – liczba falowa. Na podstawie powyższego wzoru widać, że jeżeli $x = 0$, to natężenie wiązki wchodzącej i wychodzącej jest takie samo dla wszystkich długości fali. Natomiast, gdy $x \neq 0$ i jest spełniony warunek $x = 2n\lambda$ to dochodzi do interferencji konstruktywnej, a gdy $x = (n + 1/2)\lambda$ dochodzi do interferencji destruktywnej. Zatem na interferogramie (energia docierająca do detektora w zależności od położenia lustra ruchomego interferometru Michelson'a) otrzymuje się na przemian minima i maksima natężenia. Ponieważ interferogramy są w domenie położenia lustra ruchomego (domena długości), dlatego wykonuje się transformację Fourier'a:

$$I(\nu) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi x \nu) dx. \quad (54)$$

Oprogramowanie przeprowadza transformację Fourier'a dla wiązki porównawczej i pomiarowej i po otrzymaniu natężeń w domenie liczby falowej otrzymuje się widmo transmisyjne. Aby poprawić stosunek sygnału do szumu, zebrane widmo jest skanowane n razy, interferogramy są sumowane i wtedy ten stosunek jest $n^{1/2}$ większy.

Spektroskopię FTIR zastosowano do określenia wpływu domieszki na oscylacyjne pasma absorpcyjne tj. zaniku/pojawienia nowych pasm (związane z powstaniem nowego wiązania chemicznego między molekułami matrycy i domieszki) i przesunięcia/poszerzenia wybranych pasm. Próbkę do pomiarów były w postaci pastylki wytworzonej poprzez sprasowanie pod dużym ciśnieniem mieszaniny badanego materiału oraz sproszkowanego bezwodnego KBr (niska absorpcja w zakresie IR). Badania prowadzono w funkcji temperatury.

4.5. Metoda dyfrakcji rentgenowskiej

W metodzie dyfrakcji rentgenowskiej na badaną próbkę pada monochromatyczne promieniowanie rentgenowskie i rejestruje się obrazy dyfrakcyjne tego promieniowania pod zmieniającym się kątem. Promieniowanie rentgenowskie obejmuje widmo elektromagnetyczne między promieniowaniem gamma i UV, w granicach 10^{-12} - 10^{-8} m (0,01-10 Å), ale typowo do pomiarów dyfrakcyjnych używa się fal w granicach 0,2-2,5 Å. Źródłem promieniowania rentgenowskiego są lampy rentgenowskie, które dają promieniowanie polichromatyczne (ciągłe) i charakterystyczne (o ściśle określonych długościach fali). W dyfrakcji rentgenowskiej wykorzystuje się promieniowanie charakterystyczne, które składa się z kilku linii i stosuje się monochromatory (np. filtr Ni). Do detekcji obrazów dyfrakcyjnych używa się detektorów pozycyjnych [21].

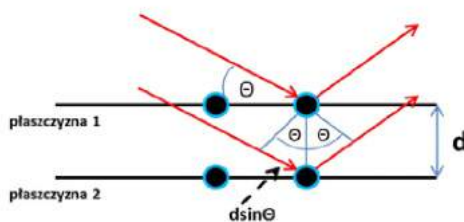
W podejściu Bragg'a-Wulf'a kierunki promieni rentgenowskich, wychodzących z atomów są traktowane, jako kierunki selektywnego interferencyjnego odbicia od kolejnych płaszczyzn sieciowych. Gdy na rodzinę płaszczyzn sieciowych o wskaźnikach Miller'a (hkl) odległych od siebie o d (odległość międzypłaszczyznowa) pada monochromatyczna wiązka promieni pod kątem θ , to następuje odbicie od każdej płaszczyzny (Rys. 11). Między dwoma promieniami odbitymi od sąsiednich płaszczyzn powstaje różnica dróg optycznych równa $2d\sin(\theta)$. Podczas interferencji promieni odbitych, dochodzi do wzmocnienia wtedy i tylko wtedy, gdy różnica dróg optycznych jest równa całkowitej wielokrotności długości fali:

$$2d\sin(\theta) = n\lambda, \quad (55)$$

gdzie n – rząd odbicia (liczba całkowita). Zatem znając długość fali padającego promieniowania oraz kąt padania na płaszczyzny sieciowe można otrzymać odległość międzypłaszczyznową. W doświadczeniu mierzony jest kąt 2θ między wiązką ugiętą i przedłużeniem wiązki padającej. Promienie o określonej długości fali λ zostają odbite od równoległych płaszczyzn (hkl) pod kątami θ_1 , θ_2 itd.. Zjawisko dyfrakcji promieni rentgenowskich zachodzi, gdy długość fali λ jest rzędu wielkości odległości międzypłaszczyznowej d :

$$\sin(\theta) = \frac{n\lambda}{2d} \leq 1. \quad (56)$$

Dla pierwszego rzędu odbicia $n = 1$ i $\lambda \leq 2d$. Dla długości fali większych niż $2d$, odbicie nie zachodzi.



Rys. 11 Ugięcie promieni rentgenowskich padających na próbkę od sąsiadujących płaszczyzn sieciowych.

Dla fazy krystalicznej, w jakiej istnieje porządek pozycyjny dalekiego zasięgu, pojawiające się refleksy są wąskie. Natomiast dla faz ciekłokrystalicznych z uporządkowaniem warstwowym, takich jak np. SmA*, SmC* występuje jedynie uporządkowanie quasi-dalekiego zasięgu, co przejawia się w postaci szerszych refleksów oraz szerokiego maksimum dyfuzyjnego. Wyróżnić można refleks dyfrakcyjny związany z grubością warstw smektycznych D ($q_D = 2\pi/D$, gdzie q_D – długość wektora rozpraszania dla refleksu niskokątowego). Ten refleks opisuje znormalizowana funkcja natężenia $I(q)$ w postaci $I(q) \sim (q - q_D)^{\eta-2}$, gdzie wykładnik η zależy m.in. od temperatury, natomiast q jest długością wektora rozpraszania, powiązanym z kątem 2θ wzorem:

$$q = \frac{4\pi\sin(\theta)}{\lambda}. \quad (57)$$

Maksima dyfuzyjne mają kształt opisywany funkcją Lorentz'a $I(q) \sim 1/(1 + (q-q_d)^2 \xi^2)$. Położenie tego maksimum zależy od średniej odległości między molekułami d ($d = 2\pi/q_d$). Z kolei szerokość połówkowa tego refleksu jest odwrotnie proporcjonalna do długości korelacji ξ .

Dyfrakcję rentgenowską zastosowano do określenia wpływu domieszki na grubość warstw smektycznych, długości korelacji i proces krystalizacji.

4.6. Metoda różnicowej kalorymetrii skaningowej

Metoda różnicowej kalorymetrii skaningowej pozwala na wyznaczenie temperatur przejść fazowych oraz związanych z nimi efektów cieplnych. Zaletą jej jest niewielka ilość substancji potrzebna do przeprowadzenia pomiaru zarówno podczas ogrzewania jak i ochładzania, w szerokim zakresie temperatur z zastosowaniem dowolnych szybkości zmian temperatury. Do pomiarów wykorzystano kalorymetr pracujący w trybie kompensacyjnym, w którym znajdują się dwie odizolowane od siebie i otoczenia komory: na próbkę referencyjną (puste naczynie pomiarowe) i próbkę badaną. W dnie każdej komory znajduje się grzałka elektryczna i układ do pomiaru temperatury. Materiały do badań odważano w naczyniach aluminiowych (30 μ l) oraz szczelnie zamykano za pomocą prasy, co zapewniało idealnie płaskie dno (ważne z punktu widzenia wymiany ciepła). Zasada działania takiego kalorymetru polega na pomiarze różnicy mocy elektrycznej dostarczanej do obu komór, przy takiej zmianie temperatury, że temperatury próbki referencyjnej oraz badanej są identyczne w każdym momencie pomiaru. Podczas przemiany fazowej w próbce, nastąpi chwilowa różnica temperatur między nią i próbką odniesienia, która natychmiast jest kompensowana przez zmianę mocy elektrycznej odpowiedniej grzałki, co jest rejestrowane przez oprogramowanie. Efektem pomiaru jest krzywa kalorymetryczna, czyli zależność tej różnicy mocy od temperatury. Podczas przemiany fazowej I-go rodzaju na krzywej pojawia się anomalia związana z istnieniem ciepła utajonego a dla przemian typu zeszklenie/odszklenie pojawia się stopień [22,23]. Temperatura początku przejścia T_o jest traktowana, jako temperatura przemiany fazowej, natomiast pole pod anomalią reprezentującą przejście fazowe jest związane ze zmianą entalpii:

$$\Delta H = \int_{T_1}^{T_2} \frac{1}{m} \frac{dP}{dT} dt dT = \int_{T_1}^{T_2} \frac{1}{mv} \frac{dP}{dT} dT, \quad (58)$$

gdzie m – masa próbki badanej, dP/dt różnica mocy cieplnych dostarczanych w określonym czasie do obu próbek, v – określa szybkość zmiany temperatury w czasie.

4.7. Metody termo-optyczne

4.7.1. Metoda pomiaru intensywności światła transmitowanego

Ze względu na dwójłomność badanych materiałów, płaszczyzna polaryzacji światła po przejściu przez próbkę ulega skręceniu i w konfiguracji skrzyżowanych polaryzatorów (płaszczyzny polaryzacji polaryzatora oraz analizatora są skręcone o 90°) część padającego światła jest przepuszczona przez analizator. Podczas pomiaru intensywności światła transmitowanego przez próbkę, badana próbka jest oświetlana światłem białym o stałym natężeniu. Intensywność światła transmitowanego zmienia się wraz ze zmianą ułożenia molekuł, zatem zmiana tej intensywności w określonej temperaturze będzie wskazywać przejście fazowe. Metoda polega na rejestracji za pomocą detektora i uśrednianiu (np. po 10ms) intensywności światła transmitowanego w określonej temperaturze. Ze względu na prostotę metody i szybkość zbierania danych oraz automatyzację pomiarów, interwały temperaturowe mogą być bardzo małe (typowo 0.1-0.5°C), co jest bardzo istotne, gdy fazy występują w bardzo wąskim zakresie temperatur. Celem tej metody jest wyznaczenie temperatur przejść fazowych II-go rodzaju, co jest zwykle trudne innymi metodami, np. metodą różnicowej kalorymetrii skaningowej. Intensywność światła transmitowanego silnie zależy od nawet małych zmian strukturalnych (dobrym przykładem jest przejście fazowe SmC*-SmC*_α, gdzie obie

fazy wykazują spiralne ułożenie molekuł, jednak różnica jest w skoku spirali). Subtelne zmiany obrazów interferencyjnych zwykle są bardzo trudne do zauważenia ludzkim okiem, zatem metoda TLI stanowi bardzo dobrą alternatywę.

Badania prowadzono na próbkach umieszczonych w komórkach ITO, tych samych, co do badań elektro-optycznych, zarówno podczas ogrzewania jak i ochładzania.

4.7.2. Metoda pomiaru kąta zwilżania

Metoda pomiaru kąta zwilżania składa się z dwóch kroków: zarejestrowania kropli na badanej powierzchni oraz analiza tej kropli. Kąt zwilżania to kąt mierzony w punkcie, w którym linia bazowa (pozioma linia reprezentująca powierzchnię, na którą naniesiono kroplę) spotyka się z krawędzią kropli (wyznaczoną automatycznie zaimplementowanym w oprogramowaniu algorytmem) [24]. Określa się nachylenie stycznej do krawędzi kropli w tym punkcie, jako $\tan\theta_{CA}$, z którego wyznacza się wartość kąta zwilżania θ_{CA} . Możliwość pomiaru kąta zwilżania związana jest z napięciem powierzchniowym. Ilościowo napięcie powierzchniowe jest związane z pracą potrzebną do wytworzenia jednostkowej powierzchni cieczy i zgodnie z definicją jest to siła styczna do powierzchni, działająca na jednostkę długości powierzchni:

$$\gamma = \frac{F}{l}, \quad (59)$$

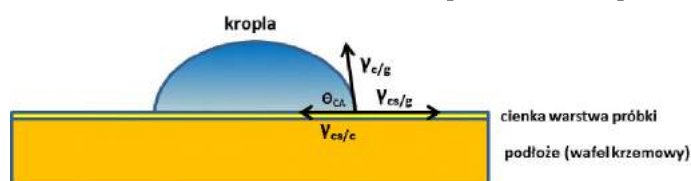
gdzie γ – napięcie powierzchniowe, F – siła napięcia powierzchniowego działająca równolegle do powierzchni, l – długość, na jakiej działa siła. Gdy kropla jest w kontakcie z powierzchnią ciała stałego, powstają trzy granice fazowe: ciało stałe-ciecz, ciało stałe-gaz (zwykle powietrze) oraz ciecz-gaz. Rys. 12 prezentuje diagram sił dla punktu, w którym krawędź kropli styka się z powierzchnią próbki (ciałem stałym). Strzałki reprezentują siły wywierane przez napięcia powierzchniowe na trzech granicach faz: ciecz-ciało stałe $\gamma_{cs/c}$, ciecz-gaz $\gamma_{c/g}$ i ciało stałe-gaz $\gamma_{cs/g}$. Jeżeli kropla jest w równowadze to siły się równoważą:

$$\gamma_{cs/c} + \cos\theta_{CA}\gamma_{c/g} = \gamma_{cs/g}, \quad (60)$$

$$\cos\theta_{CA} = \frac{\gamma_{cs/g} - \gamma_{cs/c}}{\gamma_{c/g}}. \quad (61)$$

Bazując na powyższym równaniu można wyciągnąć wnioski:

- gdzie $\gamma_{cs/g} > \gamma_{cs/c}$ wartość $\cos\theta_{CA} > 0$ i $\theta_{CA} < 90^\circ$ (kropla zwilża próbkę),
- gdzie $\gamma_{cs/g} < \gamma_{cs/c}$ wartość $\cos\theta_{CA} < 0$ i $\theta_{CA} > 90^\circ$ (kropla nie zwilża próbki).



Rys. 12 Rozkład sił dla punktu, w którym krawędź kropli styka się z powierzchnią próbki.

W celu wykonania pomiarów kąta zwilżania w pierwszym kroku przygotowano krzemowe podkłady. Wafle krzemowe o rozmiarach ok. 1x2cm oczyszczono w izopropanolu w łaźni wodnej z użyciem myjki ultradźwiękowej przez około 10min i przedmuchano sprężonym azotem w celu pozbycia się rozpuszczalnika oraz ewentualnych stałych zanieczyszczeń. Na przygotowane podkłady naniesiono badane materiały metodą odwirowania (ang. spin coating). Wytworzone w ten sposób cienkie warstwy umieszczano poziomo w komorze przystawki grzewczej. Powierzchnia badanej próbki wraz z nanoszonymi kroplami była przez cały czas trwania pomiarów oświetlona światłem białym oraz rejestrowana przez kamerę cyfrową. Badania prowadzono w funkcji temperatury: po osiągnięciu docelowej temperatury na powierzchnię próbki przez otwór w komorze dozowano pojedynczą kroplę wody destylowanej, wykonywano zdjęcie kropli a następnie ją analizowano.

5. Omówienie wyników badań

W niniejszym rozdziale przedstawione są najważniejsze wnioski płynące z przeprowadzonych badań, pogrupowane artykułami składającymi się na cykl prac, będący podstawą rozprawy doktorskiej. Artykuły uszeregowane są zgodnie z chronologią badań i ich publikacji.

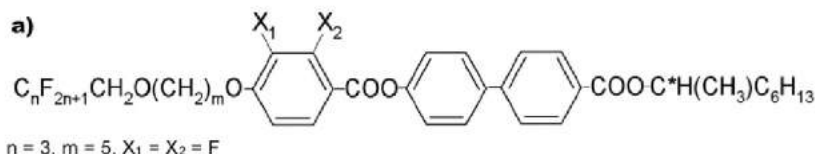
5.1. Systematyczne badania chiralnych faz smektycznych fluorowanego związku

Systematic study of the chiral smectic phases of a fluorinated compound

(Artykuł I)

S. Lalik, A. Deptuch, P. Fryń, T. Jaworska-Goląb, D. Dardas, D. Pociecha, M. Urbańska, M. Tykarska, M. Marzec

Liquid Crystals, 46(15), 2256-2268 (2019), DOI: 10.1080/02678292.2019.1622044.



Artykuł prezentuje badania podstawowe nowego materiału ciekłokrystalicznego 3F5FPhF (z szeregu homologicznego o akronimie nFmX₁PhX₂), który wykazuje bardzo szeroki zakres antyferroelektrycznej fazy SmC*_A oraz wąski zakres temperaturowy obejmujący inne fazy, w tym rzadko spotykaną pod-fazę SmC*_α. Związek stanowiący podstawę tego artykułu jest nierozdzielnie związany z tematem pracy doktorskiej, ponieważ wchodzi w skład dwuskładnikowej mieszaniny zastosowanej, jako matryca organiczna do domieszkowania submikro- i nanocząstkami BaTiO₃ (Artykuł II). Do najważniejszych wniosków płynących z tej pracy należą:

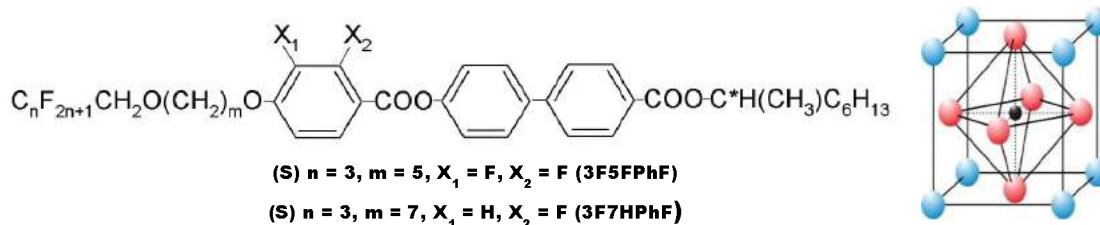
- Ciekły kryształ 3F5FPhF, oprócz szerokiego zakresu antyferroelektrycznej fazy SmC*_A, wykazuje fazę paraelektryczną SmA*, ferroelektryczną SmC* oraz, w bardzo wąskim zakresie temperaturowym, pod-fazę SmC*_α. Wszystkie zidentyfikowane fazy są enancjotropowe.
- Ze względu na wbudowanie w molekułę 3F5FPhF fluoru, zarówno w łańcuchu alifatycznym jak i jednym z pierścieni benzenowych, zarejestrowano bardzo duże wartości spontanicznej polaryzacji, dochodzące nawet do około 300 nC/cm². Z kolei wartość kąta pochylenia molekul osiąga wartość około 41° a czas przełączania wynosi poniżej 500 μs w temperaturze pokojowej.
- Związek 3F5FPhF wykazuje bardzo silne przechłodzenie fazy antyferroelektrycznej, obserwuje się przesunięcie temperatury przejścia fazowego SmC*_A-Cr w kierunku niskich temperatur o około 30°C w stosunku do przejścia Cr-SmC*_A.
- W obszarze antyferroelektrycznej fazy SmC*_A wraz z obniżaniem temperatury następuje zmniejszanie grubości warstw smektycznych do około 60°C, po czym ustala się grubość i wynosi ok. 30.5 Å.
- Trzy procesy relaksacyjne występują w antyferroelektrycznej fazie SmC*_A: dwa kolektywne fazony P_H i P_L oraz jeden molekularny – proces s (reorientacja wokół osi krótkiej molekuły), natomiast w ferroelektrycznej fazie SmC* i pod-fazie SmC*_α zidentyfikowano dwa procesy kolektywne: jeden amplitudon (proces miękki) i jeden fazon (proces Goldstone'a), w paraelektrycznej fazie SmA* tylko proces miękki.

5.2. Modyfikacja właściwości fizycznych AFLC poprzez domieszkowanie cząstkami BaTiO₃

Modification of AFLC physical properties by doping with BaTiO₃ particles

(Artykuł II)

S. Lalik, A. Deptuch, T. Jaworska-Goląb, P. Fryń, D. Dardas, O. Stefańczyk, M. Urbańska, M. Marzec
Journal of Physical Chemistry B, 124(28), 6055–6073 (2020), DOI: 10.1021/acs.jpcb.0c02401.



Artykuł prezentuje wpływ małych koncentracji zarówno submikrocząstek (280nm, 0.75%wag.) jak i nanocząstek (45nm, 0.50%wag.) na właściwości matrycy organicznej będącej mieszaniną ciekłych kryształów z jednego szeregu homologicznego 3FmXPhF (3F5FPhF i 3F7HPhF), wykazującą fazę antyferroelektryczną SmC*_A w szerokim zakresie temperatur. Zarówno cząstki o średnicy 45nm, jak i 280nm wykazywały właściwości ferroelektryczne. Do najważniejszych wniosków płynących z tej pracy należą:

- Domieszka nie wpływa na sekwencję fazową kompozytów, ale temperatury przejść fazowych zostały obniżone i pojawiła się dwuetapowa krystalizacja, bez względu na średnicę domieszki.
- Zmiany na obrazach interferencyjnych (teksturach): domieszka ma tendencję do aglomeracji w przecięciach ścianach domenowych (defekty), co powoduje obniżanie energii swobodnej tych defektów.
- Następuje obniżenie progu napięciowego dla kompozytu z domieszką nanocząstek (45nm) oraz spadek wartości spontanicznej polaryzacji bez względu na rozmiar domieszki, co jest najprawdopodobniej efektem antyrównoległego uporządkowania momentów dipolowych molekuł ciekłego kryształu oraz domieszki, z jednoczesnym pułapkowaniem pasożytniczych jonów. Zjawisko to jest odpowiedzialne za wzrost pola lokalnego działającego na molekuly organiczne, co przekłada się na skrócenie czasu przełączania oraz obniżenie lepkości rotacyjnej.
- Zarówno grubość warstw smektycznych jak i kąt pochylenia molekuł w niskich temperaturach fazy antyferroelektrycznej SmC*_A nie zmienia się po domieszkowaniu, bez względu na rozmiar domieszki.
- Domieszka wyraźnie wpływa na parametry dielektryczne matrycy organicznej, w szczególności na częstość relaksacji i wartości absorpcji, obniża także przewodność elektryczną właściwą, a nie wpływa na energie aktywacji procesów relaksacyjnych w antyferroelektrycznej fazie SmC*_A.

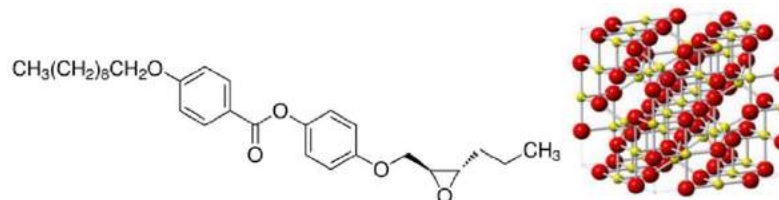
5.3. Modyfikacja właściwości fizycznych FLC poprzez domieszkowanie nanocząstkami Fe_2O_3 (część I)

Modifications of FLC physical properties through doping with Fe_2O_3 nanoparticles (part I)

(Artykuł III)

S. Lalik, O. Stefańczyk, D. Dardas, N. Górską, S.-i. Ohkoshi, M. Marzec

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Artykuł prezentuje wpływ małych koncentracji (0.3, 0.5, 0.7 i 0.9% wag.) nanocząstek maghemitu $\gamma\text{-Fe}_2\text{O}_3$ (średnica $< 50\text{nm}$, Sigma Aldrich) na właściwości organicznej matrycy będącej ciekłym kryształem EHPDB, wykazującym fazę ferroelektryczną SmC^* w szerokim zakresie temperatur. Dyskutowany jest zarówno pozytywny jak i negatywny wpływ zastosowania kwasu oleinowego, jako czynnika zapobiegającego aglomeracji nanocząstek w matrycy organicznej. Do najważniejszych wniosków płynących z tej pracy należą:

- W wyniku domieszkowania struktura krystaliczna matrycy EHPDB nie została zmieniona. Zarejestrowane dyfraktogramy dla nanokompozytów są zasadniczo takie same, jak dla czystej matrycy organicznej, a jedyną różnicą jest obecność refleksów o niskich intensywnościach pochodzących od maghemitu $\gamma\text{-Fe}_2\text{O}_3$. Morfologia powierzchni również nie została zmieniona po domieszkowaniu (bez kwasu oleinowego).
- Następuje przesuwanie temperatur przejść fazowych w kierunku niższych wartości, poszerzenie zakresu temperaturowego fazy SmA^* kosztem fazy SmC^* i zanik polimorfizmu w obszarze faz krystalicznych po domieszkowaniu matrycy organicznej.
- Domieszka powoduje pojawienie się prążkowania tekstury wachlarzowej fazy SmC^* .
- Wartości parametrów elektrycznych uległy dużym zmianom po wprowadzeniu nanocząstek do matrycy, odnotowano spadek wartości spontanicznej polaryzacji (nawet o ok. 50%), kąta pochylenia molekuł, czasu przełączania, lepkości rotacyjnej i dyspersyjnego współczynnika kotwiczenia molekuł, natomiast wzrósł skok helisy smektycznej.
- Zarejestrowana dodatkowa odpowiedź napięciowa dla nanokompozytów została przypisana obecności jonów wprowadzonych do matrycy razem z nanocząstkami.
- Nieco różną modyfikację właściwości ferroelektrycznej fazy SmC^* dla nanokompozytów o większej koncentracji nanocząstek $\gamma\text{-Fe}_2\text{O}_3$ wyjaśniono m.in. przez silny wpływ aglomeracji.
- Dodanie kwasu oleinowego znacznie zawężyło zakres temperaturowy faz ciekłokrystalicznych podczas ochładzania i spowodowało praktyczny ich zanik podczas ogrzewania, oraz spowodowało zmianę orientacji molekuł ciekłego kryształu z planarnej na homeotropową.

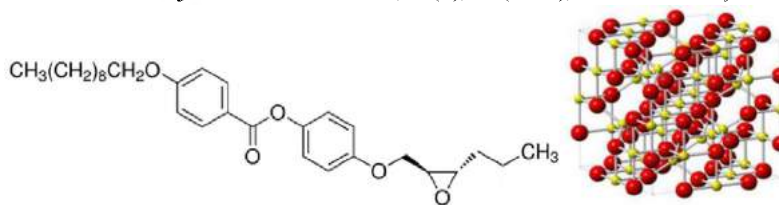
5.4. Modyfikacja właściwości fizycznych FLC poprzez domieszkowanie nanocząstkami Fe₂O₃ (część II)

Modifications of FLC physical properties through doping with Fe₂O₃ nanoparticles (part II)

(Artykuł IV)

S. Lalik, O. Stefańczyk, N. Górską, K. Kumar, S.-i. Ohkoshi, M. Marzec

International Journal of Molecular Sciences, 23(1), 50 (2022), DOI: 10.3390/ijms23010050.



Artykuł prezentuje wpływ małych koncentracji (0.3, 0.5, 0.7 i 0.9%wag.) nanocząstek maghemitu γ -Fe₂O₃ (średnica < 50nm, Sigma Aldrich) na właściwości organicznej matrycy będącej ciekłym kryształem EHPDB, wykazującym fazę ferroelektryczną SmC* w szerokim zakresie temperatur, i jest kontynuacją badań z Artykułu III. Do najważniejszych wniosków płynących z tej pracy należą:

- Występuje absorpcja światła w zakresie UV-Vis zarówno czystych jak i dekorowanych kwasem oleinowym nanocząstek γ -Fe₂O₃, a powyżej 750nm są one całkowicie transparentne.
- Bez względu na temperaturę oraz koncentrację domieszki, w zakresie 500-850nm wszystkie nanokompozyty są całkowicie transparentne. Wartości absorpcji przy wybranych długościach fali wykazują nieciągłości w temperaturach przejść fazowych z wyraźnym plateau w zakresie temperaturowym ferroelektrycznej fazy SmC*.
- Pojawienie się dodatkowych pasm absorpcyjnych w obszarze 350-600nm oraz spadek wartości absorpcji w zakresie UV po domieszkowaniu jest wynikiem obecności nanocząstek, które działają jak centra rozpraszające padające światło – ze wzrostem ich koncentracji, ilość centrów rozpraszania rośnie, zwiększając ilość rozpraszanego światła i zmniejszając absorpcję.
- Obecność nanocząstek w nanokompozytach jest odpowiedzialna za utrudnienie ruchu molekuł matrycy ciekłokrystalicznej i potrzebują one więcej czasu na reorientację, co powoduje zmniejszenie częstości relaksacji zarówno procesu molekularnego (reorientacja wokół krótkich osi molekuly) w fazie cholesterycznej N* jak i kolektywnego procesu Goldstone'a w ferroelektrycznej fazie SmC* (12-krotny wzrost czasu relaksacji).
- Dla nanokompozytów o największych koncentracjach nanocząstek (0.7 i 0.9%wag.), dodatkowy proces relaksacyjny w obszarze ferroelektrycznej fazy SmC* jest prawdopodobnie związany z ruchem nanocząstek w formie aglomeratów lub kolektywnym ruchem nanocząstek (lub ich aglomeratów) z otaczającymi je molekułami organicznymi i/lub swobodnymi jonami.
- Przewodność elektryczna właściwa rośnie wraz ze wzrostem koncentracji domieszki w całym zakresie częstotliwości.
- Ferromagnetyczne właściwości nanocząstek zostały zachowane w matrycy organicznej i w obszarze ferroelektrycznej fazy SmC* materiał jest dwufunkcyjny – wykazuje naturę ferroelektryczną (od fazy SmC*) i ferromagnetyczną (od nanocząstek). Ze wzrostem temperatury saturacja magnetyzacji nanokompozytu maleje, jako wynik większej energii termicznej, jaką nabywają nanocząstki. Z kolei wartość pola koercji zależy nie tylko od temperatury, ale także od koncentracji nanocząstek i jest większa dla nanokompozytów niż dla czystych nanocząstek. Zatem nanocząstki zanurzone w matrycy organicznej wymagają większego pola magnetycznego na wyzerowanie wartości magnetyzacji. Zastosowanie surfaktanta dodatkowo zwiększa wartość pola koercji i saturację magnetyzacji.
- W oparciu o szczegółową analizę w zakresie światła podczerwonego stwierdzono, że niektóre fragmenty matrycy organicznej, zawierające tlen, są wrażliwe na zmianę między molekularnych oddziaływań i/lub dynamikę molekularną z powodu obecności nanocząstek.

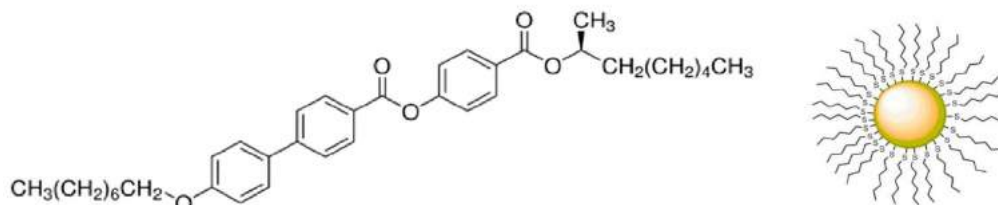
5.5. Nanokompozyty na bazie antyferroelektrycznego ciekłego kryształu (S)-MHPOBC domieszkowanego nanocząstkami Au

Nanocomposites based on antiferroelectric liquid crystal (S)-MHPOBC doping with Au nanoparticles

(Artykuł V)

S. Lalik, O. Stefańczyk, D. Dardas, A. Deptuch, T. Yevchenko, S.-i. Ohkoshi, M. Marzec

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Artykuł prezentuje wpływ małych koncentracji nanocząstek Au (0.2 i 0.5% wag.) na właściwości matrycy będącej ciekłym kryształem (S)-MHPOBC wykazującym fazę antyferroelektryczną SmC^*_A w szerokim zakresie temperatur. W tym przypadku nanocząstki złota były dekorowane pochodną tiolu i zdyspergowane w roztworze. Do najważniejszych wniosków płynących z tej pracy należą:

- Obrazy interferencyjne faz ciekłokrystalicznych SmA^* , SmC^*_α , SmC^* , SmC^*_γ , and SmC^*_A nie uległy zmianie, jednak z powodu dużej liczby defektów focal-conic nanocząstki Au akumulują w ich obszarze redukując energię swobodną tych defektów.
- Zahamowanie procesu krystalizacji wraz ze wzrostem koncentracji domieszki uwidoczniło się w postaci szerokiego zakresu temperaturowego współistnienia faz SmI^* oraz Cr_1 . Pojawił się także bogaty polimorfizm fazy krystalicznej po domieszkowaniu.
- Brak wpływu domieszki na sekwencję fazową oraz znikomy na temperatury przejść fazowych, ze znaczącym wpływem na zmiany entalpii w przejściach fazowych, szczególnie dla przejść Cr_4 - SmC^*_A oraz SmA^* -Is.
- Brak wpływu domieszki na grubość warstw smektycznych oraz wyraźny wzrost skoku helisy wytłumaczono lokalizacją większości nanocząstek między warstwami smektycznymi.
- Morfologia powierzchni cienkiej warstwy matrycy nie uległa zmianie po domieszkowaniu, jednak po wygrzaniu warstw w wysokich temperaturach zauważono pojawianie się nowych obiektów na powierzchni, co wytłumaczono aglomeracją dekorowanych nanocząstek pod wpływem wysokiej temperatury.
- Domieszka bardzo silnie zmodyfikowała wartość kąta zwilżania cienkich warstw (szczególnie w obszarze antyferroelektrycznej fazy SmC^*_A), co jest prawdopodobnie wynikiem zmian konformacyjnych łańcuchów surfaktantu. Jest to zatem prosta metoda na obniżenie zwilżalności powierzchni przez niewielkie koncentracje domieszki.
- Fluorescencja w zakresie światła zielonego i niebieskiego została wzmocniona wraz ze wzrostem koncentracji domieszki, a wzrost spontanicznej polaryzacji w obszarze wysokich temperatur fazy SmC^*_A jest wynikiem zlokalizowanego powierzchniowego rezonansu plazmonowego nanocząstek złota.

6. Podsumowanie

Jak wiadomo rozwój przemysłu stanowi siłę napędową do poszukiwania coraz bardziej wyrafinowanych, złożonych materiałów, które wykazywałyby dobrze określone właściwości. Alternatywą dla syntezy nowych związków jest domieszkowanie znanych układów, w tym ciekłokrystalicznych, komercyjnie dostępnymi materiałami o dobrze określonych właściwościach. Gwałtowny rozwój nanotechnologii na przestrzeni ostatnich kilku lat, oferuje bogactwo nanomateriałów, które mogą stanowić domieszkę do organicznej matrycy ciekłokrystalicznej. Stąd, badania w ramach rozprawy zostały ukierunkowane na syntezę układów hybrydowych (kompozytów) oraz badanie wpływu nanomateriałów na parametry matrycy ciekłokrystalicznej. Motywacją do podjęcia badań była niewielka ilość doniesień naukowych odnośnie modyfikacji za pomocą nanomateriałów związków ciekłokrystalicznych wykazujących ferroelektryczną fazę SmC^*_A oraz brak danych na temat modyfikacji antyferroelektrycznej fazy SmC^*_A .

W ramach niniejszej rozprawy wykonano badania podstawowe dla wybranych układów hybrydowych na bazie matryc organicznych wykazujących ciekłokrystaliczną fazę ferroelektryczną i/lub antyferroelektryczną domieszkowanych trzema rodzajami nanocząstek: ferroelektrycznymi, ferromagnetycznymi i o właściwościach plazmonicznych. Wybrano trzy matryce organiczne: mieszaninę dwóch homologów z szeregu 3FmXPhF (MIX: $3\text{F5FPhF}+3\text{F7HPhF}$) oraz dwa znane związki: ferroelektryczny EHPDB i antyferroelektryczny (S)-MHPOBC, na bazie których przygotowano kompozyty, których składy zaprezentowano w Tabeli 2.

Tabela 2. Składy przygotowanych i zbadanych kompozytów.

Matryca	Domieszka	Skład kompozytu
MIX	BaTiO_3 (45, 280nm)	Composite 1: 0.50%wag. 45nm Composite 2: 0.75%wag. 280nm
EHPDB	$\gamma\text{-Fe}_2\text{O}_3$ (<50nm)	Composite 1: 0.0%wag. Composite 2: 0.3%wag. Composite 3: 0.5%wag. Composite 4: 0.7%wag. Composite 5: 0.9%wag. Composite 6: 0.3%wag. + kwas oleinowy
(S)-MHPOBC	Au (2-4nm)	Composite 1: 0.0%wag. Composite 2: 0.2%wag. Composite 3: 0.5%wag.

W toku prowadzonych badań, okazało się, że proces domieszkowania matryc ciekłokrystalicznych nie jest zagadnieniem trywialnym, ze względu na liczne aspekty doświadczalne, jakie należy wziąć pod uwagę, np. higroskopijność, dobór odpowiednich koncentracji nanomateriału, dobór i ilość odpowiedniego rozpuszczalnika dla matrycy czy określenie objętości, z jakich wylewane są roztwory po procesie sonifikacji.

W ramach prowadzonych badań pokazano, że domieszkowanie matrycy ciekłego kryształu wykazującej ferroelektryczną fazę SmC^* i/lub antyferroelektryczną SmC^*_A jest bardzo obiecującą alternatywą, dzięki której w prosty sposób można otrzymać materiał o nowych, pożądanych właściwościach. Na podstawie otrzymanych wyników, stwierdzono, że zastosowane domieszki i ich koncentracje w sposób wybiórczy wpływają na właściwości fizyczne matrycy ciekłokrystalicznej, modyfikując część z nich a inne pozostawiając bez zmian. Do najważniejszych wniosków płynących z niniejszej pracy należą:

- ✓ Domieszka BaTiO_3 o dwóch różnych rozmiarach ziaren (45 i 280nm) spowodowała pozbycie się z ośrodka organicznego swobodnych jonów, które są pułapkowane blisko domieszki przez silne pole elektryczne będące wynikiem elektrycznego momentu dipolowego submikro- oraz nanocząstek BaTiO_3 . Zaobserwowana redukcja koncentracji swobodnych jonów zmodyfikowała takie parametry jak lepkość, dwójłomność, przenikalność dielektryczną oraz spontaniczną polaryzację i czas przełączania matrycy organicznej.

- ✓ Poprzez kontrolę koncentracji nanocząstek maghemitu $\gamma\text{-Fe}_2\text{O}_3$ w matrycy ferroelektrycznego ciekłego kryształu EHPDB otrzymano nowe materiały o zmodyfikowanych właściwościach względem matrycy. Należy jednak zaznaczyć, że dla tak małych koncentracji nanocząstek, modyfikacja określonej właściwości może być wypadkową kilku różnych efektów (w tym oddziaływania typu molekula-molekula, molekula-nanocząstka, nanocząstka-nanocząstka, nanocząstka-elektroda). Pokazano także, że kwas oleinowy (surfaktant do dekoracji nanocząstek) zapobiega procesowi aglomeracji nanocząstek, powodując ich lepszą homogeniczność w matrycy (co zwiększa m.in. pole koercji M_R , obniża magnetyzację saturacji M_s), jednak ma negatywny wpływ na temperatury przejść fazowych, przyczyniając się ostatecznie do zawężenia zakresu temperaturowego ciekłokrystalicznej fazy SmC^* .
- ✓ Pokazano, że nanocząstki Au wpływają zarówno na fluorescencję jak i hydrofobowość warstwy matrycy ciekłokrystalicznej, powodując ich wzrost wraz ze wzrostem koncentracji domieszki. Modyfikacji ulegają także takie parametry jak skok spirali, kąt pochylenia molekul, spontaniczna polaryzacja oraz czas przełączania. Nie odnotowano natomiast wpływu na sekwencję fazową, grubość warstw smektycznych i długość korelacji dla antyferroelektrycznej fazy SmC^*_A .

Podsumowując, otrzymane wyniki badań poszerzają znacząco zakres wiedzy w obszarze wpływu domieszkowania na właściwości faz smektycznych (w szczególności antyferroelektrycznej fazy SmC^*_A), jednak wciąż pozostaje wiele otwartych kwestii, zatem badania przeprowadzone w ramach niniejszej dysertacji nie wyczerpują tej tematyki. Pomimo przeprowadzenia badań właściwości wytworzonych układów hybrydowych (kompozytów) metodami komplementarnymi, nadal pozostają otwarte pytania np. o wpływie domieszek na parametry mechaniczne matrycy, degradację warstw w różnych środowiskach czy wpływie ciśnienia na procesy relaksacyjne. W niniejszej pracy badano wpływ domieszki na warstwy o grubościach rzędu $5\mu\text{m}$, a nie jest znany ich wpływ na warstwy zarówno grubsze jak i cieńsze. Pokazano wpływ rozmiaru domieszki BaTiO_3 (45 i 280nm), jednak można jeszcze sprawdzić wpływ rozmiaru zarówno mniejszych niż 45nm oraz pośrednich $45\text{-}280\text{nm}$ wielkości ziaren domieszki. Otwartą kwestią pozostaje także dekoracja nanocząstek surfaktantem, istotnym wydaje się zbadanie wpływu rodzaju czynnika dekorującego wybraną domieszkę. Odnotowany wybiórczy wpływ wybranych domieszek na właściwości smektycznych matrycy wydaje się być obiecujący, otwierając nowe możliwości. Ogromna ilość nanomaterialów dostępnych na rynku może posłużyć do stworzenia baz danych, niosących informację o tym, jak dana domieszka i w jakiej koncentracji zmodyfikuje dany parametr/parametry, pozostawiając inne bez zmian.

W chwili zakończenia pisania dysertacji, autor postawił sobie kolejne problemy badawcze, które są kontynuacją przeprowadzonych badań, rozszerzonych o badania mechaniczne i zwilżalność warstw różnymi cieczami:

- a) Poszukiwanie korelacji między strukturą chemiczną matrycy a domieszką. Celem niniejszego projektu jest domieszkowanie ustaloną koncentracją wybranego typu domieszki (nanocząstek) kilku przedstawicieli określonego szeregu homologicznego.
- b) Wpływ rozmiaru domieszki na właściwości fizyczne antyferroelektrycznej fazy SmC^*_A . Celem niniejszego projektu jest wybór związku wykazującego fazę SmC^*_A w szerokim zakresie temperatur (zawierającym temperatury pokojowe) i domieszkowanie kilkoma różnymi rozmiarami nanocząstek jednego typu.

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8. Przedruki artykułów



Systematic study of the chiral smectic phases of a fluorinated compound

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Systematic study of the chiral smectic phases of a fluorinated compound

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ABSTRACT

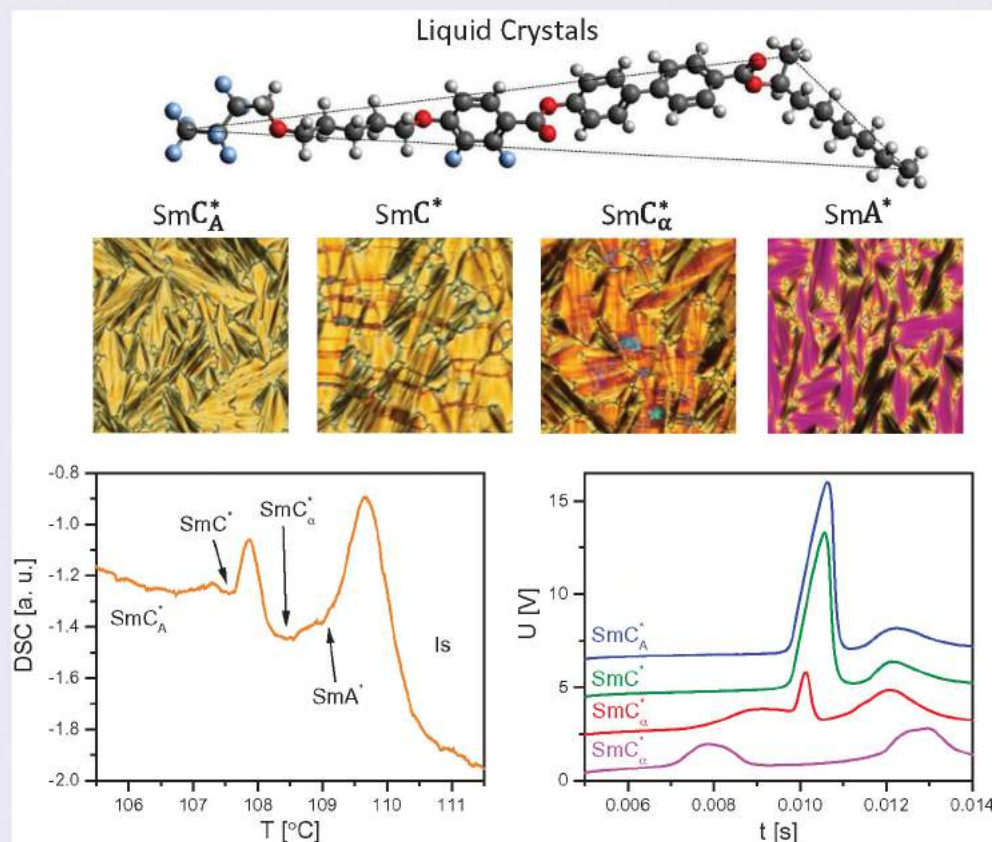
Physical properties of the partially fluorinated compound 3F5FPhF, with hockey stick-like molecules, were studied by complementary methods. Apart from the already reported paraelectric SmA^* , ferroelectric SmC^* and antiferroelectric SmC_A^* phases, the presence of the smectic C_α^* subphase in the phase sequence was proved by differential scanning calorimetry, polarising optical microscopy, electro-optic and dielectric spectroscopy methods. The temperature dependence of the smectic layer thickness and correlation length of the lateral short-range order was determined by X-ray diffraction. Based on dielectric measurements three relaxation processes were revealed in the antiferroelectric SmC_A^* phase (two collective: P_L , P_H and one molecular: s -process), two collective ones (Goldstone and soft modes) were found both in the ferroelectric SmC^* phase and SmC_α^* subphase while one relaxation process (soft mode) in the paraelectric SmA^* phase. The results were compared with that obtained for other structurally similar compounds, and it was shown that even addition of one methylene group to the side chain influences much on the physical properties.

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Antiferroelectric liquid crystal; electro-optic parameters; X-ray diffraction; subphase alpha; dielectric relaxation



1. Introduction

Liquid crystals have become interesting not only from scientific but also from the application point of view and are known from their discovery in the end of the nineteenth century [1]. These materials combine the properties of liquid (e.g. flowing) and solids (e.g. anisotropy of different physical properties). Later, the ferroelectric liquid crystalline SmC* phase was predicted and discovered by Meyer et al. in 1974 [2], which was incredible because before the ferroelectricity was assigned only to the solid state. Phenomenon of ferroelectricity appears only in chiral tilted smectic phases because the chiral atom in the molecular structure is breaking the point symmetry (the chirality removes the symmetry plane as the element of symmetry). In the ferroelectric SmC* phase the long axes of molecules in each layer are oriented in slightly different direction in comparison to adjacent layers, maintaining the constant tilt angle. This causes the helical structure of molecules with helical pitch equal to ca. 300 nm [3]. This helical arrangement of molecules leads to the helicoidal dipole moment structure, so the bulk spontaneous polarisation is zero. On the other hand, after unwinding the helix (by e.g. electric or magnetic field) the dipole moments are oriented in one direction and spontaneous polarisation occurs. That is why it is so-called improper spontaneous polarisation [4,5]. Afterwards, the antiferroelectricity in liquid crystal was discovered by Chandani et al. in 1989 [6]. In this case, the molecules in the adjacent layers are tilted in opposite directions; therefore, two helices shifted by one layer are present (looking at the odd layers we get one helix, and we get a second helix for the even layers, both twisted in the same direction) and the resultant spontaneous polarisation is zero [7]. These two helices can be unwound in the antiferroelectric phase, just like in the ferroelectric SmC* phase. Since the discovery of both phenomena, ferroelectricity and antiferroelectricity, many experimental and theoretical works have been done [8–12]. The experimental works focus mainly on the synthesis of new compounds,

preparation of mixtures and study of their physical properties [13]. Nowadays, the most common application of nematic liquid crystals is display industry; however, their use in switching devices, light modulators and temperature sensors is quite common [14–16]. The ferroelectric and antiferroelectric liquid crystals are also interesting from application point of view, for example, displays based on them (FLCD and AFLCD, respectively) provide better technical parameters, e.g. more faithful reproduction of colour [17], shorter switching time [18], usage of lower energy, in comparison to that based on the nematic phase. But it should be stressed here, however, that AFLCD has disadvantages such as loss of alignment due to mechanical shock (defects in texture) [19].

The aim of this work was to study the physical properties of a chiral fluorinated compound and discuss the results based on the properties of other compounds with similar chemical structure. For this purpose, complementary methods were used and the phase sequence, the temperature dependence of the spontaneous polarisation, the switching time, the tilt angle, the smectic layer thickness and the correlation length within the smectic layers in the liquid crystalline phases were found. Moreover, based on the temperature dependence of the relaxation frequency and dielectric increment, the dielectric processes in the smectic phases were interpreted.

2. Experimental section

Figure 1(a) presents the general chemical formula of the nFmX₁PhX₂ compounds, where n is the number of carbon atoms in fluoroalkyl chain, m – the number of methylene groups, X₁, X₂ – hydrogen/fluorine atoms (mixed configurations are possible). The studied compound (S)-4'-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[7-(2,2,3,3,4,4,4-heptafluorobutoxy)pentyl-1-oxy]-2-fluorobenzoate belongs to the homologue series 3FmFPhF [20] (X₁, X₂ = F and m = 5, in short

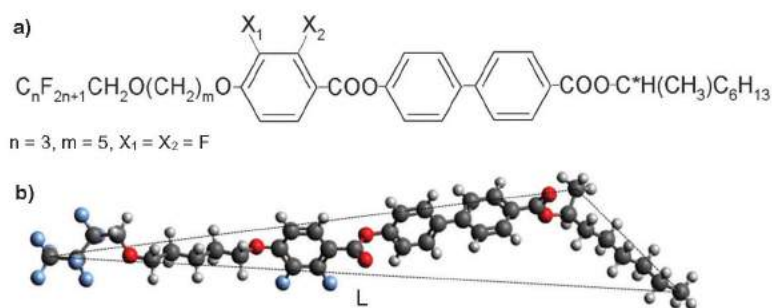


Figure 1. (Colour online) General chemical formula of the homologous series nFmX₁PhX₂ (a) and a model of 3F5FPhF molecule obtained in HyperChem 7.52 (b).

3F5FPhF). The members of this series differ by number of methylene groups in the side chain $C_3F_7CH_2OC_mH_{2m}O-$. The studied compound exhibits three enantiotropic liquid crystalline phases, namely: antiferroelectric SmC^*_A , ferroelectric SmC^* , and paraelectric SmA^* [20]. The last two appear in a very narrow temperature range while the antiferroelectric one in a wide temperature range.

2.1. Differential scanning calorimetry

Perkin Elmer DSC8000 calorimeter was used to find transition temperatures on heating and cooling. The calorimeter was calibrated by using water and indium. The polycrystalline sample of 5.21 mg was put into an aluminium 30 μ l vessel and hermetically sealed by a press. The measurements were done with chosen rates (2, 5, 10, 15, 20, 25, 30°C/min) both during heating and cooling in the temperature range from -40°C to $+130^\circ\text{C}$. The transition temperatures at so-called zero rate were calculated by a linear fit to the dependence of the onset temperature as a function of rate.

2.2. X-ray diffraction

Polycrystalline sample of 3F5FPhF, in the isotropic liquid phase, was introduced into a borosilicate glass capillary (0.3 mm diameter) by the capillary effect. The measurements were performed on Empyrean 2 (PANalytical) diffractometer with Cryostream 700 Plus (Oxford Cryosystems) temperature attachment in the geometry of a horizontal rotating capillary in the $2\theta = 2-30^\circ$ range (CuK α radiation, parallel beam geometry) at chosen temperatures between 115 and -75°C . The cooling/heating rate of 6°C/min was used with 5 min of temperature stabilisation before each measurement. The flat sample of 3F5FPhF in the form of a thin film on a silicon wafer was prepared by smearing the substance on a silicon wafer, after heating above the clearing temperature. The measurements were performed on D8 Discover (Bruker) diffractometer with Anton Paar DCS350 non-ambient attachment in $\theta/2\theta$ scan in $2\theta = 2.5-3.2^\circ$ range (CuK α radiation, parallel beam geometry) during cooling in temperatures between 116°C and 30°C. Cooling rate of 0.5°C/min was used with 20 s and 30 s of temperature stabilisation for patterns registered each 1°C and 0.1°C, respectively. Diffraction data were analysed in WinPLOTR [21] and TOPAS.

2.3. Polarising optical microscopy, electro-optic measurements

The optical textures were registered by using polarising optical microscope Nikon Eclipse LV100POL (crossed

polarisers, 90°) equipped with Fine Instruments WTMS-14C heating stage. Moreover, 33120A Agilent generator, F20-FLC Electronics amplifier and DSO6102A Agilent oscilloscope were used. The sample in the isotropic liquid state was placed into 5.1 μ m ITO cell (AWAT Company) by the capillary effect. The SE610 polymer layer with weak rubbing on the ITO electrodes provided the planar alignment of the sample. The texture observations were done both during heating and cooling with the rate equal to 2°C/min. Spontaneous polarisation, switching time and tilt angle measurements were carried out on the mono-domain during cooling. In order to obtain a uniformly oriented sample, the sample was heated up to the isotropic liquid and then slowly cooled down to the orthogonal tilted smectic phase transition, where the external electric field was applied and kept at this temperature for several minutes. Spontaneous polarisation measurements were carried out by reversal current method under triangular wave ($V_{p-p} = 60$ V, $f = 50$ Hz) while switching time measurements under rectangular wave [22–24]. In turn, the tilt angle was measured as half of the angle between the Clark–Lagerwall states [25].

The electro-optic response (EOR) was registered by using the polarising optical microscope Biolar (PZO) with crossed polarisers for the azimuth angle distant by $\alpha_0 = 22.5^\circ$ from the position of the maximum of the transmission in the SmA^* phase. The signals coming from the photodetector were amplified by PIN20 pre-amplifier (FLC Electronics, Sweden) and recorded by the lock-in amplifier SR850 (Stanford Research, USA). Measurements were done, during heating and cooling of the uniformly oriented sample placed in the ITO cell, by using Mettler heating equipment and the homemade temperature controller (temperature stabilisation with an accuracy of $\pm 0.01^\circ\text{C}$). The field frequency was equal to 440 Hz and the external AC measuring voltage was 0.5 V_{rms}. The data acquisition process was controlled by the software package developed in the Department of Liquid Crystals Physics, Institute of Molecular Physics, Polish Academy of Sciences. This software allows registering EOR measurements as a function of temperature, frequency, time and measuring voltage.

2.4. Frequency domain dielectric spectroscopy

The dielectric measurements were done in the frequency range 40–10⁷ Hz by using Agilent 4294A impedance analyser with Fine Instruments IMTA-300 Temperature Control System. The measurements were done during cooling from the isotropic liquid to 0°C. The sample was placed in the 5 μ m cell with golden electrodes (AWAT Company). The dielectric

spectra were collected every 2°C while in the vicinity of the phase transitions every 0.3°C. The influence of the temperature and the bias field on the dielectric spectra was studied.

3. Results and discussion

3.1. Molecular modelling

The initial model of the isolated molecule was obtained in the Avogadro molecular editor [26] and subjected to a geometry optimisation procedure. Then, pre-optimised molecule was subjected to a multistage geometry optimisation procedure (MM+ force field and semi-empirical MNDO methods) in HyperChem 7.52. The molecule of 3F5FPhF compound after the geometry optimisation, resembling a hockey-stick shape, is shown in Figure 1(b). The molecule's length $L = 36.6\text{\AA}$ (the length between the centres of the farthest carbon atoms in aliphatic chains) was obtained in Avogadro. The opening angle is equal to 128.3°.

3.2. Phase sequence

Differential scanning calorimetry (DSC) measurements were carried out to check thermal stability and find transition temperatures. DSC curves registered during heating and cooling at different chosen rates are presented in Figure 2. In case of cooling, there is observed a super-cooling effect [27,28] of antiferroelectric SmC^*_A phase. On DSC curves there is no visible peak corresponding to the crystallisation process for all rates except 2°C/min where a very weak anomaly, around 23°C, was registered. This result was confirmed by electro-optic and diffraction measurements (as will be shown later). During heating, depending on the rate,

several peaks are visible (Figure 2). As it is presented in the inset in Figure 2(a) four peaks (marked by vertical arrows) are visible for rates 2°C and 5°C/min, while for the higher heating rates only two well-visible peaks were registered. Figure 2(b) shows the DSC curves for heating and cooling in the high-temperature range.

Identification of the phases was done by texture observation under a polarising optical microscope (POM), and the following phases were identified both during heating and cooling: crystalline phase (Cr), antiferroelectric SmC^*_A , ferroelectric SmC^* , subphase SmC^*_α , paraelectric SmA^* and isotropic liquid (Is). As an example, characteristic textures of the non-aligned sample for each liquid crystalline and crystal phases are presented in Figure 3. Characteristic fan-shape texture of the SmA^* phase is visible in Figure 3(a). It turns out that the 3F5FPhF compound exhibits an additional subphase SmC^*_α (Figure 3(b)) as compared with the results presented in [29]. All the textures registered for smectic phases are fan-shaped. The difference in textures between SmC^* , SmC^*_α and SmC^*_A phases is mainly based on the colour change in the texture (Figure 3(b–d)), like it was shown for another compound in [30]. Moreover, the characteristic disclination lines are well visible for SmC^*_α subphase and SmC^* phase. Below the antiferroelectric SmC^*_A phase during further cooling down the texture of the crystal phase was registered (Figure 3(e)). Relating the phase sequence of the studied compound with that of compound 3F6FPhF [31], belonging to this series, it is seen that addition of one methylene group in the side chain influences much on the phase sequence. The antiferroelectric SmC^*_A phase is shifted towards lower temperatures while temperature range of the ferroelectric SmC^* phase becomes much wider as compared with the studied 3F5FPhF. On the other hand for shorter homologue belonging to this series, namely 3F3FPhF, neither the

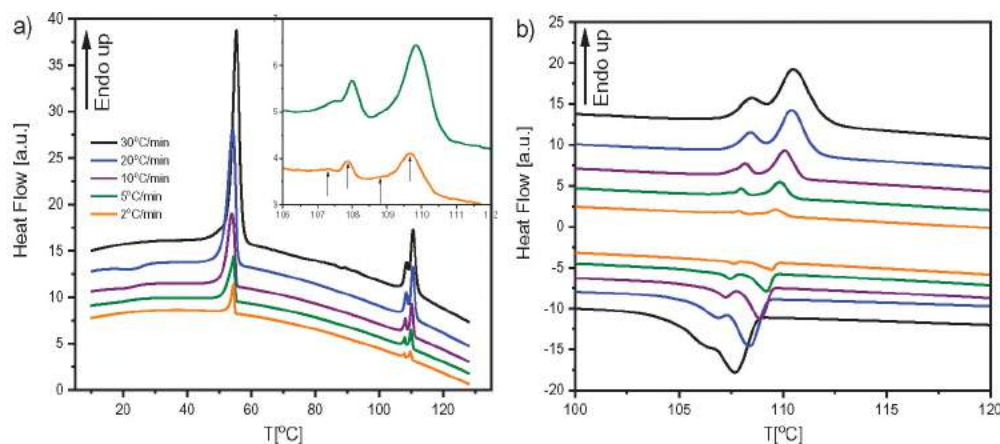


Figure 2. (Colour online) DSC curves registered for 3F5FPhF during heating in the whole temperature range (a) and during heating and cooling in a high-temperature range (b). The inset in (a) presents the chosen temperature range of DSC curves for rates 2 and 5°C/min.

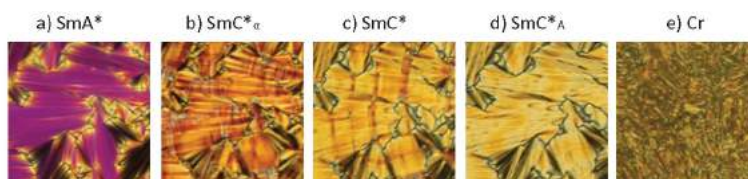


Figure 3. (Colour online) Textures of 3F5FPhF compound registered during cooling for (a) SmA*, (b) SmC*_α, (c) SmC*, (d) SmC*_α and (e) Cr.

ferroelectric SmC* nor the paraelectric SmA* phases are present [32]. In the case of similar compounds, namely 4F3(HH) and 4F3(HF), the complete disappearance of the SmA* phase is observed [33].

Further, the electro-optic response (EOR) measurements were done to find transition temperature and confirm the existence of the subphase SmC*_α. The polar phases have non-zero macroscopic spontaneous polarisation and give distinctly higher EOR than antiferroelectric SmC*_A and non-polar paraelectric SmA* phases. Figure 4 presents the temperature dependence of the linear electro-optic response. As it is seen, EOR signal in the SmA* and SmC*_A phases is weak, while in the SmC* and SmC*_α phases it is well visible, like it was observed for other compounds [34,35]. The value of EOR signal is weak in the antiferroelectric SmC*_A because there is a compensation of the polarisation in the neighbouring smectic layers. Based on the temperature dependence of the linear EOR signal the transition temperatures between SmA*–SmC*_α and SmC*–SmC*_A phases during cooling were designated (Figure 4). Additionally, the transition temperature between SmC*_α–SmC* phases

was also obtained from the saddle point. A small saddle observed during cooling is another proof of the presence of an additional polar phase between SmC* and SmA* (subphase SmC*_α). Kuczyński et al. [36] observed a similar EOR for MHPOPBC compound.

Based on the texture identification and EOR measurements, the anomalies on the DSC curves were appointed to the phase transitions: the first arrow from the left (inset in Figure 2(a)) represents SmC*_A–SmC* transition, the second SmC*–SmC*_α transition, the third weakly visible SmC*_α–SmA* transition, while the fourth SmA*–Iso transition. Summarising, the phase sequences on heating and cooling were obtained as follows:

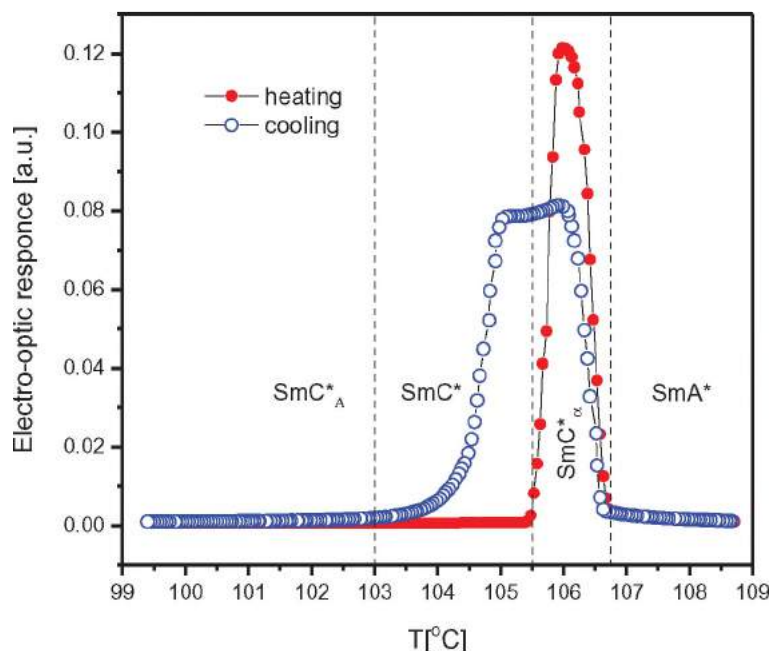
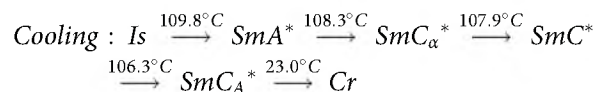
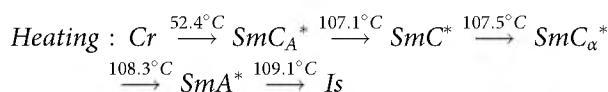


Figure 4. (Colour online) The linear electro-optic response as a function of temperature.

3.3. Structural parameters of smectic phases

Wide-angle X-ray diffraction patterns characteristic for smectic and crystal phases of the studied compound are shown in Figure 5(a). The ones collected between 110°C and 30°C are characteristic for smectic phases with a short-range order within smectic layers [37]. The sharp maximum below 3° and the wide diffuse one about 18° are well visible. The low intensity maxima which develop on cooling do not originate from the onset of the crystal phase but are the higher order peaks connected with the one characterising the layer thickness (e.g. at 40°C visible at $2\theta = 5.7^\circ$, 8.6° , and 11.5° as shown in Figure 5(a)) giving evidence about increasing quasi-long range lamellar order with decreasing temperature.

The wide maximum observed in the isotropic liquid and smectic phases can be defined by the Lorentz curve in the scattering vector space ($q = 2\pi\sin\theta/\lambda_{\text{CuK}\alpha}$). Its position

($\theta_d = 2\pi/d$) allows to calculate the average distances d between long axes of molecules within the smectic layers and the half-width at half-height is the inverse correlation length of the short-range order [37,38]. There is no considerable change in the average distances between the molecules: $5.0(1.1)\text{\AA}$ and $4.83(0.93)\text{\AA}$ at 125°C and 30°C, respectively (experimental errors are given in parenthesis). The correlation length ξ increases significantly with decreasing temperature (from $3.57(0.02)\text{\AA}$ at 125°C up to $4.37(0.03)\text{\AA}$ at 30°C). However, even in the lowest temperatures ξ is comparable with d , which means that the short-range order involves only the nearest neighbours.

The position of the sharp low angle maximum, by using the Bragg equation, allows to calculate the smectic layers thickness D . In this study, the D values were determined based on the XRD patterns registered for a flat sample in a narrow 2θ range (some examples are shown in Figure 5(b)). The temperature dependence of D ,

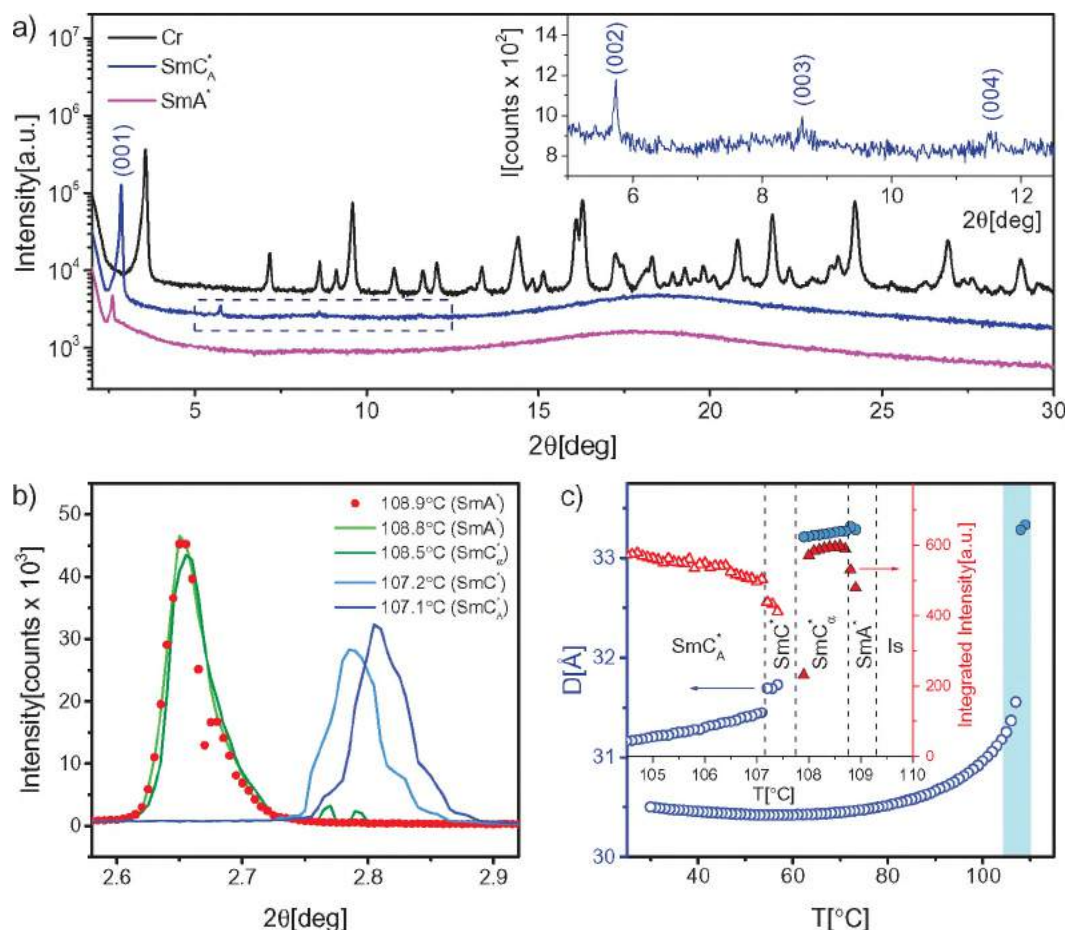


Figure 5. (Colour online) XRD patterns at chosen temperatures on cooling: for the sample measured in a capillary (a) and in the low-angle region for the sample on a zero-background holder (b) as well as the temperature dependence of the smectic layer thickness D ($\Delta D < 0.3 \text{ \AA}$) determined each 1°C (c). In (a): the plots are shifted for clarity, the region marked by the dashed rectangle is enlarged in the inset, and the rapid increase in the intensity below 2.5° comes from the experimental setup. The inset in (c) shows the shaded area in details and the integrated intensity of the low-angle peaks (triangles) is also plotted (both values are determined each 0.1°C , and solid and open symbols are related to the peaks about 2.65° and 2.8° , respectively).

obtained in the measurements performed every 1°C, is plotted in Figure 5(c) while the inset in this figure shows the D vs T behaviour in the temperature region in which the phase transitions are observed (points collected each 0.1°C).

Focusing on the position of the maximum at $2\theta = 2.65^\circ$ it is necessary to consider that initially moving to lower angles with decreasing temperature it changes this tendency about 108.7°C and starts to move towards higher 2θ values (Figure 5(b)). On further cooling, the peak at $2\theta = 2.65^\circ$ decreases and simultaneously a new one appears at about 2.8°, but in the temperature range between 107.8°C and 107.5°C the data were too noisy to calculate the layer thickness with reasonable uncertainty. The small change in the D values visible about 108.7°C (inset in Figure 5(c)), which is still in the experimental error, can be interpreted as a sign of a phase transition if one takes into account the above discussed behaviour of the Bragg maximum position about 2.65°, the temperature dependence of the integrated intensity of the low angle peak in this temperature range (inset in Figure 5(c)), and the results of complementary measurements reported in this work.

The layer thickness does not change significantly in the temperature range 108.9–107.8°C with the average value of 33.25(22) Å being about 10% smaller than the molecular length L estimated with MNDO calculations. That leads to the steric tilt angle value about 25° (estimated as $\cos(D/L)$ [39]). This relatively high value of the tilt angle together with the observations described above allows to state that the liquid crystalline phases observed in the high-temperature region are SmA^* of de Vries type [40,41] and SmC^*_{α} , and the transition temperature between them is slightly higher than 108.7°C.

On further decreasing temperature another phase transition, with an abrupt change in the D value, is observed (inset in Figure 5(c)). The layer shrinkage at this transition, calculated as $(D_{107.9^\circ\text{C}} - D_{107.4^\circ\text{C}})/D_{107.9^\circ\text{C}}$, is equal to 4.5% which means a significant increase in the tilt angle. It is known that in the SmC^*_{α} phase the tilt angle is much smaller than in the SmC^* phase and the transition between those phases is the first order transition [42]. The above allows to identify the one at 107.7°C as the transition from SmC^*_{α} to SmC^* .

The last anomaly visible in the temperature dependence of D (at 107.2°C) can be interpreted as the $\text{SmC}^* - \text{SmC}^*_A$ transition and below this transition the layer thickness decreases continuously saturating at about 30.4–30.5 Å below 70°C. Similar values of the smectic layer thickness and their temperature dependence were found for a racemic mixture MHPOBC [43], brominated [44] and not fluorinated [45] compounds.

3.4. Electro-optic parameters

Temperature dependences of the spontaneous polarisation and tilt angle are presented in Figure 6, together with sample voltage peaks. As it is seen the highest value of spontaneous polarisation, at low-temperature range of antiferroelectric SmC^*_A phase, is ca. 290 nC/cm². Large value of spontaneous polarisation is due to the transverse dipole moment coming from the carbonyl group, attached to the chiral centre. C–F polar bonds on the benzene ring and transverse dipole moment of the carbonyl group connecting benzene rings also influence a large value of the spontaneous polarisation. The replacement of fluorine atoms by hydrogen atoms causes that C–H covalent bonds are less polarised than C–F bonds, as reflected in the value of P_s . Similar values were observed for another compounds, for example MHP(F)O(13F)BC [46]. According to the theory [47] temperature dependence of the spontaneous polarisation P_s should obey the following equation:

$$P_s(T) = P_0(T_c - T)^\beta \quad (1)$$

where T_c – critical temperature (temperature of the transition between para – and ferroelectric phases), β – critical parameter describing type of the phase transition and $\beta = 0.5$ for the second order transition while $\beta = 0.25$ for the tri-critical point. Eq. (1) is valid only close to the para – ferroelectric phase transition. For the substance studied, the paraelectric – ferroelectric phase transition is characterised by the critical parameter equal to 0.23 (see Figure 6(a)), so one can assume that this is the tri-critical point ($\text{SmA}^* - \text{SmC}^*_{\alpha} - \text{SmC}^*$). As it is seen in Figure 6(a) the spontaneous polarisation becomes zero at ca. 25°C which agrees with DSC and X-ray results showing that at this temperature the crystallisation occurs. Comparing these results with the ones for compounds 3H5FPhH and 3H5HPhF the phase sequence is very similar, but the value of spontaneous polarisation is much lower (about half) over the entire temperature range [48]. In turn, for similar MHPB(3F)PBC and MHPBBBC compounds, the P_s values are almost the same as for the studied compound [49], in contrast to the MHPB(F)PBC compound for which the P_s value reaches almost 400 nC/cm² [50,51].

Figure 6(b) presents reversal voltage responses acquired for chosen temperatures. As one can see, two well-separated peaks are visible in the voltage response at higher temperature range, while at lower temperatures these separated peaks combine into one. Existence of two symmetrical peaks is an evidence of the presence of the subphase SmC^*_{α} between SmC^* and SmA^* phases

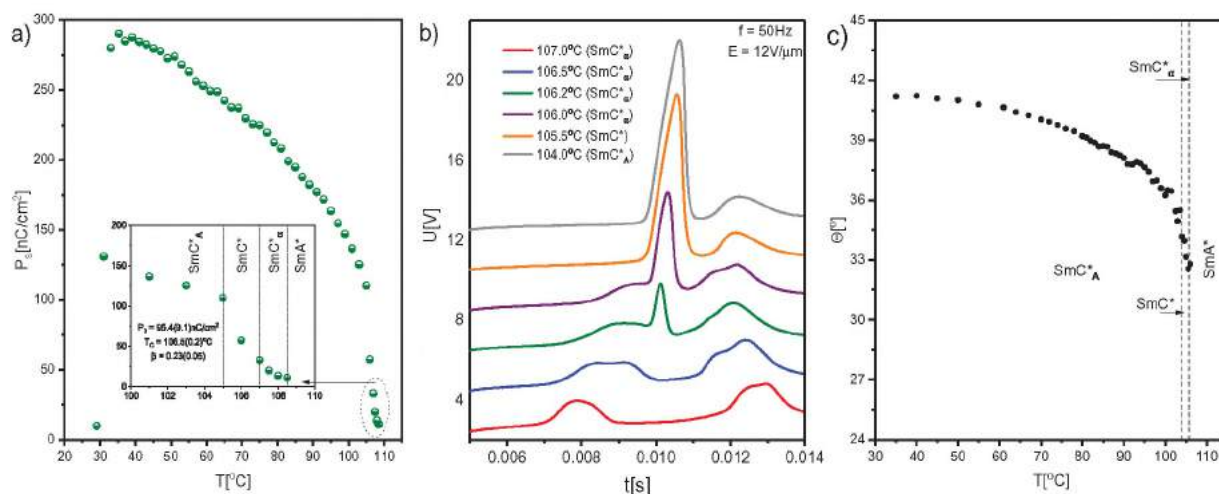


Figure 6. (Colour online) Temperature dependence of the spontaneous polarisation (a), reversal voltage peaks at selected temperatures (b) and temperature dependence of the tilt angle (c).

[46,52–54]. In the higher temperature range of SmC*_α phase, two peaks are visible. This is a characteristic behaviour for the antiferroelectric structure. However, at lower temperatures of the SmC*_α phase the formation of a third peak between them is observed (the last one begins to dominate). This is a characteristic behaviour for the ferroelectric structure [55]. Temperature dependence of the spontaneous polarisation with an anomaly just below the transition from paraelectric SmA* phase (see inset in Figure 6(a)) confirms that the SmC*_α subphase exists between the SmC* and SmA* phases.

Tilt angle reaches value ca. 40° (see Figure 6(c)), like it was found for other compounds, for example 3F6HPhF, 3F6FPhH, 3F6FPhF [56,57]. On the other hand, the 3F6HPhH compound exhibits a higher value of the tilt angle (c.a. 43° before crystallisation) [56,57]. Moreover, it was found for the studied compound that the switching time increases with decreasing temperature starting from 120 μs at high-temperature range of antiferroelectric phase up to 425 μs just before crystallisation. Such behaviour is similar to that observed for other compounds (for example 3F5HBM6 or 3F6HBM6) where the switching time is below 0.5 ms over the entire temperature range [58].

3.5. Dielectric spectroscopy results

3.5.1. Antiferroelectric SmC*_A phase

Chosen absorption curves and corresponding Cole–Cole plots registered during cooling in the antiferroelectric SmC*_A phase are presented in Figure 7(a,b). Two temperature-dependent dielectric processes are visible down to ca. 40°C (one at low frequency ca. 1 kHz and second at high frequency ca. 200 kHz), while below this temperature the low-frequency mode disappears and a new one,

high-frequency process appears at ca. 1 MHz. The relaxation frequency and dielectric increment of these processes were obtained by fitting the Cole–Cole model [59] to the experimental data:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \sum_{i=1}^n \frac{\Delta\varepsilon_i}{(1 + (2i\pi\nu_R\tau_i)^{1-\alpha_i})} - i \frac{\sigma}{2\pi\nu\varepsilon_0} \quad (2)$$

where ε^* is a complex dielectric permittivity (perpendicular component), ε' – dispersion, ε'' – absorption, ε_∞ is the dielectric permittivity at high frequency limit, $\Delta\varepsilon_i$ – the dielectric increment of i -th process, ε_0 – the dielectric permittivity at low frequency limit, ν_R – relaxation frequency, τ_i – relaxation time of i -th process, α_i – the distribution parameter of the relaxation time τ_i , ε_0 – the dielectric permittivity of vacuum, σ – the ionic conductivity.

To identify the relaxation processes, the influence of the bias field on the dielectric spectra in the antiferroelectric SmC*_A phase was studied. It is worth to stress here that the bias field much influences the dielectric behaviour in the antiferroelectric SmC*_A. As it is seen in Figure 8(a), the intensity of absorption increases with increasing the bias voltage up to $V_B = 16$ V (compare the results for $V_B = 8$ V and $V_B = 16$ V), while for higher values both dielectric processes become gradually suppressed and completely disappear at $V_B = 25$ V. Moreover, from a qualitative point of view, dielectric spectra collected without and with the bias field ($E_B = 16$ V/5 μm) are similar (compare Figure 7(a,b) with 7(c,d), respectively).

Figure 8(b) presents the Arrhenius plot and the temperature dependence of the relaxation frequency for all modes revealed in the liquid crystalline phases (both with

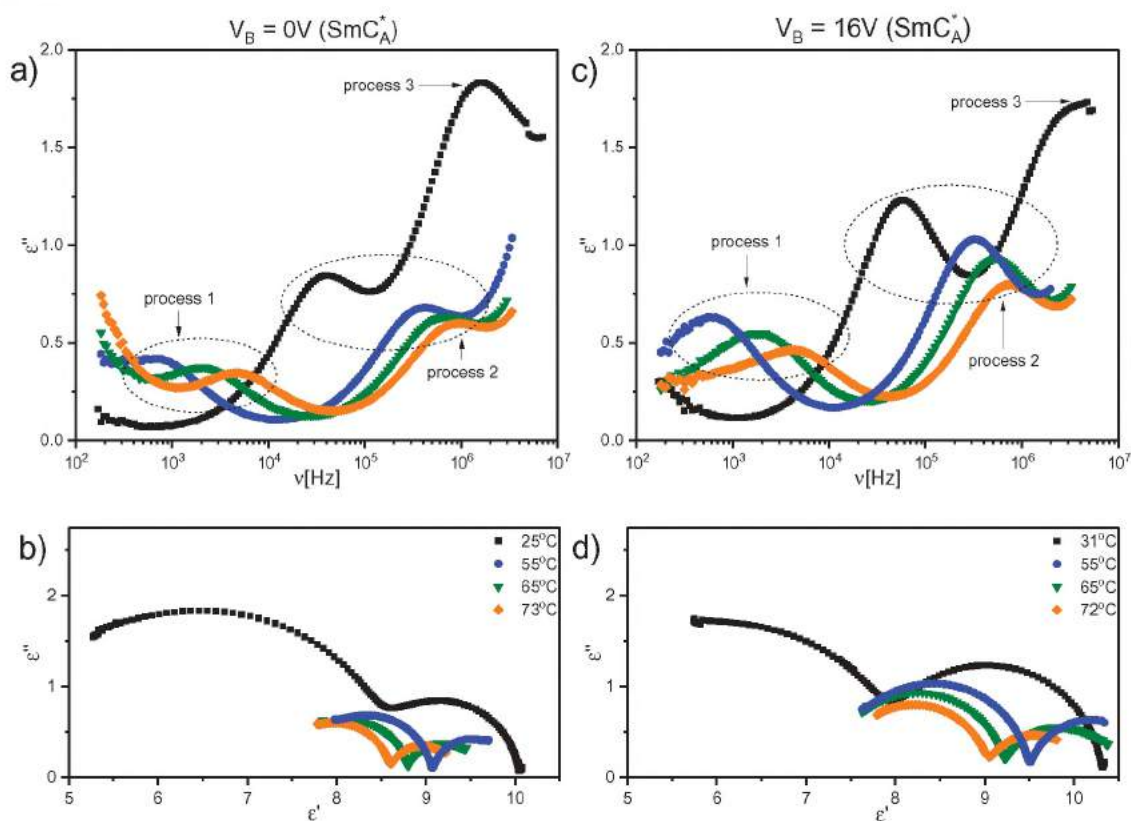


Figure 7. (Colour online) The dielectric absorption curves and the Cole–Cole plot of 3F5FPhF registered in the SmC^*_A phase at chosen temperatures: for $V_B = 0\text{V}$ (a, b) and $V_B = 16\text{V}$ (c, d).

and without the bias field). The activation energies of the processes appearing in the antiferroelectric SmC^*_A phase were calculated by fitting to the experimental data the following formula:

$$\ln \nu_R = \ln \nu_0 - E_A / (RT) \quad (3)$$

where ν_R is relaxation frequency, E_A – the activation energy, R – gas constant, T – temperature in the absolute scale. The activation energies of these processes obtained using Eq. (3) are gathered in Table 1. In the case of process 2, it was necessary to fit two lines to the experimental data: for the low- and high-temperature range, respectively. The break has occurred at the point where the process 1

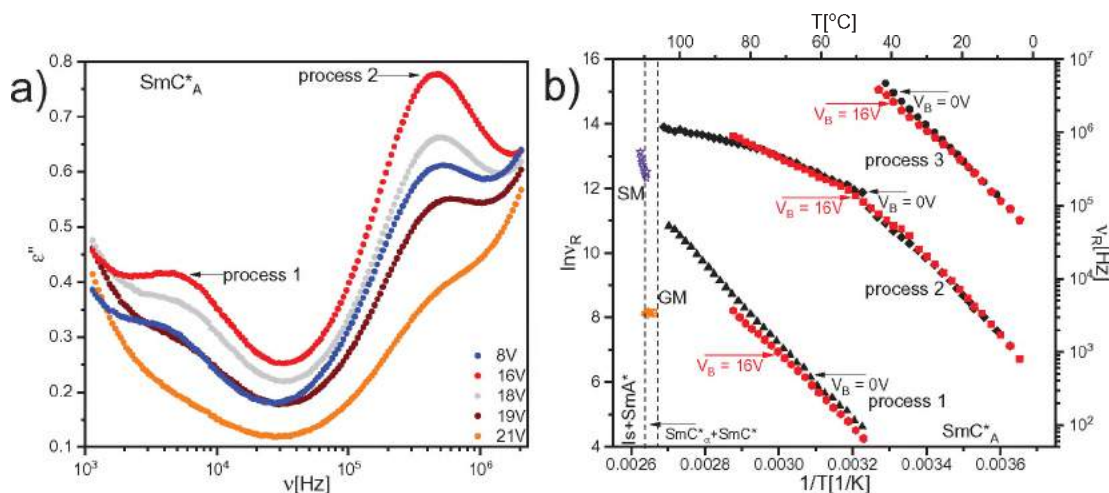


Figure 8. (Colour online) Influence of the bias field on the dielectric absorption in the SmC^*_A phase, $T = \text{const.}$ (a) and Arrhenius plot for all processes registered in the SmC^*_A phase (b).

Table 1. Activation energy of the dielectric processes revealed in the SmC^*_A phase.

E_A [kJ/mole]	Process 1	Process 2 (low T)	Process 2 (high T)	Process 3
($V_\text{DC} = 0.0\text{V}$)	100.63 (0.55)	91.43 (1.41)	31.04 (9.09)	95.86 (1.11)
($V_\text{DC} = 16.0\text{V}$)	92.27 (0.69)	93.96 (1.72)	45.83 (0.43)	86.55 (0.98)

disappeared and the process 3 appeared. At lower temperature range of the SmC^*_A phase, the bias field does not influence much the activation energy of the process 2 (see Table 1). Processes 1 and 2 are slower than the process 3 (see Figures 7 and 8(b)), which is an evidence of their phase character. Moreover, because the bias field of 25V completely suppressed both processes 1 and 2 (see Figure 8(a)), it can be concluded that these processes (1 and 2) can be interpreted as collective ones:

- process 1 as P_L , in-phase fluctuations of the director's phase in adjacent layers (named also as the antiferroelectric Goldstone mode [60]), existing up to appearing of process 3;
- process 2 as P_H , anti-phase fluctuations of the director's phase in adjacent layers (named also as the anti-phase antiferroelectric Goldstone mode [60]), existing in the whole temperature range of the antiferroelectric SmC^*_A phase.

Process 3, independent of the applied bias field, with activation energy close to 100 kJ/mole, seems to be reorientation around the short axes (s-process), like it was found for other compounds, for example, 3F3HPhF [28], MHPNBC [52] or 12OBP1M7 [61].

3.5.2. Paraelectric SmA^* phase, subphase SmC^*_α and ferroelectric SmC^* phase

Except the antiferroelectric SmC^*_A phase, the dielectric studies were carried out for other liquid crystalline phases. Without bias field applied, in the ferroelectric SmC^* and paraelectric SmA^* phases one dielectric process was revealed, while two processes in the SmC^*_α subphase (two relaxation processes in this phase were also reported for other compounds [62,63]). Under the bias field, in all of the above-mentioned phases (SmA^* , SmC^* and SmC^*_α), only one dielectric process was registered (Figure 9(a)).

To identify these dielectric processes, the temperature dependence of the relaxation frequency (Figure 8(b)) and the inverse of the dielectric increment (Figure 9(b)) were plotted. Temperature independent process in the ferroelectric SmC^* phase was interpreted as the Goldstone mode (GM), while the process present in the SmA^* phase – soft mode (SM) (similar behaviour was observed, for example, in [64–67]). In turn, in the SmC^*_α phase, both the Goldstone and soft modes were revealed. After

suppression of the Goldstone mode, by applying a strong bias field ($E_\text{B} = 16\text{V}/5\mu\text{m}$), the soft mode has been revealed in the paraelectric and ferroelectric liquid crystalline phases as well as in the subphase SmC^*_α (Figure 9(a)). Based on the Landau phase transition theory, R. Blinc and B. Žekš [68] described the behaviour of the soft mode in the vicinity of the phase transition between paraelectric SmA^* and ferroelectric SmC^* phases as characteristic V-shape in the temperature dependence of relaxation frequency and inverse of dielectric increment. According to the prediction of this theory the ratio of the slope of the straight lines fitted to the temperature dependence of relaxation frequency or inverse of dielectric increment on both sides of the transition should be equal to -2 for the second-order transition. For the studied 3F5FPhF, a characteristic decrease and subsequent increase of $\Delta\epsilon^{-1}$ of the SM is indeed observed during cooling (Figure 9(b)) and the ratio of the fitted lines' slopes is equal to -1.81. However, this is not exactly the V-shape dependence [41,69], because in the very narrow temperature range (between 107.8°C and 107.2°C) $\Delta\epsilon^{-1}$ is constant. It confirms the existence of the

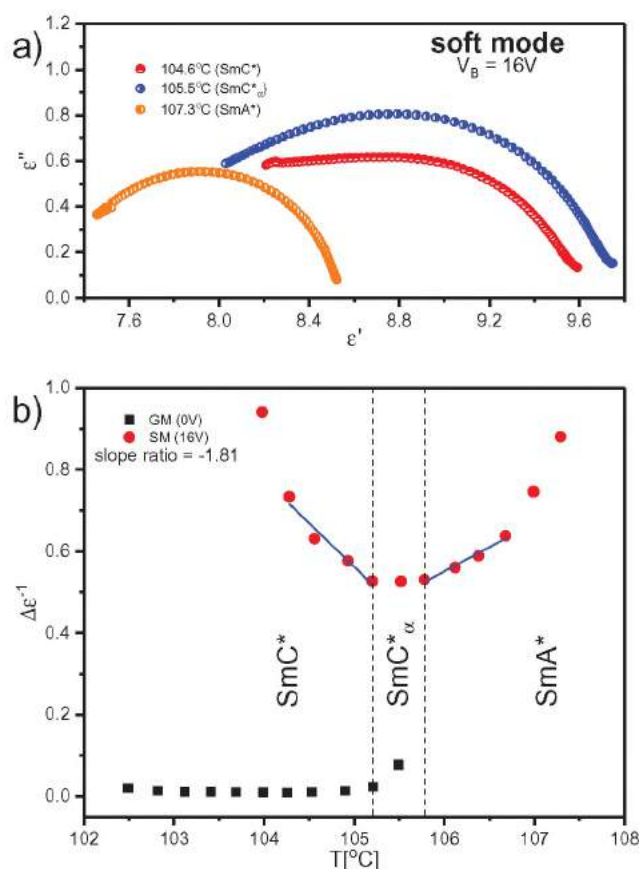


Figure 9. (Colour online) The Cole–Cole plot under the bias voltage ($V_\text{B} = 16\text{V}$) for the ferroelectric SmC^* , subphase SmC^*_α , paraelectric SmA^* phases (a) and temperature dependence of the inverse of dielectric increment for SM and GM in different phases (b).

SmC*_α subphase between SmA* and SmC* phases, as it was revealed in the texture observations (Figure 3), EOR (Figure 4), X-ray diffraction (Figure 5(c)) and spontaneous polarisation (Figure 6(a)) measurements.

4. Summary and conclusions

In this article, physical properties of 3F5FPhF compound were examined by complementary methods. The results were compared with that obtained for other compounds, and it was shown that the addition of one methylene group to the side chain influences much on the physical properties. Particularly, for the studied compound it was found:

- The modelled molecule has a hockey stick shape in the most extended conformation.
- Next to the antiferroelectric SmC*_A phase, the paraelectric SmA* and ferroelectric SmC* phases the subphase SmC*_α appears during heating and cooling as well.
- The smectic layer thickness decreases with decreasing temperature and then at about 60°C saturates at 30.5 Å.
- The spontaneous polarisation increases with decreasing temperature (up to 290 nC/cm²) while the tilt angle increases rapidly up to ca. 40.5° and then slightly increases over the entire temperature range.
- Three relaxation processes were revealed in the antiferroelectric SmC*_A phase: two collective ones: in-phase (P_L) and anti-phase (P_H) fluctuations of the director's phase in the adjacent layers and molecular one – reorientation around the short axis (s-process). In turn, two collective relaxation processes (Goldstone and soft modes) were found in the ferroelectric SmC* phase and SmC*_α subphase, while one relaxation process (soft mode) in the paraelectric SmA* phase.

Summarising, the substance is thermally and electrically stable and is characterised by good, from application point of view, parameters like spontaneous polarisation, switching time and tilt angle of molecules. It seems that the usage of this compound as a component of multi-component mixture may be desired for applications.

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Disclosure statement

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Modification of AFLC Physical Properties by Doping with BaTiO₃ Particles

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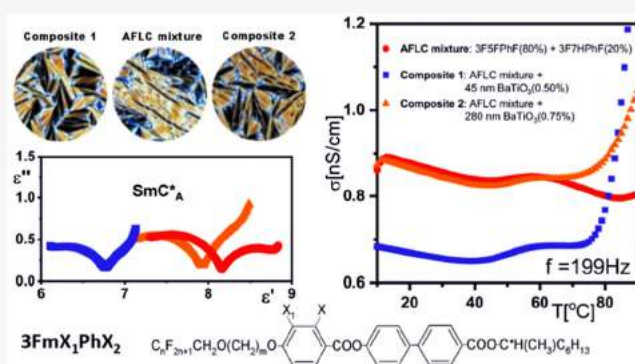
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ABSTRACT: In this paper, for the first time, the influence of the BaTiO₃ particles on the antiferroelectric liquid crystalline phase was shown. Low concentrations and two different sizes of BaTiO₃ particles (nano- and submicroparticles) were used. It was found that admixture of the ferroelectric particles causes a decrease in the concentration of free ions in the liquid crystal matrix. Despite the small amount of admixture, a decrease in spontaneous polarization, switching time and rotational viscosity, was observed, while the tilt angle of molecules and the smectic layer thickness did not change. It turns out that BaTiO₃ particles have a very large impact on the dielectric spectra not only in the antiferroelectric phase but also in the ferroelectric and paraelectric phases of the polymorphic mixture studied. The dopants affect also the complex conductivity. In this paper, we explain why some properties are modified by BaTiO₃ particles and others are not.



1. INTRODUCTION

The development of industry requires searching for new materials with precisely defined properties.¹ Therefore, there are synthesized new materials, and their properties are studied in a detailed manner. However, the synthesis routes of such compounds are very complex. In contrary to time-consuming and very expensive methods of chemical synthesis, the process of doping already synthesized materials, such as liquid crystals, is relatively simple and has great potential.

As it is known, the antiferroelectric liquid crystals (AFLCs) have attracted attention as materials with a response time in microseconds, capable of forming a gray scale, having a large optical contrast and hemisphere view angle, and eliminating ghost effects.² From a chemical point of view, the liquid crystal's molecules have an anisotropic shape, e.g., rodlike, disclike, banana shape, etc. The typical factors necessary for the liquid crystal materials to be ferroelectric/antiferroelectric are chiral carbon atom in the molecular terminal chain and a non-zero component of the dipole moment perpendicular to the long molecular axis.³ The temperature range of an antiferroelectric smectic phase can be changed by substituting hydrogen atoms with fluorine atoms in the core of molecule and/or in the achiral terminal chain.^{4–7}

On the other hand, the continuous increase of nanotechnology and ease of access to nanomaterials such as metallic and dielectric nanoparticles, quantum dots, carbon nanotubes, etc. opens new possibilities to design complex advanced

materials. In recent years, liquid crystal nanocomposites/nanocolloids have been formed by doping the liquid crystal (LC) matrix with nanomaterials, which has led to the emergence of a new branch of soft matter physics.^{8–18} It turns out that the connection of anisotropic liquid crystals with nanomaterials gave curious results: the enhancement of electro-optic properties, changes in the electric conductivity, faster response, etc.^{19–27} For example, the admixture of carbon nanotubes to the ferroelectric liquid crystal (FLC) matrix leads to a reduction in switching time, an increase of spontaneous polarization and modification of dielectric properties (change the dielectric permittivity, shift in relaxation frequency of the Goldstone mode)¹⁶ while the addition of dye strongly reduces the spontaneous polarization and leads to increase a response time.²⁸

The admixture of large particles (diameter of ca. several micrometers) causes defects in the LC matrix due to strong deformation of the liquid crystal director. Moreover, these defects can form complex structures. However, the admixture of small particles (nanoparticles) has a little effect on the behavior

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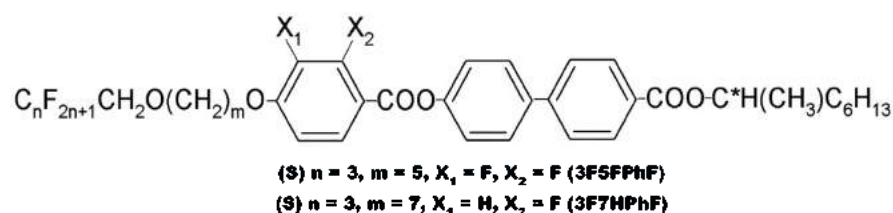


Figure 1. General molecular structure of 3FmX₁PhX₂ homologous series.

of the liquid crystal director. On the other hand, nanoparticles (e.g., BaTiO₃, LiNbO₃) are big enough to maintain their ferroelectric properties and share these intrinsic properties with LC matrix.²⁹ Additionally, the low concentration of nanoparticles and the sonication process in LC host prevent both agglomeration of nano-objects and the formation of defects. Sometimes surfactants (like oleic acid) are used to modify nanoparticles surface, which reduces their agglomeration, but at the same time, in many cases, this surfactant impairs the properties of the LC matrix.³⁰ In turn, Meeker et al.¹¹ showed that if the nanoparticle concentration is large enough, rigid suspensions can be obtained. It turns out that by changing the concentration and the type of nanoparticles, one can control properties of the LC matrix (e.g., dielectric constant, birefringence, switching time, phase transition temperatures, etc.).^{19–27} Doping the ferroelectric liquid crystal matrix by ferroelectric nanoparticles causes a strong interaction between dipole moments of both materials, which leads to a change in the optical and dielectric anisotropy of the doped material. For example, carbon nanotubes have a beneficial effect on the electro-optic answer, quantum dots modify helical pitch in the cholesteric liquid crystals, and ferroelectric nanoparticles reduce the threshold voltage for electrical response.³¹

The constantly developing industry is showing a demand for materials with precisely defined properties. An additional requirement is a relatively simple and inexpensive way of obtaining such materials. Many research groups are making efforts and trying to create new liquid crystal nanocomposites. And so, in one recent paper, Pandey et al.³² doped 6CHBT with silver nanoparticles of 50 nm. In addition to reducing the transition temperatures, a decrease in dielectric anisotropy was observed. Similarly, Yadav et al.³³ doped the nematic phase with Fe₂O₃ nanoparticles of 20 nm and showed that as the amount of dopant increases, the birefringence decreases. This behavior was explained by changing the molecular orientation by admixture. Pushpavathi et al.³⁴ doped 5CB with 25 nm ZnO nanoparticles and noticed that even for high dopant concentration (5% by weight) the N–Is transition temperature did not change whereas the enthalpy of the transition changed, which was explained by the energy transfer between liquid crystal molecules and nanoparticles. In addition, with the increase in the concentration of nanoparticles, an increase in conductivity, a decrease in birefringence and the Fredericksz effect at higher voltage were observed. Despite the development of many composites based on liquid crystals, most of them are based on the nematic phase. Therefore, the motivation for us was to study the effect of the BaTiO₃ admixture on the antiferroelectric phase.

In this paper, we present the influence of BaTiO₃ particles with two different diameters on the physical properties of the binary antiferroelectric mixture. We particularly focus on the effect of the admixture on the antiferroelectric phase, which in principle has not been reported before. The influence of the

particle size is analyzed. It turns out that ferroelectric particles dispersed in a liquid crystal matrix cause a decrease in the concentration of free ions in this matrix. Many material properties are also changed by admixture.

2. EXPERIMENTAL SECTION

2.1. Samples. Components of the binary antiferroelectric liquid crystal mixture studied belong to the homologous series 3FmX₁PhX₂³⁵ (X₁, X₂ = H, F) with general chemical formula presented in Figure 1. They differ by number of methylene groups in the terminal chain and the number of fluorine atoms substituted to the phenyl ring and both were examined by us earlier.^{36,37} The mixture has the following composition: 80 wt. % 3F5FPPhF and 20 wt. % 3F7HPhF. The pure mixture was then doped by commercially available BaTiO₃ particles (delivered by Nanografi Co. Ltd.) to create two composites:

Composite 1: AFLC mixture + 0.50 wt. % of 45 nm BaTiO₃ nanoparticle,

Composite 2: AFLC mixture + 0.75 wt. % of 280 nm BaTiO₃ submicroparticle.

Low concentrations of particles were used in order to not alter the liquid crystal order and the direction of the director in the individual smectic layers. Moreover, the particles have non-zero dipole moments and for higher concentrations their interactions may result in uncontrolled aggregation.³¹ Special attention has to be paid to disperse the particles well in the liquid crystal host so that the average distance between the particles is large enough (objects do not agglomerate then).

To get the AFLC/BaTiO₃ composites in the first step the adequate amounts of AFLC mixture and BaTiO₃ particles (58.17 mg of AFLC + 0.30 mg of 45 nm BaTiO₃, 23.76 mg of AFLC + 0.18 mg of 280 nm BaTiO₃) were mixed and quenched with 2 mL of chloroform. Prepared solutions were sonicated in 50 s (on)/10 s (off) mode for 20 min and poured into a microscopic slide, which was then placed on the heating plate (80 °C) for several minutes to pre-evaporate of most of the solvent and next left at normal condition for a few hours. Obtained composites were peeled off with a blade and used to measurements.

2.2. Raman Spectroscopy. Raman measurements for powder samples of commercially available BaTiO₃ particles (45 and 280 nm; delivered by Nanografi Co. Ltd.) were carried out with a JASCO NRS-5500 Confocal Raman Microscope (JASCO, Japan, $\lambda_{\text{exc}} = 532$ nm, $P = 9.5$ mW, $t_{\text{exp}} = 1$ s) equipped with a 1024 pixel CCD detector in 3800–100 cm^{−1} Raman shift range. For each sample experiments were performed using set up 1, objective = MPLFLN 20×, slit size = 0.01 × 1 mm, and aperture = 4 mm; and set up 2, objective = MPLFLN 50×, slit size = 0.05 × 1 mm, and aperture = 4 mm. The results are shown in Figure 2.

The obtained Raman spectra are identical for both size of the particles. The narrow bands at 175 and 304 cm^{−1} and the broad ones at 267, 522, and 715 cm^{−1} are present confirming the

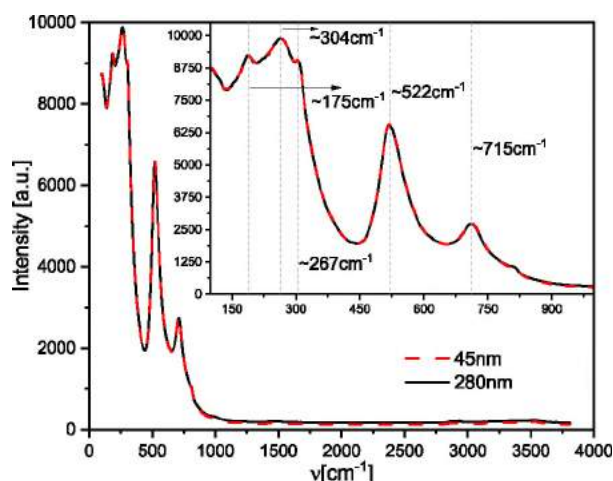


Figure 2. Raman spectra of the 45 and 280 nm BaTiO₃ particles. The inset shows the wavenumber range with the maxima corresponding to the tetragonal structure.

tetragonal phase^{40,41} of both 45 nm nanoparticles and 280 nm submicroparticles. That means that both BaTiO₃ particles used in our research are ferroelectric materials, even if by manufacturer the 45 nm nanoparticles were described as cubic ones (without a dipole moment). One should keep in mind that the tetragonal structure is strongly dependent on crystallinity and grain size^{38,39} and even the smallest BaTiO₃ nanoparticles can reveal the ferroelectric behavior.⁴⁰ The above results are essential for the reported studies.

2.3. Differential Scanning Calorimetry. Calorimetric measurements were carried out in the temperature range from −20 to +150 °C at heating and cooling (rates: 10, 15, 20 °C/min) by using PerkinElmer DSC8000 differential scanning calorimeter (DSC), calibrated on melting points of water and indium. The samples of ca. 5 mg were placed into the 30 μL aluminum pans and sealed by the press. Results were analyzed by using Pyris software and Origin 2017. Calorimetric method was used to find phase transition temperatures. The transition temperatures at so-called zero rate were obtained by a linear fit to the dependence of the onset temperature versus heating/cooling rate.

2.4. Polarizing Optical Microscopy and Electro-optic Measurements. Texture observations and electric measurements were carried out by means of a polarizing optical microscope Nikon Eclipse LV100POL equipped with a Fine Instruments WTMS-14C heating stage. The experimental setup also consists of a 33120A Agilent generator, an F20-FLC Electronics amplifier, and a dual channel DSO6102A Agilent oscilloscope. Nikon camera was used to texture acquisition during heating and cooling with the rate equal to 2 °C/min while measurements of transmitted light intensities were performed by using photodetector. Pure AFLC mixture and composites were placed into sandwich type ITO electro-optic cells (thickness, ca. 8.1 μm; surface of electrodes, 25 mm²; planar alignment, AWAT Company) in the isotropic liquid phase by capillary effect. The electric and electro-optic measurements (spontaneous polarization, switching time, tilt angle) were carried out on the uniformly oriented samples. In order to obtain the monodomain, all the samples were heated to the isotropic phase and then slowly cooled to the first tilted smectic phase—SmC*_α. In this phase the external electric field was applied and kept at this phase by several hours. The tilt angle was measured as a half of

the angle between the Clark–Lagerwall states,⁴² the switching time by the method described in^{43–45} while the reversal current method was used to measure spontaneous polarization^{43,46–48} with the resistor of 100 kΩ connected in series. All electric and electro-optic measurements are subjected to the systematic temperature uncertainty of 0.1 °C. The accuracy of the surface area determination in the sample response (numerical integral) was estimated at 2% and was included in the calculation of the spontaneous polarization uncertainty. In turn, during a series of switching time measurements, the oscilloscope time base did not change for each sample, the waveforms were averaged over four cycles, and the switching time was calculated in Origin after the sample response was transferred to the computer.

2.5. X-ray Diffraction. Diffraction method was used to determine the smectic layer thickness and the distance between the long axes of the molecules in the smectic layers. The measurements (Cu Kα radiation) were performed on cooling, for samples in a horizontal rotating capillary using an Empyrean 2 (PANalytical) diffractometer with a Cryostream 700 Plus (Oxford Cryosystems) temperature controller. The details of the sample preparation and experimental set-up are the same as for, reported earlier, pure 3F5FPhF.³⁶ Diffraction data were analyzed by using WinPLOTR.⁴⁹

2.6. Frequency Domain Dielectric Spectroscopy. Dielectric measurements were carried out by means of Agilent 4294A analyzer linked with the Fine Instruments IMTA-300 Temperature Control System. AFLC mixture and both composites were placed in the sandwich type cells with golden electrodes (ca. 5.0 μm, active area 25 mm², planar alignment, AWAT Company) by capillary effect. The perpendicular component of the electric permittivity ϵ^* was measured in the frequency range 40 Hz to 50 MHz (measuring voltage $V_m = 0.1$ V) in the temperature range 110–0 °C (at cooling). Spectra were collected every 2 °C in a wide antiferroelectric phase and every 0.3 °C in the other phases. In addition, the effect of the bias field on the dielectric spectra was studied. Additionally, a Novocontrol Technologies Concept 81 dielectric spectrometer was used to measure AC electric conductivity versus temperature in the frequency range 1 Hz to 2.5 MHz.

2.7. Birefringence Measurements. Birefringence measurements have been performed by using a Photoelastic Modulator (PEM-100, Hinds Instruments). The length of the light emitted was 532 nm. Application of a light emitting diode for the light source simplifies the optical setup and enables measurement by using polarizing microscope. Temperature dependence of the birefringence of AFLC mixture and both composites was studied at cooling using PEM system. It is worth noting that measurements with the use of a photoelectric modulator are most often made with the use of polarized laser light. Unfortunately, there is no overview of the quality of sample ordering, which is very important in the case of liquid crystals, especially in ferro- and antiferroelectric phases, where the value of optical anisotropy may be much lower. In this method the lock-in amplifiers measure a voltage at the first and second harmonic frequency of the PEM that correspond to the output of the system at that frequency.⁵⁰ For small amplitudes the output of each amplifier can be given by

$$I = I_0 \left(\frac{1}{2} (1 - J_0 \cos B) + J_1 \sin B \cos \omega t + J_2 \cos B \cos 2\omega t \right) \quad (1)$$

where J_0 , J_1 , and J_2 are Bessel functions of the PEM retardation and B is the retardation of the liquid crystal.^{51,52} In this

configuration only two signals were detected: (1) a lock-in amplifier detects the rms voltage V_{1f} of the detector signal at the PEM frequency $1f$; (2) a lock-in amplifier detects the rms voltage V_{2f} of the detector signal at the PEM frequency $2f$. The ratios of V_{1f} to V_{DC} and V_{2f} to V_{DC} are insensitive to fluctuations in the light source intensity, changes in optical transmission, etc. (eq 3), but in consequence, the signals of the constant component have been reduced:

$$R_{1f} = \frac{V_{1f}}{V_{DC}}, R_{2f} = \frac{V_{2f}}{V_{DC}} \quad (2)$$

On the basis of PEM theory,⁵⁰ it is known that

$$B = a \tan \left(\frac{V_{1f} J_2(A)}{V_{2f} J_1(A)} \right) \quad (3)$$

Therefore

$$\Delta n = \frac{B}{2\pi d} \quad (4)$$

where Δn denotes the birefringence of the sample and d the thickness of the cell. Measurements were made in ca. $8.1 \mu\text{m}$ thick cells in the absence of an external electric field without using an additional ordering procedure (ordering was only due to the orienting layers and the temperature gradient). The quality of the obtained orientation was evaluated by means of polarizing optical microscopy. The measurements were done in the temperature range 110 – 60°C , on cooling. When using this measuring method, it is necessary to be sensitive to a change in angle—an oscillation between 0 and 180° —which may have a significant influence on the final result. The low temperature limit is related to restrictions of the equipment used.

3. RESULTS AND DISCUSSION

3.1. Texture Observations. The characteristic textures of the paraelectric SmA^* , subphase SmC^*_α , ferroelectric SmC^* , and antiferroelectric SmC^*_A phases registered for pure AFLC mixture and both composites are presented in Figure 3. The typical fan-shaped texture was observed in the SmA^* phase for pure AFLC mixture and both composites (Figure 3a). Texture of the SmA^* phase for composite 1 appears to be more defective than for the same phase in the AFLC mixture. In the case of ferroelectric SmC^* phase the broken fan-shaped texture was visible for all materials studied (Figure 3c). The difference between the textures of the SmC^* and SmC^*_α is the change of color and the appearance of fringes for the latter (compare parts b and c of Figure 3). Additionally, for the SmC^*_α subphase, one can see inclusions of the focal–conic texture that is broken at the transition to the SmC^* phase for all the samples. Moreover, the striation⁵³ is quite visible in the SmC^*_α subphase, especially for the AFLC mixture and composite 2 (Figure 3b) while there are more focal–conic texture inclusions for composite 1. In the SmC^* phase, except for the fan-shaped texture, broken focal–conic inclusions were visible for all the samples. Additionally, the polygonal texture was registered for AFLC mixture and composite 2 in the SmC^* phase and in the SmC^*_α subphase for AFLC mixture (for composites polygonal texture is strongly suppressed in the SmC^*_α subphase).

In the antiferroelectric SmC^*_A phase, a characteristic fan-shaped texture with fingers⁵⁴ was registered (Figure 3d) which slightly changes color and the fingers disappear as the temperature decreases (Figure 3e). The polygonal inclusions

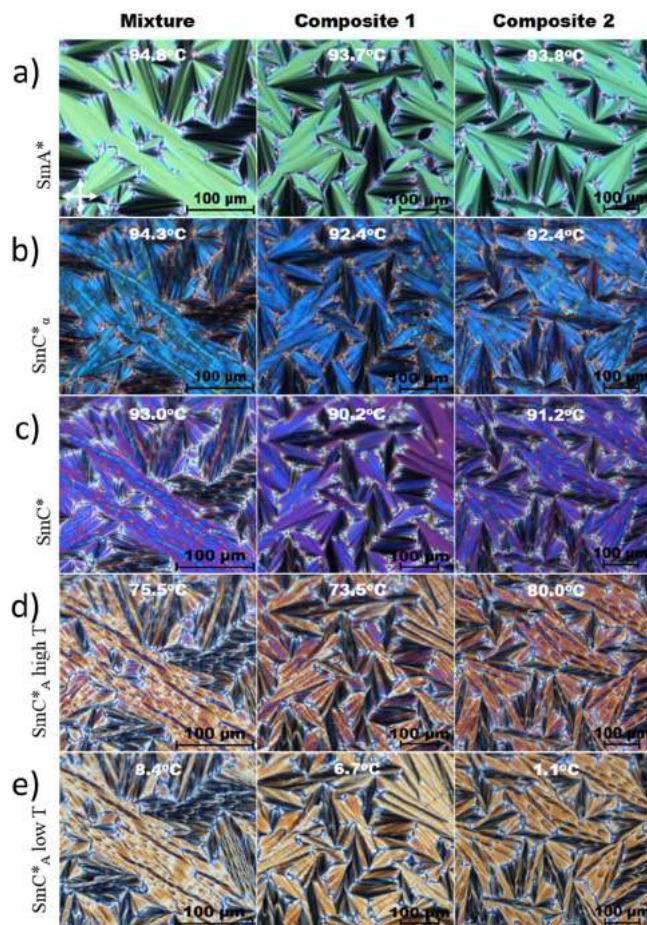


Figure 3. Textures of the liquid crystalline phases of AFLC mixture and both composites registered during cooling without external electric field applied, rate $2^\circ\text{C}/\text{min}$.

exist in the texture of the antiferroelectric SmC^*_A phase both for AFLC mixture and composite 2. It is impressive that starting from the SmC^*_α phase the number of polygonal inclusions are strongly growing and reach a large number in the last liquid crystalline phase for composite 2. It seems that small BaTiO_3 particles (45 nm) are reasonable for elimination of polygonal texture inclusions (but not focal–conic defects). Interestingly, this type of particles affects stronger the striation in the antiferroelectric phase (especially at lower temperature range).

Generally, all the textures registered for composite 2 are very similar to those for AFLC mixture, while for composite 1 are different. It is likely that larger particles (280 nm in composite 2) agglomerate faster and accumulate in already existing defects (e.g., domain boundaries). It is also not excluded that, in the filling process, particles have agglomerated at the edge of the cell and did not enter its interior (this requires further studies). To sum up, the following phases were distinguished for studied materials: the SmA^* phase with the fan-shaped texture, the SmC^*_α subphase with fan-shaped texture (with visible striation for AFLC mixture and composite 2), the SmC^* phase with broken fan-shaped texture with visible broken focal–conic inclusions, and the SmC^*_A phase with the fan-shaped texture containing fingers. The polygonal inclusions were observed only for AFLC mixture and composite 2.

3.2. Calorimetric Measurements. As an example, the DSC curves registered during cooling and heating are presented in Figure 4. As one can see, for all the samples studied, the

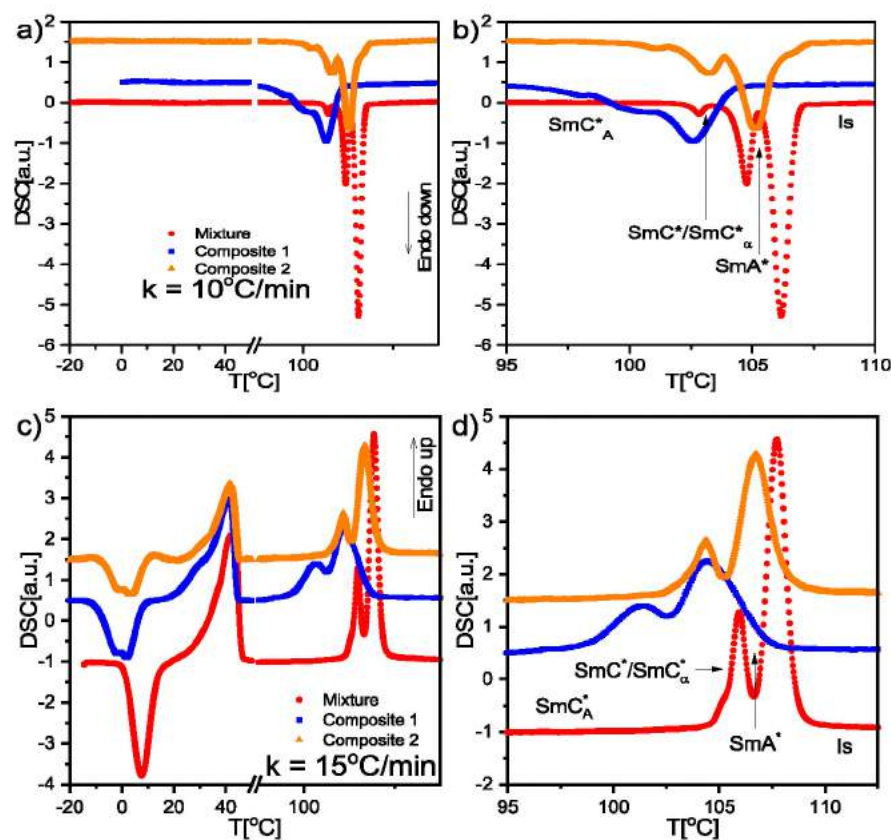


Figure 4. DSC curves obtained during cooling (a) and heating (c) for all the samples studied and the enlarged area during cooling (b) and heating (d).

anomalies were registered only in the high temperature range during cooling to -20°C (Figure 4a). Therefore, the very narrow high temperature range is enlarged in Figure 4b to compare the DSC curves. The heating cycles of the whole temperature range and the enlarged high temperature range are presented in parts c and d of Figure 4, respectively. As is seen, the doping process does not cause the vanishing of any phases present in the pure AFLC mixture while the transition temperatures, both at heating and cooling, are visibly shifted toward lower values after doping with BaTiO_3 (in contrary to nematic liquid crystal doped with BaTiO_3 ⁵⁵). This is a very interesting conclusion because Kumar et al.⁵⁶ by doping the BCN with BaTiO_3 particles (10–200 nm, tetragonal structure) obtained the transition temperature of the nematic–isotropic liquid at higher values. In the nematic phase, particles have much greater freedom of movement than in layered phases such as smectics. Due to the stable dipole moment, ferroelectric particles generate strong electric fields around them, which affects the orientation of liquid crystal molecules and interactions, which in turn increases the nematic order parameter, and thus increases the transition temperature. Large restrictions of molecular movement in the smectic phases strongly limit (or even hinder) the increase of the order parameter in such a phase, which means that a decrease in phase transition temperatures for composites is observed. For example, the Is–smectic phase transition temperature is shifted about ca. 4°C for composite 1 and 1°C for composite 2 compared with pure AFLC mixture. As one can see, no transition to the crystal phase was registered during cooling, while the crystallization process is visible during subsequent heating for pure AFLC mixture and both composites (Figure 4c,d), what is in good agreement with the texture observations. Interestingly, the

crystallization process for both composites is a two-step process, as evidenced by two anomalies close together. During heating, a small hump is visible only for AFLC mixture (Figure 4d), which probably represents the transition from the antiferroelectric SmC^*_A to the ferroelectric SmC^* phase. As is known, the second order transition is not visible in DSC study because it is not accompanied by a thermal effect. In our case the $\text{SmA}^*-\text{SmC}^*_\alpha$ transition is not visible while the $\text{SmC}^*-\text{SmC}^*_\text{A}$ phase transition is associated with a very low heat effect. The DSC measurements were repeated after 2 and 4 weeks, and the results obtained are identical with those presented here, which indicates the thermal stability of the pure antiferroelectric mixture and both composites.

3.3. Transmitted Light Intensity Measurements. As it was mentioned above, some phase transitions were not registered by DSC measurements, therefore the optical method was used. Transmitted light intensity versus temperatures is presented in Figure 5. As one can see, in the antiferroelectric SmC^*_A phase the intensity decreases down to ca. 30°C and then continuously increases with decreasing temperature for all the samples. In turn, in the high temperature range, a step, corresponding to the phase transition, is well visible for all the samples. As an example, the high temperature range for AFLC mixture is presented in the inset. As one can see, the gradual increase in the transmitted light intensity is visible which allows determining the phase transition temperatures between narrow liquid crystalline phases. Three characteristic intensity jumps indicate phase transitions between the Is– SmA^* , $\text{SmA}^*-\text{SmC}^*_\alpha$ and $\text{SmC}^*-\text{SmC}^*_\text{A}$ phases. Due to the fact that the SmC^*_α subphase exists in a very narrow temperature range, the $\text{SmC}^*_\alpha-\text{SmC}^*$ phase transition was not registered by this method.

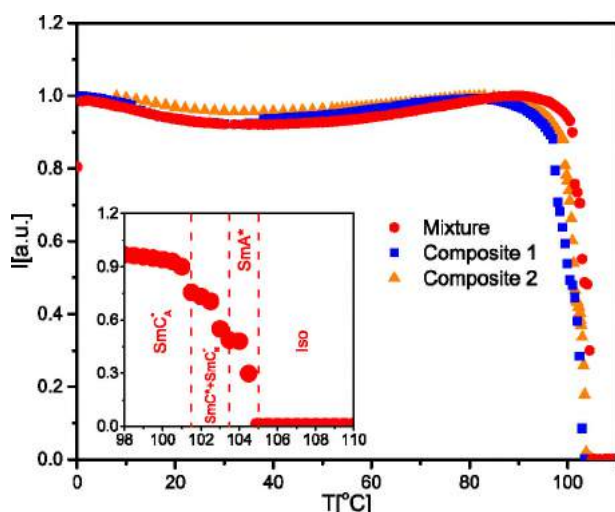


Figure 5. Transmitted light intensity versus temperature for pure AFLC mixture and both composites. The inset shows the high temperature range of the AFLC mixture; the dashed lines marked the transition between liquid crystalline phases.

3.4. Phase Sequence. Using complementary methods, mentioned above, the phase sequences for the AFLC mixture and both composites were determined. Table 1 presents the

Table 1. Phase Sequences on Cooling for the AFLC Mixture and Both Composites, $\Delta T = 0.4^\circ\text{C}$

sample	phase sequence					
mixture	Is	$\xrightarrow{107.2^\circ\text{C}}$	SmA*	$\xrightarrow{105.9^\circ\text{C}}$	SmC*_ α	$\xrightarrow{105.6^\circ\text{C}}$ SmC* $\xrightarrow{103.7^\circ\text{C}}$ SmC*_A
composite 1	Is	$\xrightarrow{104.6^\circ\text{C}}$	SmA*	$\xrightarrow{102.0^\circ\text{C}}$	SmC*_ α	$\xrightarrow{101.6^\circ\text{C}}$ SmC* $\xrightarrow{99.9^\circ\text{C}}$ SmC*_A
composite 2	Is	$\xrightarrow{106.1^\circ\text{C}}$	SmA*	$\xrightarrow{104.4^\circ\text{C}}$	SmC*_ α	$\xrightarrow{104.1^\circ\text{C}}$ SmC* $\xrightarrow{102.0^\circ\text{C}}$ SmC*_A

phase sequences on cooling for all the samples studied. The phase transition between antiferroelectric SmC*_A and Cr phases was not observed at cooling. However, if the sample was kept for a long time at 0°C or lower temperature (after cooling from the isotropic phase), crystallization was observed after several dozen minutes. The studies of the crystallization process of AFLC mixture and both composites are the focus of further research. As one can see in Table 1, the doping AFLC mixture with particles decreases the transition temperatures.

3.5. Electro-optic Measurements. Spontaneous polarization measurements were performed on uniformly aligned samples. Alignment conditions (frequency, signal shape, and

applied voltage) were selected on the experimental way and were different for each sample. An external electric field was applied to the samples during cooling in the first tilted smectic phase. As an example, the process of forming a uniform texture (monodomain) for the AFLC mixture over time is presented in Figure 6. Although only an area of $500\ \mu\text{m} \times 500\ \mu\text{m}$ is presented in the figure, the sample was uniformly oriented in the entire area of the electrodes ($25\ \text{mm}^2$).

First, the effect of doping particles on the spontaneous polarization was checked. As it is seen in Figure 7 the threshold

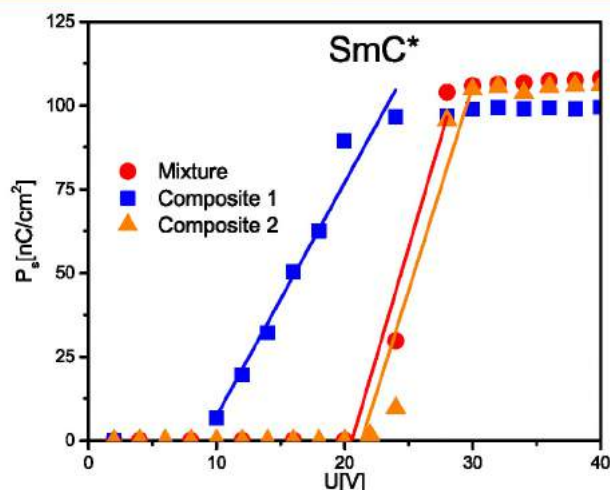


Figure 7. Influence of the applied voltage on the spontaneous polarization in the ferroelectric SmC* phase for AFLC mixture and both composites.

voltage, at which the molecules began to reorient in the electric field, is modified by particles. The threshold voltage was obtained by fitting the straight line to the experimental data in the low voltage range and is equal to 20.57, 8.96, and 21.35 V for AFLC mixture, composite 1, and composite 2, respectively. At higher voltages, spontaneous polarization increases slightly for all the samples, although the smallest values were registered for composite 1. In turn, the opposite behavior, in the high voltage range, was observed by Coondoo et al.⁵⁷ and Ganguly et al.⁵⁸ for other compounds in the ferroelectric phase. It may be that the addition of oleic acid⁵⁷ or deionized water⁵⁸ has an effect on discrepancies at higher voltages. However, it should be stressed here that the above-mentioned papers^{57,58} describe P_s behavior in the middle of the ferroelectric phase existing in a very wide temperature range (about 70°C), while in our case the ferroelectric phase covers at most 2°C . It seems that the effect of

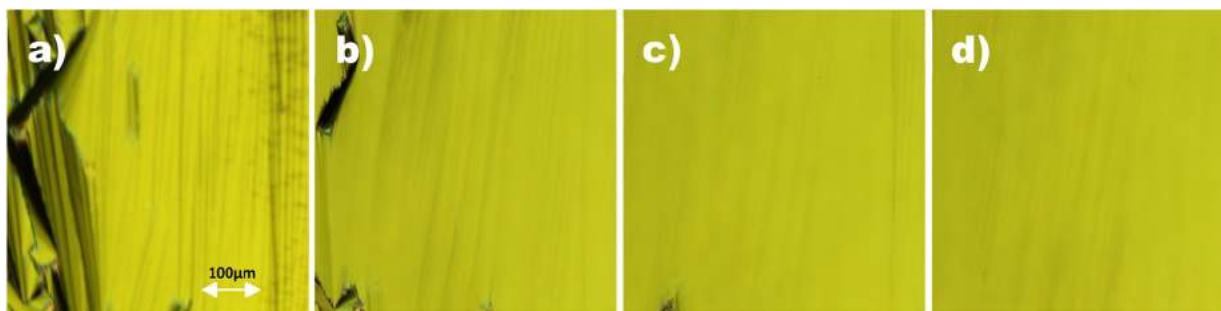


Figure 6. Alignment process of AFLC mixture: texture taken after a few minutes after applying a sinusoidal wave of $U = 50\ \text{V}$ (a), after another 17 min (b), after another 51 min (c) and after another 83 min (d). All photos are of $500\ \mu\text{m} \times 500\ \mu\text{m}$ size.

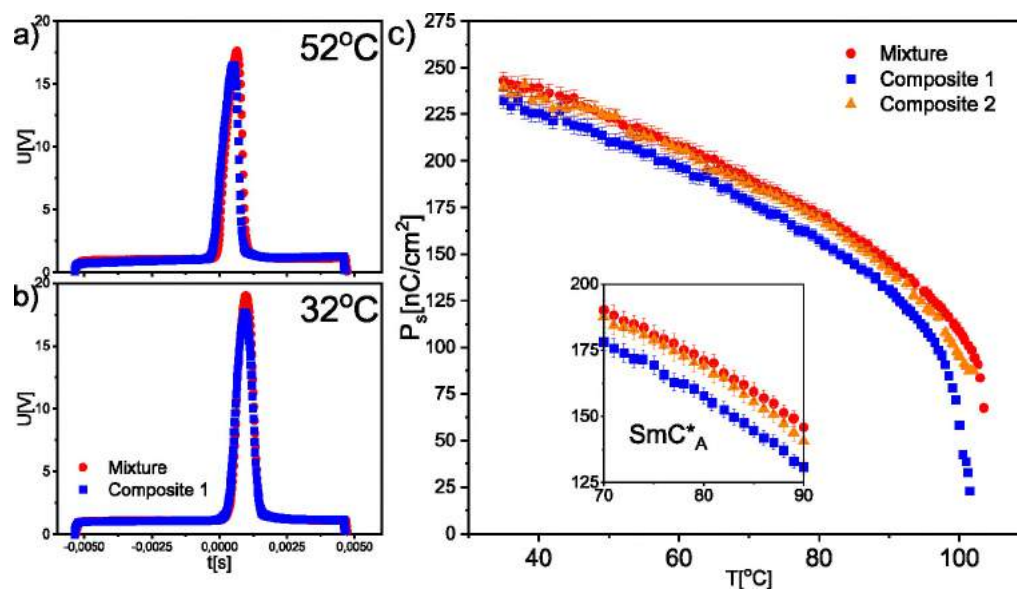


Figure 8. Voltage response for AFLC mixture and composite 1 at 52 (a) and 32 °C (b) together with the temperature dependence of the spontaneous polarization for AFLC mixture and composites (c); $f = 50$ Hz, $U = 120$ V.

doping with $BaTiO_3$ particles on the $P_s(U)$ behavior may depend on many factors (including the chemical structure of the compound), which requires further studies.

As an example, the voltage responses at two chosen temperatures (in the antiferroelectric phase) for AFLC mixture and composite 1 are presented in parts a and b of Figure 8. It is clearly visible that the voltage response for AFLC mixture is higher than that for composite 1. The temperature dependence of the spontaneous polarization for all the samples studied is presented in Figure 8c.

As one can see in the inset in Figure 8c, the significant decrease in the P_s value is visible for composite 1 as compared to the pure AFLC mixture while it is very subtle for composite 2. For example, the spontaneous polarization at 82 °C is equal to 166.3, 152.5, and 164.5 nC/cm² for the AFLC mixture, composite 1, and composite 2, respectively. Because the effect of doping of ferroelectric particles on the antiferroelectric phase has not been published so far, our studies can be compared with the results describing the effect of ferroelectric particles on the ferroelectric phase.^{59,60} In both mentioned articles, the spontaneous polarization in the ferroelectric phase decreases after doping the liquid crystal compound with ferroelectric particles $LiNbO_3$ and $BaTiO_3$, like in our case in the antiferroelectric phase. We can therefore conclude that the $BaTiO_3$ admixture reduces the spontaneous polarization in both the ferroelectric and antiferroelectric phases. The temperature behavior of P_s is similar for all of the samples and no saturation was observed even at the lowest temperature. It is easy to notice the second order transition between SmA^* and SmC^*_A subphases. Interestingly, such large polarization values in the antiferroelectric phase were also observed in the antiferroelectric phase by Mukherjee et al.⁴⁵ for another compound (MOPBIC), which was not fluorinated.

We suppose that the decrease in the P_s value for composites is associated with the antiparallel orientation of the dipole moments of the liquid crystal molecules (AFLC mixture) and ferroelectric particles.⁶¹ Interestingly, despite the use of a larger concentration of $BaTiO_3$ particles with average diameter equal to 280 nm, the polarization change is more pronounced for

composite 1 (AFLC + 45 nm $BaTiO_3$). At this stage, we have to consider the size of the liquid crystal molecules and the particles used. The average molecule length of 3F5FPhF compound is ca. 37 Å = 3.7 nm while the diameter of particles is 45 and 280 nm. Therefore the ratio of objects mixed in the composites is ca. 12 and 76 for composite 1 and 2, respectively. Assuming an equal density of used particles in both composites (according to manufacturer true density is equal to 5.90 g/cm³), it is easy to state that in a 1:1 weight ratio there are ca. 240 particles with 45 nm of diameter per 1 particle with diameter of 280 nm ($V_{280\text{ nm}}/V_{45\text{ nm}} \approx 240$). The particle concentrations used were 0.50 wt. % for composite 1 and 0.75 wt. % for composite 2. Thus, the weight ratio used is like 1:1.5 what means 120 nanoparticles of 45 nm diameter to 1 submicroparticle of 280 nm diameter. Another important aspect, that should be considered, is the P_s value of $BaTiO_3$:^{40,62} for crystal form (single crystal) the P_s value is equal to 26 $\mu\text{C}/\text{cm}^2$. However, Shieh et al.⁶² have shown that the theoretical value 26 $\mu\text{C}/\text{cm}^2$ changes under compressive stress for 5 mmx5 mmx2 mm single crystal while for nanoparticles around 50 nm is ca. 2.2 $\mu\text{C}/\text{cm}^2$. In our case, despite the higher concentration of particles for composite 2, more individual particles are present in composite 1 and each of particle contributes with its dipole moment. The total spontaneous polarization for composites can be expressed by the following relation:⁶³

$$P_s^{com} = wP_s^{LC} + (1 - w)P_s^{NP} \quad (5)$$

where w is the weight ratio of the AFLC mixture, $(1 - w)$ is the weight ratio of the $BaTiO_3$ particles, and polarizations next to weight ratios are for AFLC mixture and particles, respectively. As is shown in Figure 8c the spontaneous polarization for composites is lower than that for the AFLC mixture. Thus, the dipole moments associated with particles and molecules of the AFLC matrix have to be antiparallel oriented. Moreover, the decrease of spontaneous polarization after doping by nano- and submicroparticles can be caused by an increase in surface area. As is seen in Figure 7 the spontaneous polarization is higher for nanoparticles, even if the concentration of the submicroparticles is higher, which results in a measurement of less polarization.

The temperature dependence of the tilt angle for AFLC mixture and both composites are shown in Figure 9. Just like for

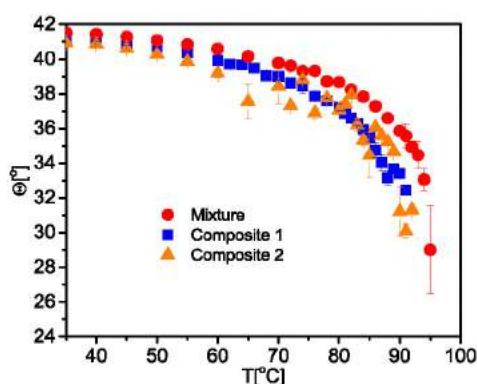


Figure 9. Tilt angle versus temperature for AFLC mixture and both composites.

spontaneous polarization close to the $\text{SmA}^*-\text{SmC}^*_\alpha$ phase transition, there is visible a jump in Θ values. It is known that the spontaneous polarization is coupled to the tilt angle but as one can see, the doping process does not change much the tilt angle (a primary order parameter⁶⁴), although the large dispersion in its temperature dependence is visible for composite 2. Therefore it is impossible to determine the influence of submicroparticles on the tilt angle of molecules. As it will be shown below, from the results of XRD one can conclude that the tilt angle of both composites should be the same within the error limits. Invariability of the tilt angle indicates no structural changes in the composites as compared to the AFLC mixture.⁶⁵

Summarizing, the admixture of BaTiO_3 particles does not disturb the liquid crystal order in the smectic layers. Especially, in the antiferroelectric phase the orthoconic nature is not disturbed and at room temperature the tilt angle reaches ca. 42° for all the samples.⁶⁶ Interestingly, very similar behavior was observed for the tilt angle during doping ferroelectric liquid crystal with noble metal nanoparticles.⁶⁷

Temperature dependence of the switching time in the antiferroelectric SmC^*_α phase is presented in Figure 10. Switching time for both composites is shorter than that for pure AFLC mixture about the same value in the whole temperature range of this phase, and it increases with decreasing temperature. Malik et al.⁶⁸ presented similar behavior for response time during doped ferroelectric liquid crystal by copper

oxide nanoparticles decorated by multiwalled nanotubes. This typical behavior is a consequence of the increasing of the rotational viscosity with decreasing temperature. The switching times at 34°C are equal to 225, 216, and $197.5\ \mu\text{s}$ for AFLC mixture, composite 1, and composite 2, respectively. Four physical quantities, namely spontaneous polarization P_s , switching time τ , rotational viscosity γ , and local electric field E are related as follows:^{69–71}

$$\gamma = P_s E \tau \quad (6)$$

The applied field was used in the calculation of rotational viscosity. As one can see in Figure 10b, the influence of BaTiO_3 particles on the rotational viscosity is quite visible, and for example, at 40°C , γ is equal to 6.03, 5.15, and $5.08\ \text{Pa}\cdot\text{s}$ for the AFLC mixture, composite 1, and composite 2, respectively. As can be seen, the viscosity of composites within the uncertainty range does not coincide with the viscosity values for the pure mixture. Khushboo et al.⁷² and Chaudhary et al.⁷³ observed similar decreasing of the rotational viscosity after doping a ferroelectric liquid crystal with nickel–ferrite as well as silica nanoparticles. In turn, completely different behavior was observed by Shukla et al.⁷⁴ after doping a ferroelectric liquid crystal by carbon dots. On the basis of the results presented above, one can conclude that addition of BaTiO_3 particles into the liquid crystal matrix can help to design new materials with faster switching time and lower spontaneous polarization. It seems that in the future, by controlling the dopant dispersed in the LC host, it will be possible to produce advanced materials with specific parameters without using complex chemical pathway.

During cooling from isotropic liquid, particles gather at the domain boundaries of fan-shaped texture what is demonstrated in Figure 11 for the SmC^*_α phase of composite 1. As it is visible without analyzer (Figure 11b), nanoparticles aggregate at the intersections of domain walls. Domain wall intersections are large defects which carry large elastic energies. Thus, the nanoparticles accumulate there, because this leads to a reduction in the total free energy of the system. However, this issue requires further research. Similar behavior was reported by Al-Zangana et al.⁶³

3.6. X-ray Measurements. The XRD patterns of the pure AFLC mixture and two composites are presented in Figure 12. In the non-doped sample, the low angle peak arising from the smectic layer order appears at 107.8°C (Figure 12a). The temperature dependence of the smectic layer thickness, determined by the Bragg equation from the position of the

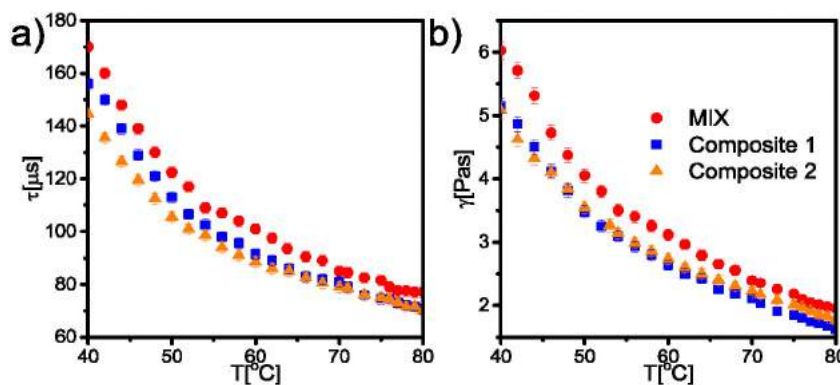


Figure 10. Switching time (a) and rotational viscosity (b) as a function of temperature in the antiferroelectric SmC^*_α phase for AFLC mixture and both composites, $\Delta\tau = 2\ \mu\text{s}$.

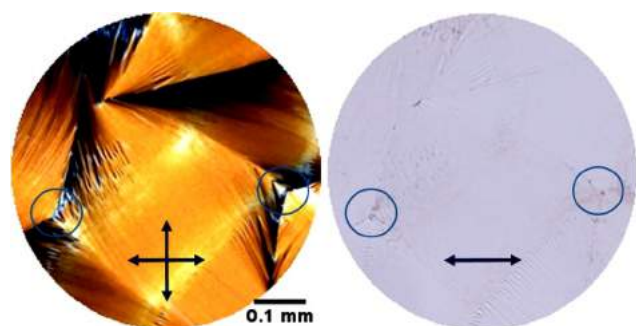


Figure 11. Fan-shaped texture of the SmC_A^* phase for composite 1 with crossed polarizers (a) and without analyzer (b). Circles surround the intersections of domain walls.

low angle peak, is shown in Figure 13. Between 107.8 and 105.8 °C, a single diffraction peak at $2\theta = 2.6^\circ$ is observed, which corresponds with either the paraelectric SmA^* phase or the SmC_α^* subphase. Our previous XRD results for the pure 3F5FPhF compound³⁶ proved that the smectic layer thickness is almost the same in these two phases because of the relatively low tilt angle value in the SmC_α^* subphase.⁵³ At 105.8 °C, the second low angle peak at $2\theta = 2.7^\circ$ appears, which is the sign of the transition to the tilted ferroelectric SmC^* phase. The SmC^* phase is stable in a narrow temperature range, and the small discontinuity in the smectic layer thickness at 104.2 °C can be interpreted as the transition to the antiferroelectric SmC_A^* phase. During further cooling, the smectic layer thickness decreases, and its value below the saturation temperature is close to 31 Å, which is the intermediate value between the smectic layer thickness deep in the SmC_A^* phase obtained for the 3F5FPhF (30.5 Å³⁶) and the 3F7HPhF (31.8 Å³⁷) homologues.

In the XRD patterns of both composites no low angle peak is observed at 107.8 °C (Figures 12b,c). For the composite 2 the low angle diffraction peak develops at 98.6 °C at $2\theta = 2.7^\circ$. The determined smectic layer thickness values (Figure 13) imply that this peak originates from the tilted ferroelectric SmC^* or antiferroelectric SmC_A^* phase. For the composite 1 the sharp diffraction peak at $2\theta = 2.8^\circ$ appears at even lower temperature (90 °C) where the sample is in the antiferroelectric SmC_A^* phase (Figure 12c). The absence of the low angle diffraction peak at $2\theta = 2.6^\circ$, expected from the SmA^* and SmC_α^* phases, in the patterns of the doped mixtures can be explained as follows: impurities (e.g., nanoparticles and submicroparticles) increase

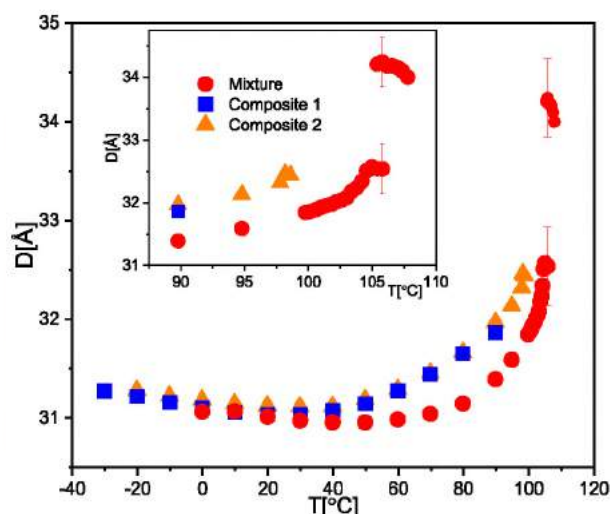


Figure 13. Smectic layer thickness in the AFLC mixture and both composites. The inset shows the temperature region close to the clearing point. For clarity, the error bars are marked only in the vicinity of the clearing point (their highest values).

the number of defects and decrease the average size of domains. This leads to widening and decrease in height of the diffraction peak originating from the smectic layer order, making the small peak invisible in the registered patterns. This effect is stronger for composite 1 because the interactions between liquid crystal molecules and particles increase with decreasing difference between smectic layer thickness and particle size.⁸ It is in accordance with texture observations, where addition of 45 nm particles to the AFLC mixture results in a larger number of defects.

Although the BaTiO_3 dopant significantly influences the phase transitions in the vicinity of the clearing point, both non-doped and doped samples develop the antiferroelectric SmC_A^* phase below 90 °C. For the doped mixtures there is no difference in the smectic layer thickness of the SmC_A^* phase. The value is slightly higher than the one determined for the non-doped sample but the difference is very small and completely vanishes below ca. 40 °C (Figure 13). This result together with the tilt angle measurements reported above prove that addition of BaTiO_3 particles (submicroparticles or nanoparticles) in the used concentration does not disturb the smectic layer spacing deep in the antiferroelectric SmC_A^* phase. There was also not

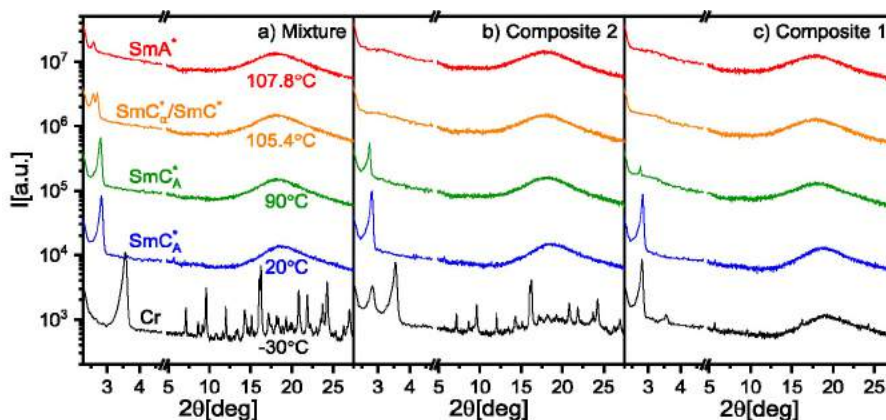


Figure 12. Diffraction patterns of the AFLC mixture (a), composite 2 (b), and composite 1 (c). The patterns in each panel are registered on cooling at 107.8, 105.4, 90, 20, and -30°C (in the same order).

observed any influence of the BaTiO₃ dopant on the distances between molecules within the smectic layers: the wide maximum visible in the diffraction patterns of the smectic phases about $2\theta = 18^\circ$ corresponds with the average intralayer distances of 4.7–5 Å for all studied samples and do not differ from the distances determined at the same temperatures for pure 3F5FPhF and 3F7HPhF.³⁷

The presence of particles has also an influence on the crystallization process, as it is visible comparing the diffraction patterns collected at -30°C (Figure 12, bottom pattern in each panel). In the non-doped AFLC mixture, the $\text{SmC}^*_\text{A} \rightarrow$ crystal transition is observed at 0°C , and at -30°C , the pattern of the well crystallized sample is observed. In composite 2, the crystallization process also begins at 0°C , but it is considerably slowed down, and at -30°C two low angle peaks are observed in the diffraction pattern: the one at $2\theta = 2.9^\circ$ originating from the antiferroelectric SmC^*_A phase and the second one at $2\theta = 3.6^\circ$ from the crystal phase. The integrated intensity of the $2\theta = 2.9^\circ$ peak at -30°C is equal to 49% of the integrated intensity of this peak at the onset of crystallization at 0°C . It means that about 50% of the composite 2 is still in the antiferroelectric SmC^*_A phase at -30°C . The addition of 45 nm nanoparticles has even stronger hindering effect on the crystallization process: although the onset of crystallization is visible at 0°C , at -30°C still only small sharp peaks from a crystal phase are visible (Figure 12c) and most of the sample is in the smectic phase. Presence of impurities is usually expected to enhance crystallization by lowering the energy barrier for nucleation.⁷⁵ Indeed, both in non-doped and doped samples crystallization starts at the same temperature. That means that the addition of particles does not hinder nucleation itself but rather may slow down the growth of stable nuclei, which is the next stage of crystallization.

3.7. Birefringence Measurements. Figure 14 shows the results of birefringence measurements in the materials studied.

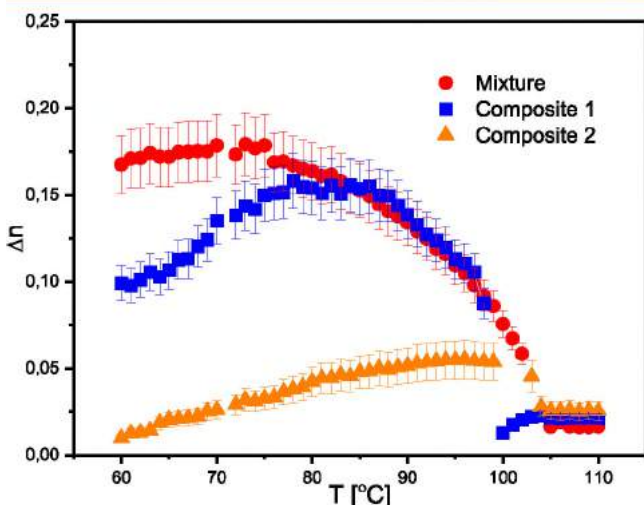


Figure 14. Birefringence as a function of temperature for the pure AFLC mixture and both composites.

As one can see, between 60–75 °C the optical anisotropy for the AFLC mixture is greater than for both composites. At the highest temperatures (in the SmA^* phase), the birefringences for AFLC mixture and composite 1 are approximately the same, but for composite 2, the value of birefringence is much lower. At the $\text{SmA}^* \rightarrow \text{SmC}^*_\text{A}$ phase transition, the abrupt jump for all materials is visible. As one can see, the phase transition

temperatures are shifted for composites what is in good agreement with the DSC results. It turns out, at lower temperatures—below 75 °C (in the SmC^*_A phase)—the measured birefringence Δn for both composites are smaller than for the pure AFLC mixture. It suggests that the addition of BaTiO₃ particles into LC matrix decreases the optical anisotropy. Much smaller values for composite 2 than composite 1 are probably associated with the particles size. Interestingly, from 80 °C to higher temperatures, the values of birefringence for the mixture and composite 1 are the same, whereas below there are discrepancies. On the basis of these results, one can conclude that the larger BaTiO₃ particles cause faster disappearance of optical anisotropy than the smaller ones. However, this requires further investigation. It seems that changes in optical anisotropy may result from the strong interaction between dipole moments of the liquid crystal host and particles. In the measurements of optical anisotropy, a guest–host effect may appear. The larger the particles of the admixture, the more difficult it is for them to fit into the double-twisted structure, which can disrupt the order of the liquid crystal. Birefringence measurements suggest that the liquid crystal arrangement is affected. In particular, this behavior is visible for composite 2. Differences appearing in birefringence measurements relative to diffraction and electric measurements may be due to the fact that measurements of the tilt angle were made on uniformly aligned samples, while birefringence without using the ordering field.

3.8. Ions Trapping Phenomenon. The results presented above show that it is possible to modulate the physical properties of the liquid crystal host by doping with BaTiO₃ particles, without disturbing the liquid crystal order. BaTiO₃ particles are ferroelectric, so their addition to the LC matrix changes the local electric field. As a result, the liquid crystal molecules are subjected to this modified electric field. We assume that the shorter switching time of the investigated composites results from the phenomenon of free ions trapping on the surface of particles—between free ions and particles Coulomb interaction occurs. Almost all liquid crystalline materials contain free ions (as impurities after the synthesis process) that affect conductivity. Moreover, if we consider liquid crystalline material in an electro-optic cell, free ions can also come from polymer alignment layers, spacers and filling process (ions from atmosphere). The electric field at a distance r from the middle of ferroelectric BaTiO₃ particle has a dipole form:^{31,76}

$$\vec{E}_{\text{NP}} = \frac{R^3 P}{3\epsilon_0 r^3} (2 \cos \theta \hat{r} + \sin \theta \hat{\theta}) \quad (7)$$

Here R is the radius of particles (in our case the diameter were equal to 45 and 280 nm), P is the polarization of particles, r is the distance from the middle of particle, and ϵ_0 is the vacuum permittivity. The electric field E_{NP} at a distance of several nanometers from the surface of the particle is of the order of 10^{10} V/m; e.g., it is 4 orders of magnitude higher than the external electric field applied to the electro-optic cell (15×10^6 V/m). The E_{NP} field decreases very fast as the distance increases; thus, all mobile ions surrounded by particle are trapped. Schematic ions transport in a pure AFLC mixture is shown in Figure 15a. When an external electric field is applied, free ions will move to the polarized bounding surfaces. In turn, the phenomena of free ions trapping in a doped AFLC mixture hinder the migration of ions to the appropriate electrodes, as schematically presented in Figure 15b. This trapping of free ions by BaTiO₃ particles is

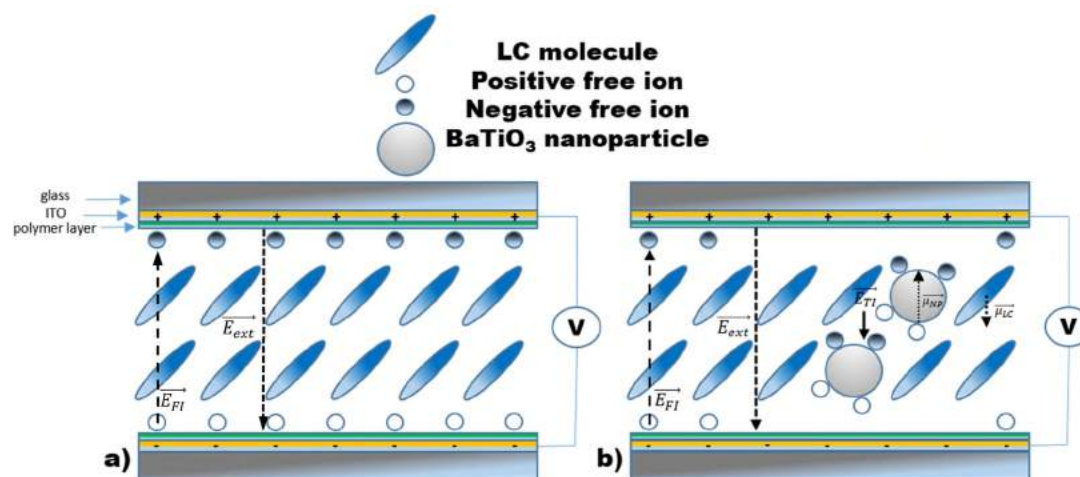


Figure 15. Scheme of the resultant electric field in the not doped (a) and doped by ferroelectric BaTiO₃ particles (b) LC matrix placed in the electro-optic cell. The scale is not preserved. Symbols used: E_{ext} external electric field; E_{FI} electric field of free ions; E_{TI} electric field of trapped ions; μ_{NP} dipole moment of particle; μ_{LC} dipole moment of liquid crystal molecule. The drawing presents the situation for unwound helices in the SmC*_A phase.

responsible for the modification of the local electric field, which is higher in the case of the doped rather than the pure AFLC mixture. So, the switching time for both composites should be shorter than for pure AFLC mixture, as it was measured by us (see Figure 10) and observed by Shukla et al.⁵⁹ Additionally, fewer free ions reduce rotational viscosity. In turn, the change of the spontaneous polarization in the composites can be explained by antiparallel dipole–dipole correlations between the liquid crystal molecules and particles. In the case of not doped sample, molecules are subjected to a resultant electric field $E_{res} = E_{ext} + E_{inter}$ (where E_{ext} is an external electric field applied while E_{inter} is an electric field from the neighbors). The resultant electric field E_{res} is weakened by opposite directed electric field E_{FI} coming from free ions on the electrodes (eq 8):

$$\vec{E}_{notdoped} = \vec{E}_{res} + \vec{E}_{FI} \quad (8)$$

In the case of the doped sample, in addition to the electric fields E_{res} and E_{FI} , there is an extra electric field coming from the trapped ions (E_{TI}), which direction is the same as the external field (eq 9):

$$\vec{E}_{doped} = \vec{E}_{res} + \vec{E}_{FI} + \vec{E}_{TI} \quad (9)$$

Thus, the local electric field is modified by particles and increases its value:

$$|\vec{E}_{notdoped}| < |\vec{E}_{doped}| \quad (10)$$

3.9. Dielectric Measurements. It is known that several collective processes exist in the antiferroelectric, ferroelectric and paraelectric liquid crystalline phases. The low frequency, temperature independent process, Goldstone mode, is connected with collective reorientation of the polarization vector along a cone with an opening angle 2Θ (Θ is the tilt angle of molecules).⁷⁷ The strong enough bias field can suppress the Goldstone mode and then relaxation processes like domain mode or soft mode can be revealed.^{78,79} The soft mode is strongly dependent on temperature while the bias voltage does not have influence on the relaxation frequency of this dielectric process. Usually, the soft mode is observed near to the SmC*–SmA* phase transition but there are also compounds with the soft mode registered in the whole temperature range of the

ferroelectric SmC* phase and even in the antiferroelectric SmC*_A phase.⁸⁰ There are possible three dielectric processes in the antiferroelectric SmC*_A denoted here as P_H, P_L (so-called the antiferroelectric-like Goldstone mode), and molecular s-process that was reported earlier by us and others.^{80–83}

Figure 16 presents the dielectric absorption as a function of frequency and temperature for pure AFLC mixture and both composites in the antiferroelectric SmC*_A phase registered without (left column) and with (right column) applied bias field. As one can see, in the case without bias field applied, the absorption ϵ'' of all the processes registered is the lowest for the composite 1 in the SmC*_A phase. Moreover, the relaxation frequency of the processes registered in both composites is shifted to lower values as compared with the pure AFLC mixture. After applying the bias field, the P_L mode, practically not visible in composites, was registered (Figure 16d,f) and the relaxation frequencies of P_L and P_H are shifted to higher values.

Figure 17 presents the influence of the bias field on the dielectric spectra for both composites in the antiferroelectric SmC*_A (70 °C) and paraelectric SmA* (100 °C) phases. As one can see, the influence of the bias field on the high frequency dielectric process P_H in the antiferroelectric phase is negligible while the low frequency mode P_L becomes weaker and its relaxation frequency decreases with increasing the bias field for both composites. The relaxation frequency for the P_L process (at 7 V) is equal to 3649, 3404, and 2963 Hz while the absorption value for this relaxation process (at 7 V) is equal to 0.042, 0.316, and 0.392 for the AFLC mixture, composite 1, and composite 2, respectively.

In turn, in the paraelectric SmA* phase only one relaxation process—soft mode is visible and the influence of particles on the dielectric spectra is noticeable (Figure 17c,d). Despite the fact that the bias voltage does not change the relaxation frequency of the soft mode ($\nu_r = 204$ kHz at 0 and 10 V for both composites), dielectric absorption values differ significantly. As it is seen, for the LC matrix with an admixture of smaller BaTiO₃ nanoparticles (45 nm), the dielectric losses of the soft mode in the SmA* phase is twice as low as for a matrix doped with larger particles (Figure 17c, d).

The dielectric increment and relaxation frequency of the dielectric processes registered in the liquid crystalline phases

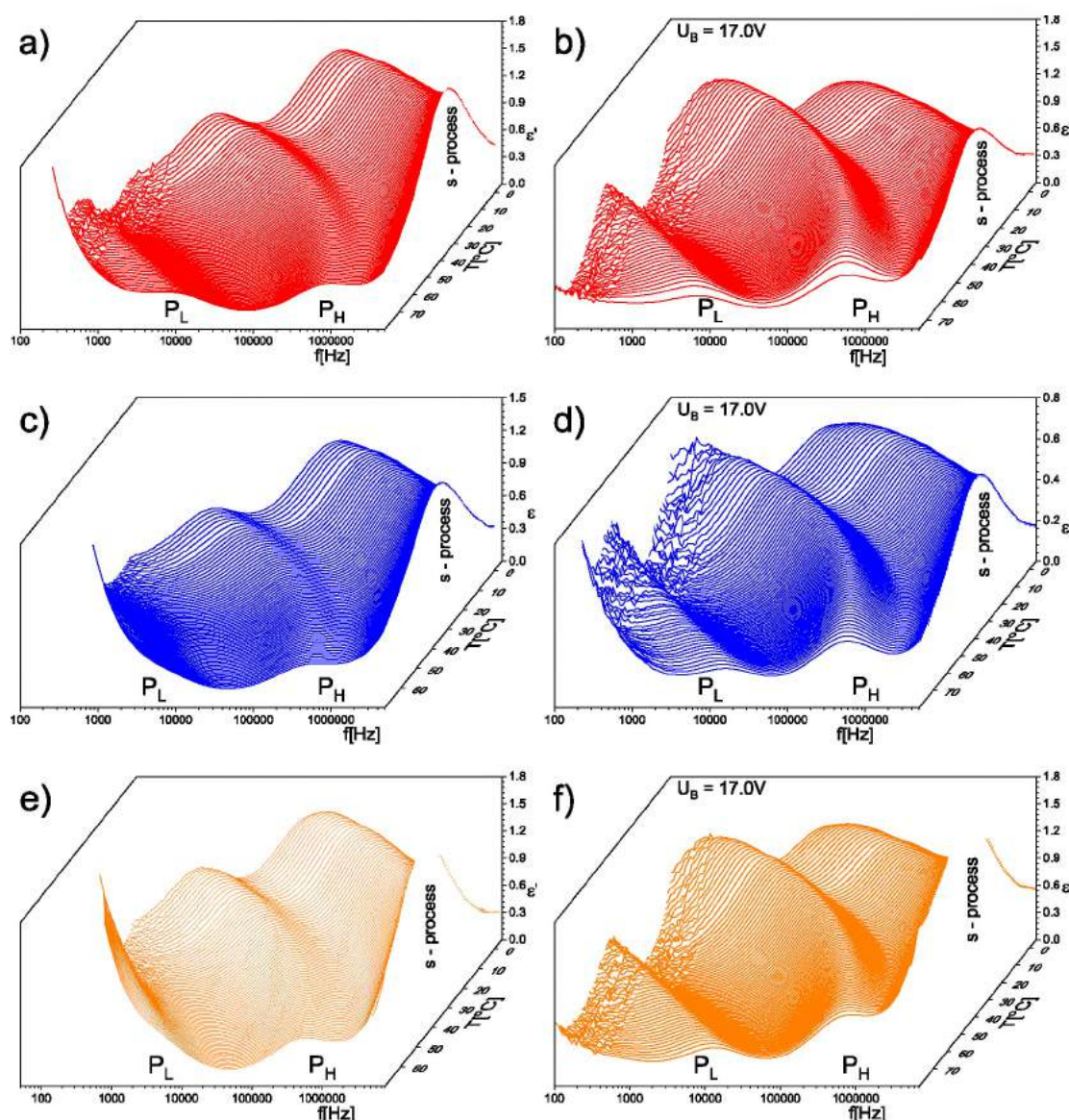


Figure 16. 3D plots of the dielectric absorption as a function of frequency and temperature for AFLC mixture (a, b), composite 1 (c, d), and composite 2 (e, f). The first column represents dielectric data registered without bias voltage and the second one with $V_B = 17.0$ V.

were obtained by fitting the Cole–Cole formula^{84,85} to the experimental data. The characteristic V-shape in the temperature dependence of the relaxation frequency and the inverse of dielectric increment, for all the samples studied, in the vicinity of the $\text{SmA}^*-\text{SmC}^*_\alpha-\text{SmC}^*$ phase transition is presented in Figure 18. On the basis of the Blinc and Žekš theory,⁸⁶ the ratio of the slope of the straight lines fitted on both sides of the $\text{SmA}^*-\text{SmC}^*$ transition is equal to -2 for the second order transition. For the studied samples these values are equal to -2.81 ± 0.85 , -2.66 ± 0.74 , and -2.76 ± 0.33 for the AFLC mixture, composite 1 and composite 2, respectively. It is seen that the calculated slope ratios, within the error limits, are generally close to -2 , as predicted by the theory. However, it should be stressed here that the theory⁸⁶ concerns the transition between the paraelectric SmA^* and ferroelectric SmC^* phases, while the compounds studied exhibit an additional narrow subphase SmC^*_α between them, which usually affects the slope factor. This is well visible for composite 2, where the slope ratio does not equal -2 within experimental error. The relaxation frequency at the $\text{SmA}^*-\text{SmC}^*_\alpha$ phase transition is equal to ca.

200 kHz for the AFLC mixture and composite 1 while for composite 2 is ca. 275 kHz. This is another proof that by addition of BaTiO_3 particles to the liquid crystal matrix its properties can be modified.

The Arrhenius plot for dielectric processes revealed in the antiferroelectric SmC^*_A phase is presented in Figure 19. The activation energy of each process, gathered in Table 2, was obtained by using the Arrhenius equation.⁸⁷ As one can see, three processes are well visible for all the samples studied. At lower temperatures P_H mode and reorientation around short axis (s-process) are present while at higher temperatures P_H and P_L modes were detected. In the case of P_H process, two values of activation energy were obtained: in the low and high temperature range (marked as 1 and 2 in Figure 19 and Table 2). As it is visible, the activation energy of P_H is almost double for low than high temperature range, for the pure AFLC mixture and both composites. Moreover, the activation energies for the AFLC mixture and both composites are comparable. Thus, the particles admixture does not influence the activation energies of

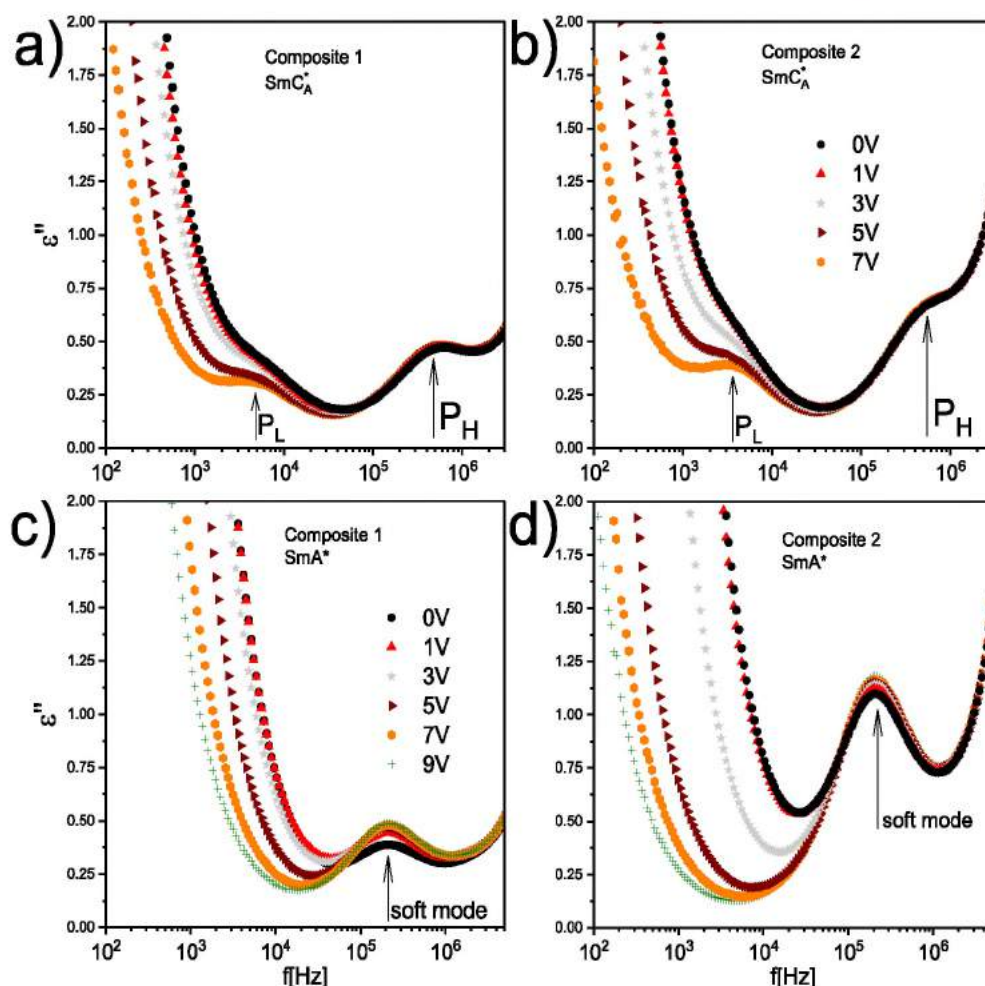


Figure 17. Influence of the bias voltage on the dielectric absorption in the antiferroelectric SmC_A^* phase (a, b) and paraelectric SmA^* phase (c, d) for composite 1 (a, c) and composite 2 (b, d).

the relaxation processes revealed in the antiferroelectric SmC_A^* phase.

3.10. Ionic Conductivity Measurements. In the pure AFLC mixture, after applying the electric field, free ions (positive and negative) go to properly polarized electrodes. After reversing the electric field direction, they move to the opposite electrodes. Their movement is responsible for ionic current in the LC host. Ionic conductivity is proportional to the amount of free ions in the sample. So, the conductivity measurement is therefore a good way to determine the amount of free ions in a sample. The conductivity is a complex quantity depending on frequency:⁸⁸

$$\begin{aligned}\sigma_{\perp}^*(\omega) &= \sigma'(\omega) + i\sigma''(\omega) = i\omega\epsilon_{\perp}^*(\omega) \\ &= i\omega(\epsilon'(\omega) - i\epsilon''(\omega)) = \omega\epsilon''(\omega) + i\omega\epsilon'(\omega)\end{aligned}\quad (11)$$

$$\sigma \equiv |\sigma_{\perp}^*| = \sqrt{(\sigma')^2 + (\sigma'')^2} \quad (12)$$

$$\begin{aligned}\sigma'(\omega) &= \omega\epsilon''(\omega) = \omega \frac{\Delta\epsilon}{1 + \omega^2\tau^2} \omega\tau \\ \sigma''(\omega) &= \omega\epsilon'(\omega) = \omega \left(\epsilon_{\infty} + \frac{\Delta\epsilon}{1 + \omega^2\tau^2} \right)\end{aligned}\quad (13)$$

where σ' , σ'' , ϵ' , ϵ'' are real and imaginary part of complex conductivity and complex permittivity, ϵ^* is complex

permittivity (perpendicular component), ω is the angular frequency ($\omega = 2\pi f = 2\pi/\tau$), τ is the relaxation time of the medium, and $\Delta\epsilon$ is the dielectric increment.

AC conductivity as a function of frequency at three freely chosen temperatures for each sample and as a function of temperature is presented in Figure 20 and 21, respectively. As one can see, the absolute conductivity in the composite 1 is smaller than for pure AFLC mixture and composite 2 as well. This indicates the trapping of free ions by particles. In turn, for composite 2, there is not visible change in comparison with the AFLC mixture. So, the admixture of smaller particles significantly reduces ionic conductivity compared to a pure mixture.

To show that the conductivity value for composite 1 drops significantly compared to the pure mixture, in Figure 21 we can see how the low frequency conductivity changes with temperature. At high frequencies, we already have a completely different conductivity regime, which is not discussed in this work. The conductivity values are lower for both composites than for the mixture at low temperatures. Higher values at high temperatures than for a pure mixture may be due to the fact that the particles introduced into the matrix also contained a certain amount of ions. The value of ionic conductivity for both composites increases then (approximately 65 °C), because trapped ions gain sufficiently high thermal energy that allow them to detach from the local field of dopant particles, and they

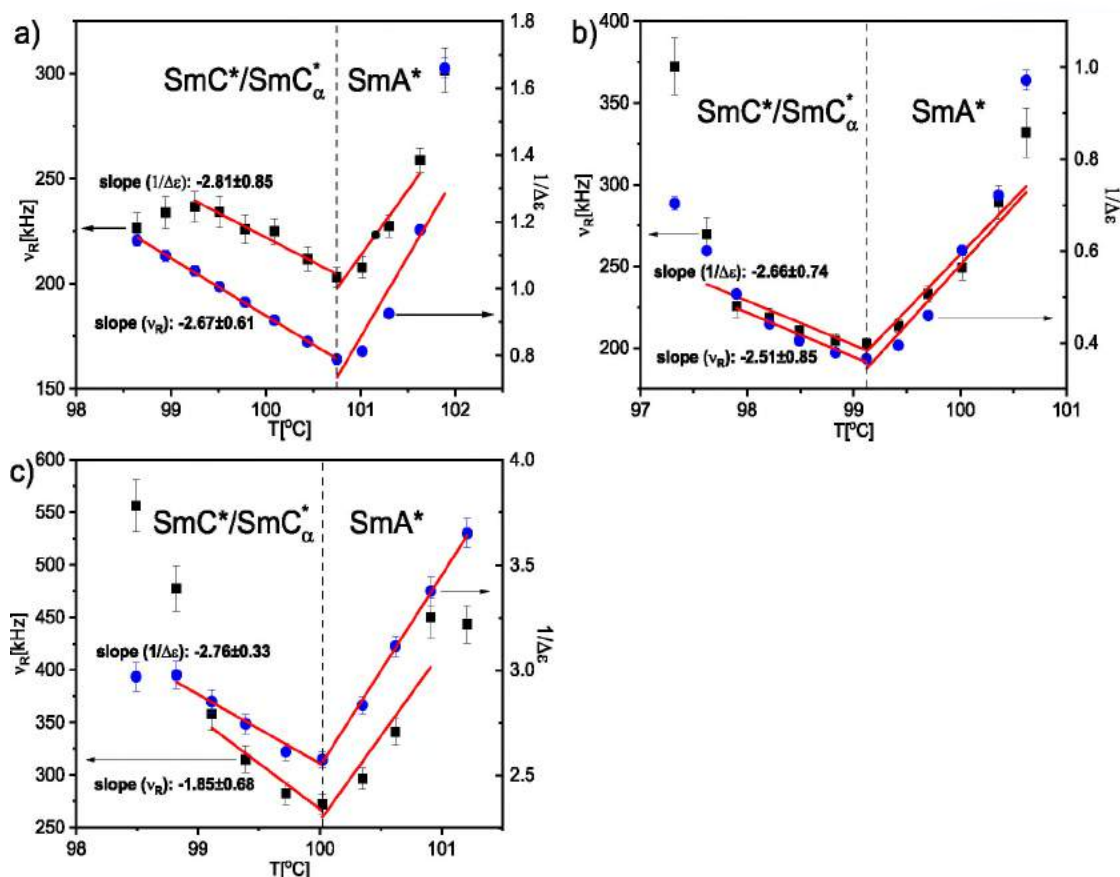


Figure 18. Temperature dependence of the inverse of dielectric increment and relaxation frequency in the vicinity of the SmA^* – SmC^*_α phase transition for the AFLC mixture (a), composite 1 (b), and composite 2 (c).

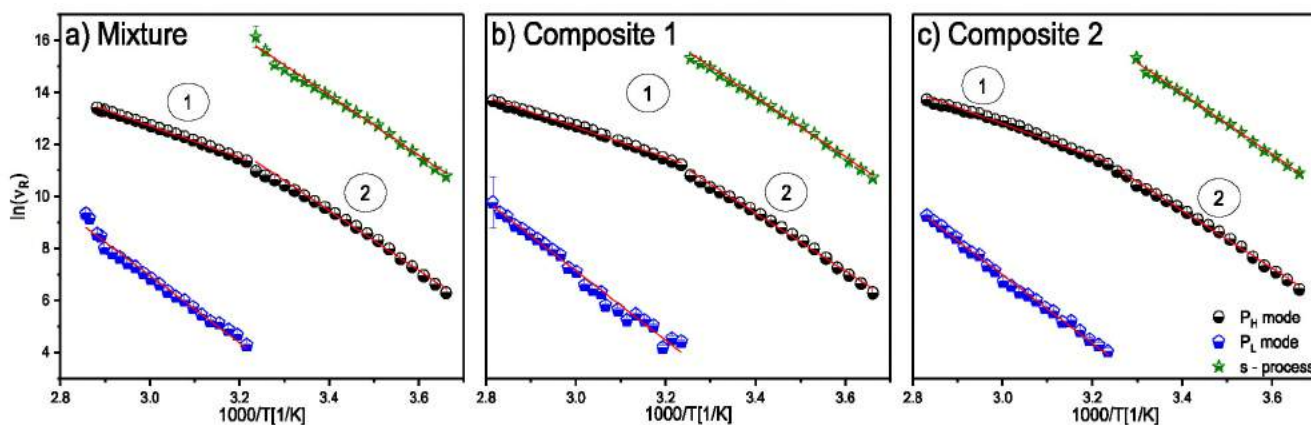


Figure 19. Arrhenius plots for all the dielectric processes in the SmC^*_α phase for AFLC mixture (a), composite 1 (b), and composite 2 (c).

Table 2. Activation Energies for All the Dielectric Processes Revealed in the SmC^*_α Phase for the AFLC Mixture and Both Composites

sample/process	activation energy [kJ/mol]			
	P_L	P_H 1	P_H 2	s-process
mixture	107.4 ± 3.2	50.5 ± 0.7	95.7 ± 1.8	96.1 ± 1.6
composite 1	111.3 ± 2.9	48.6 ± 0.8	92.5 ± 1.6	95.9 ± 1.3
composite 2	109.2 ± 2.0	51.8 ± 0.2	92.2 ± 1.5	97.5 ± 1.0

become mobile. Hsiao et al.⁸⁹ obtained similar ionic conductivity behavior for nematic liquid crystal E44 doped

with ferroelectric BaTiO_3 nanoparticles (30–50 nm, concentration 0.1 and 0.55% by weight).

According to Garbovskiy et al.,^{90–92} liquid crystals obtained by doping with nano-/microparticles can be purified or contaminated with ions, or there will be no change in the concentration of these ions in the sample, depending on the chemical purity of the liquid crystal matrix and dopant particles. According to Garbovskiy's assumptions, if the original concentration of mobile ions in the matrix is less than the critical concentration (characteristic parameter for a given liquid crystal material), then the dispersed dopant particles will cause an increase in ion concentration. In addition, if the introduced particles are heavily contaminated with ions (the amount of

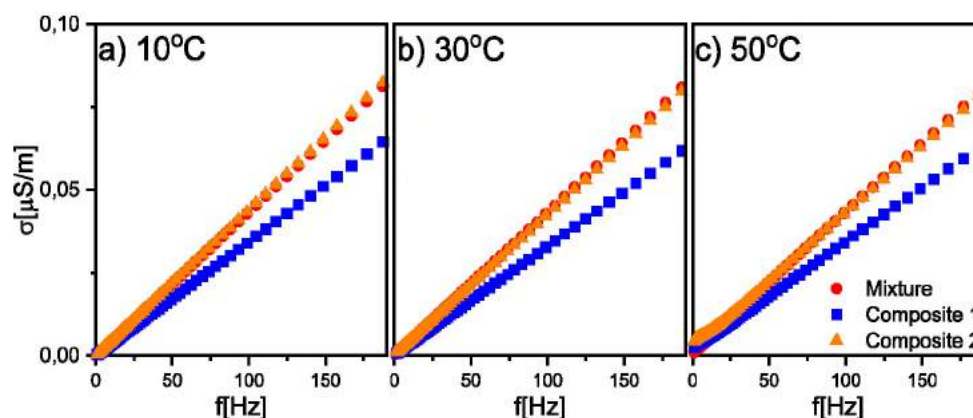


Figure 20. Frequency dependence of the absolute value of the complex conductivity for the AFLC mixture and both composites at chosen temperatures.

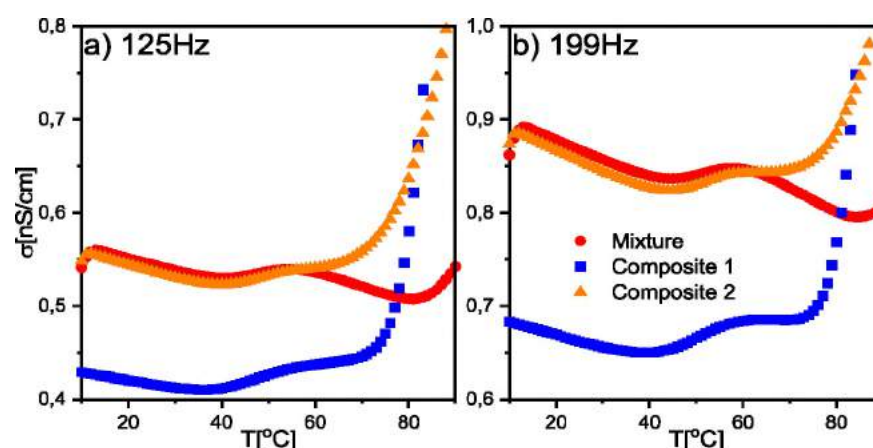


Figure 21. Temperature dependence of absolute value of complex conductivity for the AFLC mixture and both composites at two chosen frequencies, $\Delta\sigma = 10^{-4}$ nS/cm.

impurities exceeds the critical value), then the amount of mobile ions in the composite will also increase. In turn, if the ion concentration in the liquid crystal matrix is higher than the critical concentration and the doped particles are relatively pure, then the matrix will be purified of ions. Intermediate cases, e.g., an ionic pure liquid crystal matrix and ionic enriched dopant particles will cause the concentration of mobile ions in the composite to be substantially constant. Tomylo et al.⁹³ confirmed that there are changes in the ionic conductivity of pure and ion-contaminated liquid crystal E7 doped with diamond nanoparticles, whereas Shcherbinin et al.⁹⁴ showed such changes through the doping of a nematic pure liquid crystal with ionically contaminated titanium dioxide nanoparticles. The particles used in our experiments exhibit purity of 99.95%. The results of conductivity measurements at low frequencies (Figures 20 and 21) clearly show that the concentration of free ions in both studied composites is lower than that in the pure AFLC matrix. Thus, it can be qualitatively concluded that the liquid crystal matrix used exceeds the critical ion concentration and the particles used are sufficiently pure. Moreover, as Garbovskiy and Glushchenko⁹⁵ showed, the ions present in a typical cell filled with a liquid crystal or a liquid crystal-based composite may come from the process of liquid crystal synthesis, impurities derived from the ordering polymer layer, glue, and ions adsorbed on the surface of the particles. Therefore, the process of controlling the amount of moving ions

is very important from the point of view of the production of materials with strictly defined properties.

It seems that despite larger particles concentration in composite 2, there are fewer particles because their size is over six times bigger than 45 nm particles ($r_{280\text{ nm}}/r_{45\text{ nm}} \approx 6.22$, while volume ratio $V_{280\text{ nm}}/V_{45\text{ nm}} \approx 240$). However, it should be pointed out here that the concentration of particles in composite 2 may be less than 0.75% due to possible aggregation of particles during cell filling. The absolute value of complex conductivity for composite 1 is lower than for the AFLC mixture in the whole temperature range, as it is seen in Figure 20. Also the absolute value of complex conductivity for composite 2 is lower than for the AFLC mixture, but in this case, the influence of particles is much less. Based on the results presented in Figure 20 and Figure 21, it can be clearly stated that the admixture of BaTiO₃ particles traps free ions in the LC matrix, which reduces the conductivity. The same phenomenon was observed by Basu et al.³¹

4. CONCLUSIONS

The influence of the ferroelectric BaTiO₃ particles on the properties of AFLC mixture were studied by complementary methods. On the basis of the results obtained, it may be concluded:

- The admixture does not affect the phase sequence, however changes in the texture are noticeable (particles

tend to aggregate at domain walls intersections, in order to reduce the free energy of defects) and the phase transition temperatures are shifted to the lower temperatures. Moreover, as compared to the undoped mixture, the two-stage crystallization appears in both composites.

- The admixture does not shorten the time for alignment of the sample, and it takes ca. 2 h for AFLC mixture and both composites. However, it is possible to decrease the threshold voltage by doping at low concentrations of BaTiO₃ nanoparticles (45 nm size).
- The decrease in the spontaneous polarization for both composites can be explained by the antiparallel ordering of the dipole moments of liquid crystalline molecules and the dopant particles together with the ion trapping phenomenon. These also increase the local field acting on a single molecule and that is why the decrease in switching time and rotational viscosity for the composites is observed.
- On the basis of X-ray diffraction and electro-optic measurements, we have shown that admixture of BaTiO₃ nano- and submicroparticles influence neither the smectic layer spacing nor the tilt angle in the SmC*_A phase below 40 °C.
- The addition of particles affects the dielectric parameters of composites, such as the relaxation frequency and absorption values; moreover, the decrease in the ionic conductivity is observed.
- In turn, no influence of the admixture on the activation energies of the processes in the antiferroelectric SmC*_A phase was observed. DC conductivity is suppressed by bias field in the pure AFLC mixture the same in both composites.

Summarizing, the reported studies confirmed that it is possible to get rid of free ions from the liquid crystal matrix by doping with ferroelectric particles. It turns out that free ions are trapped close to the particles by a strong electric field, which is the result of the dipole moment possessed by particles. Reduction of the concentration of free ions in the liquid crystal matrix significantly modifies the properties of the LC host material, such as spontaneous polarization, rotational viscosity, switching time, dielectric constant, or optical anisotropy.

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Notes

The authors declare no competing financial interest.

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Article

Modifications of FLC Physical Properties through Doping with Fe₂O₃ Nanoparticles (Part I)

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Abstract: The aim of this paper is to show, by systematic studies, the influence of γ -Fe₂O₃ nanoparticles on the physical parameters of the liquid crystalline matrix, exhibiting a ferroelectric phase in a wide temperature range. The detailed research was carried out by using diffraction (PXRD), microscopic (OM, SEM, FCPM, POM), thermal (DSC), optical (TLI), electric and spectroscopic (FTIR) methods. We show that even the smallest concentration of γ -Fe₂O₃ nanoparticles largely modifies the parameters of the ferroelectric SmC* phase, such as spontaneous polarization, switching time, tilt angle, rotational viscosity, dispersion anchoring energy coefficient and helix pitch. The admixture also causes a significant reduction in the temperature of phase transitions, broadening the SmA* phase at the expense of the SmC* phase and strong streaking of the texture. We present and explain the non-monotonic modification of these parameters with an increase in the nanoparticle concentration. The influence of oleic acid admixture on these parameters is also widely discussed. We have shown that certain parameters of organic-metal nanocomposites can be controlled by the appropriate amount of metal admixture.

Keywords: ferroelectric liquid crystal; γ -Fe₂O₃ nanoparticles; oleic acid; aggregation; metal-organic nanocomposite



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1. Introduction

The continuous industry development and various areas of social life cause an increase in the demand for materials with precisely defined physical and chemical properties. Nowadays, the soft matter discipline is not limited to widely understood science of organic materials. In recent years, new branches have emerged, e.g., involving organometallic materials. This group of materials is divided into two classes: (1) with and (2) without the presence of a chemical bond between a metal atom and an organic ligand. The above-mentioned classes of hybrid materials are one of the ways to meet the growing demand for specialized materials. Another way is the chemical synthesis of extremely complex organic materials, including the use of longer alkyl substituents, increasing the number of benzene rings in a rigid core and the presence of heteroatoms (such as S, N) [1–4]. Another possibility is, for example, to introduce lactate groups into the structure of organic compounds or fabrication of a polymer-dispersed liquid crystal [5,6]. In many cases, the latter approach is very costly, time-consuming and requires multiple intermediates and catalysts. In addition, the yields of the end products may be relatively low and/or the material has to be further purified. Therefore, it seems only natural that creating hybrid materials based on existing ones is a good alternative. However, it should be noted that the chemical synthesis of complex compounds makes it possible to predict some of their properties, for example the modification of phase transition temperatures, while the

properties of the created composites' organic material-metal component are practically unpredictable. One of the reasons is the very poor database of these materials. On the other hand, the possibilities of creating hybrid materials are practically unlimited, starting with the choice of matrix (liquid crystal, polymer, gel, sol, resin, silicone, etc.) and ending with the choice of dispersed material (metal, non-metal, isolator, element, chemical compound). Additionally, the dispersed material can be in various forms: crystal, amorphous material, glass, solution, powder, granules, etc. Thanks to the nanotechnology development, it has become possible to synthesize materials with sizes in the order of several nanometers. This is very important because the size of such objects is usually only a few times larger than the single organic molecule that forms the matrix of such a nanocomposite. The commercial cost of the nanoparticles is usually negligible compared to the organic matrix; however, both the cost and the nanoparticles' diameter depends on the synthesis method [7].

Soft materials, such as liquid crystals (LC), can only exhibit a ferroelectric phase if they are composed of molecules having a non-zero dipole moment and chiral center. Typically, for a new liquid crystalline material, a chiral center is created during its synthesis. However, the easiest way to obtain the chiral liquid crystal material is to introduce a chiral dopant (even a small amount) into the non-chiral matrix [8]. In the case of doping of liquid crystals, the most important issue is the concentration and type of nanoparticles used. Interestingly, different liquid crystalline phases (nematic, smectics, cholesteric) react in a different way to the same admixture.

Until now, many scientists have been involved in the creation and research of new composite materials based on a liquid crystal matrix doped with various types of nanoparticles. Shiraishi et al. doped two nematic liquid crystals NLC-1 and NLC-2 (differing in dielectric anisotropy) with Pd nanoparticles (ca. 2.5 nm with 1, 5, 10 wt.%), and showed that the highest transmission in the on state is for the smallest impurity concentration, and as the frequency increases, the threshold voltage drops drastically for switching to the off state [9]. Joshi et al. doped ferroelectric liquid crystal KCFLC by ZnO nanoparticles (ca. 7 nm) and showed that the admixture improves the alignment of organic molecules in low concentrations (1 wt.%) and the spontaneous polarization and viscosity increase significantly after doping [10]. In turn, Kumar et al. observed nine-fold photoluminescence intensity improvement after doping the ferroelectric liquid crystal LAHS19 with Au nanoparticles (ca. 15–20 nm) [11]. Prakash et al. observed a memory effect due to charge transfer from LC molecules of FLC 6304 to Au nanoparticles (ca. 15–20 nm) [12]. Li et al. also used the non-synthetic method to modify liquid crystal properties and showed that for the MLC-6609 nematic mixture, after doping with BaTiO₃ nanoparticles (ca. 30–50 nm), the nematic–isotropic liquid phase transition temperature increases by almost 40 °C, as well as an increase in dielectric and optical anisotropy is observed [13]. By doping antiferroelectric liquid crystal mixture with BaTiO₃ nanoparticles, we obtained faster molecular switching, a drop in threshold voltage and spontaneous polarization, as a result of modification of the local electric field [14]. In turn, Manepalli et al. showed that the self-organization of ZnO nanoparticles (ca. 61 nm, 1 wt.%) added to 9OBA and 11OBA liquid crystals causes changes in their textures, and transmittance for each functional group increases after 9OBA is doped [15]. Kopčanský et al. doped nematic 6CHBT with Fe₃O₄ (0.0001 vol.%), and as a result, a decrease in the specific resistance and an increase in the relaxation time were observed [16]. Manna et al., by doping MHPOBC with BaTiO₃ nanoparticles (ca. 25 nm, 5 wt.%), significantly decreased the SmA*–SmC* transition temperature and spontaneous polarization, which in turn increases the entropy of the nanocomposite system [17]. Neeraj et al. showed that by doping ferroelectric liquid crystal with Ni nanoparticles (ca. 2–8 nm, 0.5 wt.%), the switching time is shortened, the absorbance in the UV region is improved, the spontaneous polarization and tilt angle (to a small extent) are increased while the conductivity is not significantly changed [18]. The increase in spontaneous polarization, tilt angle and transmittance is explained by the strong interactions between the dipole moments of Ni nanoparticles and surrounding organic molecules in an external electric field. Interestingly, Ni nanoparticles reduced zig-zag structure defects and improved

contrast [18]. Roy et al. showed that after doping an antiferroelectric liquid crystal with Na_2TiO_3 nanoparticles (ca. 70–80 nm, up to 13 wt.%), the photoluminescence of nanocomposites increased (depending on their concentration) [19]. Additionally, they observed a red shift for the emission bands [19]. Rudzki et al. doped ferroelectric liquid crystal MHOB4 with ZnO (ca. 50 nm, 0.2 wt.%) and Ag (ca. 100 nm, 0.2 wt.%) nanoparticles [20]. Both admixtures do not affect the molecular tilt angle (the smectic layer's thickness is constant), but the spontaneous polarization is decreased in both cases while the switching time increased, even by five times [20]. Rožić et al. doped ferroelectric liquid crystal Felix 015/100 with ferromagnetic nanoparticles $\gamma\text{-Fe}_2\text{O}_3$ (ca. 18 nm, $T_B > 380$ K), and suggested that the orientation of magnetic nanoparticles is directly coupled to the liquid crystal director field [21]. This coupling concerns the magnetization of nanoparticles and the liquid crystal polarization. These hybrid materials (named soft magnetoelectrics) exhibit both ferromagnetism and ferroelectricity. An additional advantage of these magnetoelectrics is that the external fields well-align nanoparticles by ordering the organic molecules. Moreover, the low dopant concentration (0.14 wt.%) decreased the $\text{SmA}^* \rightarrow \text{SmC}^*$ phase transition temperature. Rožić's group expressed an important conclusion that the magnetic susceptibility anisotropy follows the temperature evolution of the tilt angle in such hybrid systems. This is direct proof of a certain coupling between the liquid crystal director and the magnetization of nanoparticles. In another paper, Rožić et al. presented that the admixture of Fe_2O_3 nanoparticles (ca. 20 nm in toluene; 10, 14 wt.%) to ferroelectric liquid crystal SCE9 suppressed both the Goldstone and soft modes in the SmC^* phase [22]. Both modes are suppressed after adding nanoparticles. Likely, a high dopant concentration results in a loss of liquid crystal properties. Due to a very low volume concentration of dopant, changes in material parameters may result from the formation of an electric double layer on the electrode–liquid crystal interface [16]. It should be noted that Fe_2O_3 nanoparticles have different magnetic parameters depending on size [23]: very small Fe_2O_3 nanoparticles are a superparamagnetic material, while larger-diameter nanoparticles are a ferromagnetic material. In addition, the large diameter distribution of nanoparticles causes the blocking temperatures for each diameter to overlap, and the final result may be impossible to determine.

The influence of the Fe_2O_3 nanoparticles on the nematic liquid crystals has been widely studied. Thus, Yadav et al. and Gao et al. obtained a decrease for rise and fall time by doping nematic liquid crystal with Fe_2O_3 nanoparticles [24,25], just like Koo et al., who additionally obtained a decrease of threshold voltage and the enhanced dielectric constant, which were explained by the charging of Fe_2O_3 nanoparticles in the external field and trapping impurity ions [26]. In turn, Katiyar et al. obtained shorter response times in nanocomposites, which was explained by the trapping ions phenomenon on the surface of TiO_2 nanoparticles [27]. In turn, by doping to 10OBA and 11OBA with Fe_3O_4 nanoparticles (ca. 70–80 nm, 0.5 and 1.0 wt.%), Sivasri et al. obtained a decrease in conductivity, phase transition temperatures, enthalpy changes and transmittance, as well as broadening of the nematic phase temperature range [28].

On the other hand, only a few scientists have reported on the influence of Fe_2O_3 nanoparticles on the ferro- or anti-ferro-electric liquid crystals. For example, after doping the ZLI-3654 liquid crystalline mixture with Fe_2O_3 nanoparticles (ca. 24 nm, 0.25 and 1.25×10^{-5} wt.%), stripe-like domains were observed under crossed polarizers, which were explained by the chain-like alignment of nanoparticles in the LC matrix [29]. In turn, the increase in spontaneous polarization versus applied voltage after doping was explained based on the magnetoelectric coupling resulting from the strong interaction between the nanoparticles' exchange field (unpaired electron) and the molecular director field [29]. Meanwhile, the rotational viscosity and response time decrease with increasing the voltage in relation to pure ZLI-3654 (modification of the electric field of electric dipoles by a nanoparticle magnetic field). The memory effect was well-observed, especially in the dielectric spectra [29]. Novotná et al. doped the ferroelectric liquid crystal 9HL with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (ca. 4 nm), which were superparamagnetic at high temperatures,

obtaining a super-paramagneto-ferroelectric in the SmC* phase [30]. In turn, Romero-Hasler et al., thanks to the doping of a ferroelectric liquid crystal based on pyrimidine with FeCo nanoparticles (ca. 2–3 nm, 0.53–10.80 wt.%), obtained a multiferroic system in which the magnetic field can be generated by an electric field and vice versa, and the phase transition temperature as well as spontaneous polarization (to a slight extent) drop [31]. As a dopant to the liquid crystal matrix, other chemical objects such as dyes can also be also used [32].

Moreover, it is well-known that when reducing the size of the dopant material to the nanometric scale, the physical and chemical properties are changing [33], and in the case of nanoparticles, their properties strongly depend on their diameter [27].

Our goal was to obtain multifunctional material with advantageous electric, optic and magnetic properties. As is known, liquid crystal can be used as a medium for self-assembly of low concentrations of nanoparticles, due to its orientational and positional order [30]. In this paper, we present the influence of Fe₂O₃ nanoparticles with diameter below 50 nm on the physical properties of the liquid crystalline matrix. We have chosen Fe₂O₃ nanoparticles as an admixture because they have various unusual physical properties, are easy to synthesize and inexpensive, are non-toxic and have pronounced antibacterial properties; moreover, they are stable in an interesting temperature range (0–110 °C) [26,34–36]. Currently, the main obstacle to the use of the ferroelectric liquid crystal in display technology is the shock problem, i.e., irreversible destruction of an aligned LC layer by mechanical stress, although Pozhidaev et al. have recently reported on the synthesis of shock-free ferroelectric liquid crystal FLC-595 [37]. Nevertheless, we believe that the nanoparticles introduced into the ferroelectric liquid crystal matrix can also eliminate the shock problem. However, it requires a lot of studies using various types of nanoparticles with different concentrations. In this paper, we particularly focused on the effect of the admixture on the ferroelectric SmC* phase, and it was found that many of the LC matrix properties were changed after doping (in the synthesized soft magnetoelectric composites).

2. Materials and Methods

2.1. Samples

As a ferroelectric liquid crystal matrix, we used a commercially available compound (short name EHPDB) (Sigma Aldrich Co., Saint Louis, MO, USA), belonging to the homologous series of epoxides, with the chemical formula presented in Figure 1. The epoxides are organic chemical compounds which contain a three-membered cyclic group consisting of an oxygen atom and two carbon atoms. The pure EHPDB compound was then doped with commercially available Fe₂O₃ nanoparticles (diameter < 50 nm, Sigma Aldrich Co., Saint Louis, MO, USA) to create six nanocomposites: Composites 1–5, with the concentrations of Fe₂O₃ nanoparticles equal to 0.0, 0.3, 0.5, 0.7 and 0.9 wt.%, respectively (Composite 1 is in fact the pure EHPDB matrix). The concentrations of nanoparticles used were very low so as not to alter the liquid crystal order and the director in the individual smectic layers. Moreover, at higher concentrations, the nanoparticles can interact strongly with each other, causing uncontrolled aggregation (typical for various types of nanoparticles) [31]. Therefore, it is important to pay special attention to disperse the nanoparticles well in the liquid crystal host. Composites 2–5 were prepared according to the same scheme:

1. The adequate amounts of pure EHPDB and Fe₂O₃ nanoparticles were weighed into separate vials (see Table 1).
2. 1.5 mL of chloroform was added to the weighed amounts of nanoparticles at room temperature, and the solution was sonicated in 50 s(on)/10 s(off) mode for 45 min (A = 30%, ice blanket).
3. The nanoparticle solution was sequentially poured into a vial with pure matrix EHPDB and chloroform was added to 2 mL, then the solution was left for 15 min to dissolve the EHPDB.
4. The solution (EHPDB + Fe₂O₃ + chloroform) was sonicated in 50 s(on)/10 s(off) mode for 30 min (A = 30%, ice blanket).

5. The solution (EHPDB + Fe₂O₃ + chloroform) was kept on the heating plate (80 °C) for about 150 min in order to obtain about 1 mL of solution.
6. The solution (EHPDB + Fe₂O₃ + chloroform) was sonicated in 50 s(on)/10 s(off) mode for 15 min (A = 30%, ice blanket).
7. The prepared solution was poured into microscopic slides and dried for at least 36 h at room temperature to evaporate the chloroform.
8. Obtained composites were peeled off with a blade and used for measurements.

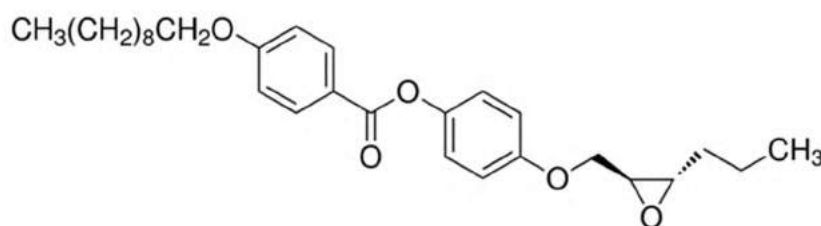


Figure 1. Molecular structure of the EHPDB matrix. The two chiral centers are on the carbons of the epoxy group.

Table 1. Mass compositions of Composites 1–6 and Fe₂O₃ samples with and without oleic acid.

Composite	Amount of EHPDB	Amount of Fe ₂ O ₃	Amount of Oleic Acid
Composite 1 (0.0 wt.%)	40.52 mg	0.00 mg	–
Composite 2 (0.3 wt.%)	40.32 mg	0.12 mg	–
Composite 3 (0.5 wt.%)	40.20 mg	0.20 mg	–
Composite 4 (0.7 wt.%)	40.91 mg	0.29 mg	–
Composite 5 (0.9 wt.%)	40.20 mg	0.37 mg	–
Composite 6 (0.3 wt.% + OA)	40.07 mg	0.12 mg	0.5 µL
		Amount of Fe ₂ O ₃	Amount of Oleic Acid
Sample 1		36.00 mg	–
Sample 2		36.01 mg	150.0 µL

Composite 1 (pure EHPDB) was prepared in the same way, but steps related to weighing and sonication of nanoparticles were omitted. Due to the use of very low concentrations of nanoparticles and the multi-stage sonication process, it was decided not to use a surfactant (e.g., oleic acid) in the composites. However, to check the influence of oleic acid on the composites' parameters, we prepared Composite 6, where the concentration of nanoparticles was equal to 0.3 wt.% (like in Composite 2), but they were decorated with oleic acid before being put into the EHPDB matrix (see the Supplementary Materials). Additionally, we prepared two samples of Fe₂O₃ nanoparticles (see the Supplementary Materials) to check the difference between pure nanoparticles (Sample 1) and nanoparticles decorated with oleic acid (Sample 2). Mass compositions of Composites 1–6 and Samples 1 and 2 are presented in Table 1.

2.2. Powder X-ray Diffraction (PXRD)

Powder XRD diffractograms for samples studied were collected on a RIGAKU Mini-Flex600 diffractometer (Rigaku, Tokyo, Japan) equipped with monochromatic Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$). Powder samples were placed in zero-diffraction Si plates and diffraction patterns were collected over a 2θ range of 5–90°, at a scanning speed of 10°/min. This method was also used to characterize the Fe₂O₃ nanoparticles and to check how small concentrations of nanoparticles modify the structure of the liquid crystalline matrix.

2.3. Optical Microscopy (OM)

Digital optical microscopy images have been collected at room temperature by using a Keyence VHX-7000 digital microscope (Keyence Corporation, Osaka, Japan). Images

were obtained in transmittance mode at 80 $\times$, 400 $\times$, 2000 $\times$ and 6000 $\times$ magnifications, for samples manually placed on a microscope glass slide of 1 mm thickness. The high-resolution optical microscopy method was used to characterize the surface morphology and the distribution of nanoparticles in nanocomposites, and moreover to obtain preliminary information about the influence of oleic acid on the nanoparticles.

2.4. Scanning Electron Microscopy (SEM)

A Keyence VHX-D510 scanning electron microscope (Keyence Corporation, Osaka, Japan) was used to register the topography of the studied materials. Samples were mounted to the SEM specimen stubs with the double-sided adhesive copper tape without an additional sputter-coating with metal to preserve the original color and morphology of materials. Detailed imaging of all samples has been performed at 100 $\times$, 1000 $\times$, 5000 $\times$ and 10,000 $\times$ magnifications at room temperature.

2.5. Differential Scanning Calorimetry (DSC)

The calorimetric curves for Composites 1–6 were collected in the temperature range from 0.0 to 110.0 $^{\circ}\text{C}$ during heating and cooling at several chosen rates (5, 10, 12, 15, 20 $^{\circ}\text{C}/\text{min}$) by using a PerkinElmer DSC8000 differential scanning calorimeter (Perkin Elmer, Waltham, MA, USA), calibrated on melting points of water and indium. The samples of exactly 5.13 mg were placed into aluminum pans and sealed by the press. Results were analyzed by using Pyris software (Perkin Elmer, Waltham, MA, USA) and Origin 2018 (OriginLab, Northampton, UK). Based on this method, the phase transition temperatures at so-called zero rate were determined by a linear fit to the dependence of the onset temperature versus the heating/cooling rate.

2.6. Polarizing Optical Microscopy (POM) and Electro-Optic Measurements (EOM)

A Nikon Eclipse LV100POL polarizing optical microscope (Nikon, Tokyo, Japan) equipped with the Fine Instruments WTMS-14C heating stage (liquid nitrogen as a coolant, temperature uncertainty of 0.1 $^{\circ}\text{C}$) was used for texture observations. The experimental setup including the above-mentioned microscope additionally consisted of the 33120A Agilent generator, the F20-FLC Electronics amplifier, the DSO6102A Agilent oscilloscope and the INSTEC PD02 photo-detector, and a system of tunable resistors (a 100 k Ω resistor was used in each case) was used for electric and electro-optic measurements. The digital camera Canon EOS600D (Canon, Tokyo, Japan) was used for texture acquisition during heating and cooling, with a rate equal to 2 $^{\circ}\text{C}/\text{min}$, whereas the tilt angle and transmitted light intensities (TLI) measurements were performed by using a photo-detector. Composites 1–6 were placed by the capillary effect into sandwich-type ITO electro-optic cells (AWAT Company, Warsaw, Poland) (4.9 μm thick, 25 mm² active electrodes surface) with the planar alignment [38–40], guaranteed by a thin polyimide layer (AWAT Company, Los Angeles, CA, USA). The uniformly aligned samples were obtained by heating to the isotropic phase and then slowly cooling down to the first tilted smectic phase, SmC*, where an external electric field was applied for a few minutes to align the samples and obtain the monodomain. The reversal current method was used to measure spontaneous polarization [41,42], tilt angle was measured as half of the angle between the Clark and Lagerwall states [43], while the switching time was measured as the time delay in the sample response [42,44]. An alternating voltage of 60 V_{pp} was used to measure spontaneous polarization, switching time and tilt angle. The surface area determination in the sample response by numerical integration is subject to uncertainty at the level of 2%, while the tilt angles for the off states are determined with a systematic uncertainty equal to 0.1 $^{\circ}$. All raw data were collected by specially prepared software, while the analysis was performed using Origin 2018.

The helix pitch of Composites 1–5 was measured for free droplets by using the BX-53F Olympus microscope (Olympus, Tokyo, Japan) equipped with the Instec ST402 hot stage and mK1000 temperature stabilizer. The images were registered during very slow cooling

(0.1 °C/min) from the isotropic phase, after a one-minute isothermal time before each measurement to produce strips corresponding to the helix length. The phase transition temperatures in this experiment are shifted to higher temperatures due to the nature of the measurement (free droplet placed on the microscope slide is heated only from the bottom). Due to the large helix pitch, it was not possible to use UV-Vis spectroscopy [45].

Transmitted light intensity (TLI) through the sample placed in the ITO cell was measured to find the transition temperature. A standard measuring set as for electric measurements with a photo-detector was used (INSTECH, Boulder, CO, USA).

2.7. Fluorescent Confocal Polarizing Microscopy (FCPM)

The confocal microscopy is a recognized technique of three-dimensional imaging, long used in biological and medical sciences, and recently also for the soft matter research [46,47]. In our studies, we employed the Olympus FLUOVIEW FV1000 IX81 confocal microscope (Olympus, Tokyo, Japan) in the reflection mode with a diode laser ($\lambda_D = 473$ nm, beam power = 1.24 mW) [48]. To obtain a 3D image of a sample, a focused beam scans the sample in a horizontal plane (x, y directions) at different depths of the sample (z direction). Before measurement, each sample was treated with chloroform and then poured onto a microscope slide. After the evaporation of chloroform, the slide was subjected to the microscopic imaging.

2.8. FT-MIR (Fourier Transform-Middle Infrared Spectroscopy)

Fourier transform-middle infrared absorption measurements were performed in transmission mode using the Bruker VERTEX 70v vacuum spectrometer (Bruker, Billerica, MA, USA). The spectra were carried out in the range of 4000–450 cm^{-1} with spectral resolution of 2 cm^{-1} and 32 scans per each spectrum. All spectra processing was performed using Bruker OPUS software (Version 7.0, Bruker, Billerica, MA, USA). All samples were mixed with KBr, compressed into pellets and measured in two subsequent steps: first during heating from 20 up to 100 °C, and then cooling from 100 down to 10 °C. Additionally, pure oleic acid has been measured in the same measurement sequence for comparison. As the sample is a liquid, it was spread between two KBr pellets before measurement.

EHPDB (FTIR): 3113, 3102, 3070 $\nu(\text{CH})_{\text{ar}}$; 2957, 2933; 2920s $\nu_{\text{as}}(\text{CH}_2)_{\text{al}}$; 2873; 2850m $\nu_{\text{s}}(\text{CH}_2)_{\text{al}}$; 1724s $\nu(\text{C=O})$, 1730sh; 1607s, 1582, 1510s $\nu(\text{C=C})_{\text{ar}}$; 1472, 1466m $\delta_{\text{as}}(\text{CH}_2)_{\text{al}}$; 1451m, 1420w $\nu(\text{C=C})_{\text{ar}}$; 1392w, 1379w $\delta_{\text{s}}(\text{CH}_3)_{\text{al}}$; 1360w; 1342sh; 1313; 1300sh, 1288, 1278sh, 1257s, 1247sh $\nu_{\text{as}}((\text{C}_{\text{ar}}-\text{O}-\text{C}))$; 1200s $\nu_{\text{as}}((\text{C}=\text{O})-\text{C})$, 1170s $\nu_{\text{s}}((\text{C}=\text{O})-\text{C})$; 1106w, 1087s, 1080sh $\nu(\text{C}-\text{O})$; 1064, 1051w $\nu_{\text{s}}((\text{C}_{\text{ar}}-\text{O}-\text{C}))$; 1025sh, 1019s, 1010s $\delta_{\text{ip}}(\text{CH})_{\text{ar}}$; 996sh, 971w; 902m $\nu(\text{C}-\text{O})_{\text{epoxy}}$, 879m, 865; 850m $\delta_{\text{oop}}(\text{CH})_{\text{ar}}$; 829, 803m, 780m, 762s; 752sh, 741w; 725sh, 721m $\rho(\text{CH}_2)_{\text{n}}$; 694m, 653, 632, 594m, 536sh, 527m $\delta_{\text{oop}}(\text{ring})_{\text{ar}}$ cm^{-1} (where, s—strong, m—medium, w—weak, br—broad, sh—shoulder, ρ —rocking, ip—in plane, oop—out of plane, ar—aromatic, al—aliphatic, epoxy—in epoxy group, n—chain, S_s—symmetric, as—asymmetric).

3. Results and Discussion

3.1. PXRD Results

Figure 2a,b show the diffractograms of Sample 1 (Fe_2O_3) and Sample 2 ($\text{Fe}_2\text{O}_3 + \text{OA}$) as well as reference materials (hematite $\alpha\text{-Fe}_2\text{O}_3$, metastable $\beta\text{-Fe}_2\text{O}_3$, maghemite $\gamma\text{-Fe}_2\text{O}_3$, Luogufengite $\varepsilon\text{-Fe}_2\text{O}_3$ and magnetite Fe_3O_4) [49–58]. The analysis of these data led to the conclusion that the Fe_2O_3 nanoparticles used in the syntheses of Composites 2–6 consist mainly of maghemite ($\gamma\text{-Fe}_2\text{O}_3$), however, very small impurities of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4), by-products in the preparation of maghemite, may occur. Moreover, the broad amorphous peak of oleic acid with a maximum around 20° is recognized in the $\text{Fe}_2\text{O}_3 + \text{OA}$ diffractogram.

Diffraction patterns of Composites 1–6 and Sample 1 are shown in Figure 2c,d. For all hybrid materials containing EHPDB liquid crystal matrix and Fe_2O_3 nanoparticles (Composites 2–6), the diffraction patterns are similar to pure EHPDB (Composite 1), sup-

plemented with low-intensity peaks characteristic of maghemite, the intensity of which increases with increasing Fe_2O_3 concentration, confirming the presence of both components in these investigated samples.

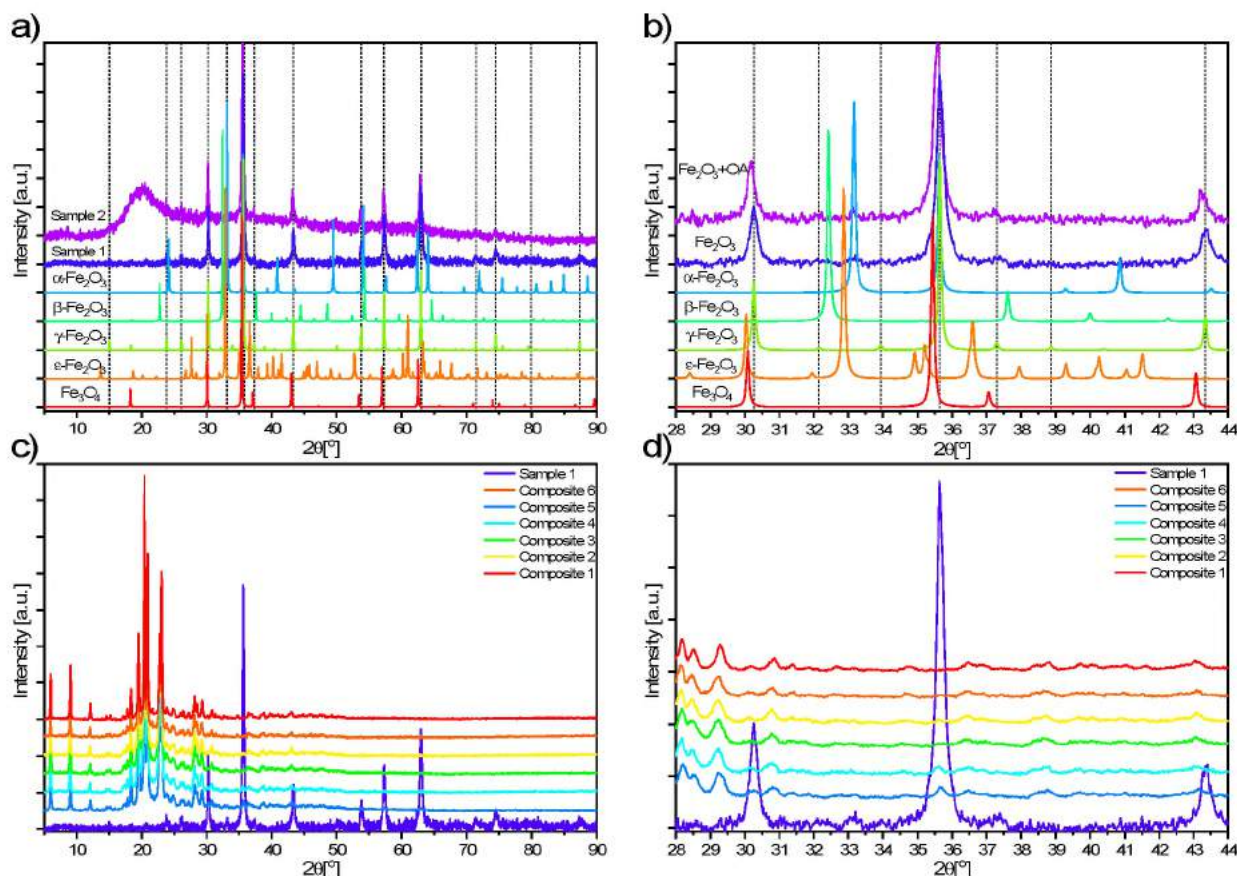


Figure 2. (a) XRD patterns of Sample 1 (Fe_2O_3), Sample 2 ($\text{Fe}_2\text{O}_3 + \text{OA}$) and reference materials in the ranges 5–90° and (b) 28–44°. (c) Dashed lines correspond to the positions of diffraction peaks for maghemite. XRD diffractograms of Composites 1–6 and Sample 1 registered in the ranges 5–90° and (d) 28–44°.

3.2. OM Results

The Fe_2O_3 nanoparticles (Sample 1) adopted the form of brown/orange powder, consisting of the agglomerates of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles with a size of approximately 100 nm, which can be recognized as black dots in the image at 6000× magnification (Supplementary Figure S1). In turn, Sample 2 ($\text{Fe}_2\text{O}_3 + \text{OA}$) is much more homogenous without the large agglomerates of nanoparticles, while Composite 1 (pure EHPDB) forms colorless/white conglomerates of crystallites without any characteristic morphological features (see Supplementary Figure S1). Images for Composites 2–5 are similar (Figure 3), showing yellowish-white areas with orange inclusions of various sizes (corresponding to nanoparticle agglomerates), the color intensity of which is proportional to the concentration of nanoparticles. The agglomerates (orange islands) are quite clearly visible for Composites 4 and 5, especially at 400× and 2000× magnification, while they are not observed for nanocomposites with lower concentrations of nanoparticles (Composites 2 and 3, see Figure 3). It is worth emphasizing that in the sample fragments that appear uniform, single, well-dispersed Fe_2O_3 nanoparticles are visible in the form of small dark dots in images with a magnification of 6000 times (Figure 3).

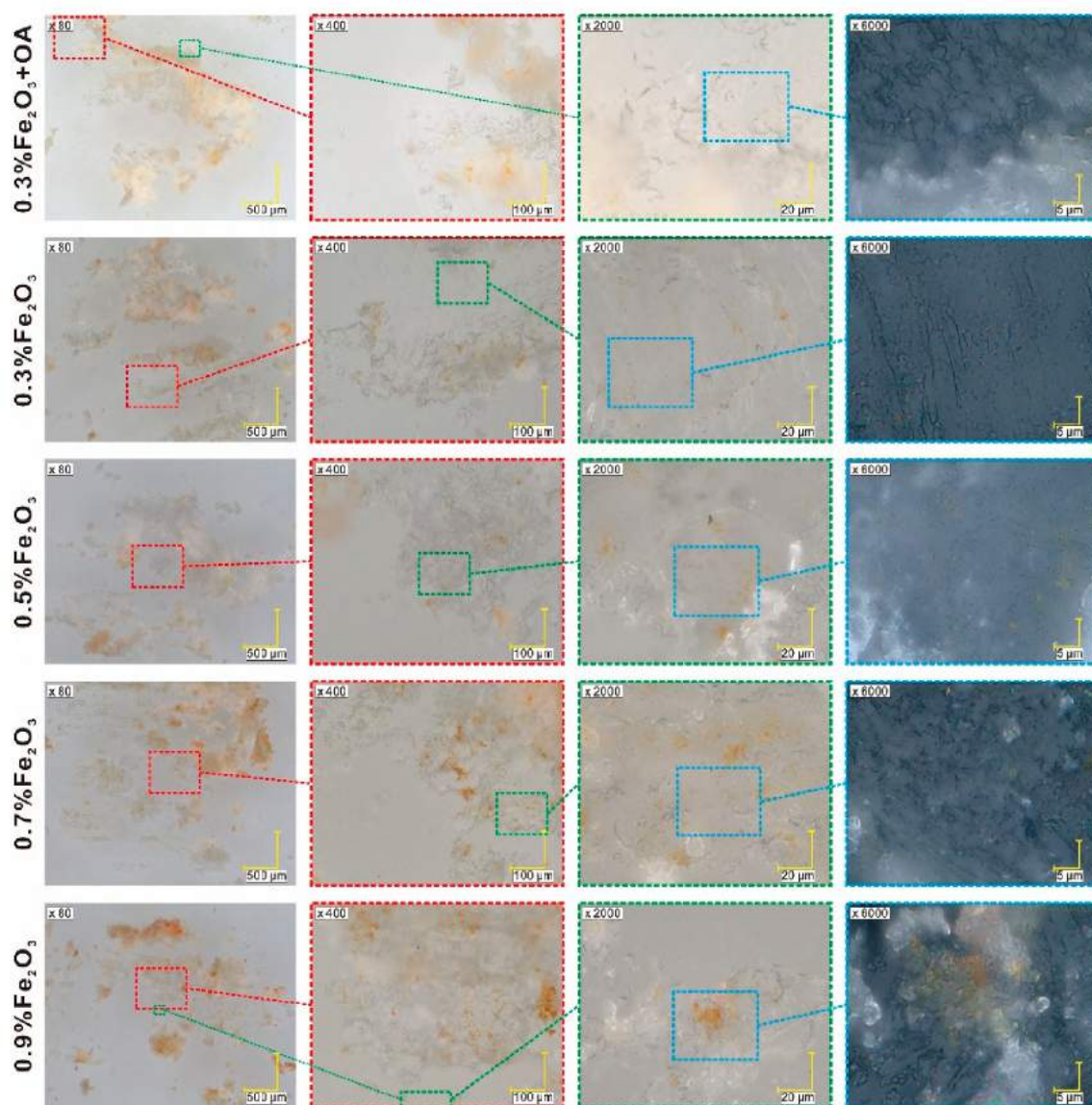


Figure 3. Digital optical images of Composites 1–5. The magnification is shown in the images, where colored dotted squares correspond to the enlarged areas.

3.3. SEM Results

The SEM imaging of Sample 1 (Fe_2O_3 nanoparticles) revealed that the sample contained nanoparticle aggregates smaller than 100 nm in size (Supplementary Figure S2, first row). The addition of oleic acid to nanoparticles (Sample 2) makes the surface smoother, which proves good dispersion of nanoparticles and no agglomeration. Analysis of Composite 6 (0.3 wt.% Fe_2O_3 + OA) images showed that the sample surface is smoother than Composites 2–5, with few ripples on the surface. Morphologies of Composites 2–5 are very similar, and the domains of the EHPDB matrix are clearly visible, however, these domains are not visibly modified by the dopant material even at 10,000 $\times$ magnification (Supplementary Figure S2). The highest magnification of the microscope used is 10,000 $\times$, so we were not able to visualize individual nanoparticles and determine their exact size distribution, or even observe smaller aggregates. However, based on the images obtained, we can confirm that oleic acid prevents aggregation.

3.4. FCPM Results

As we have shown above, the use of a surfactant (oleic acid) to decorate nanoparticles aims to eliminate the aggregation process. However, when the matrix is doped with a low concentration of nanoparticles, the surfactant is an additional chemical agent that can act on both the organic matrix and the nanoparticles. In our opinion, for such small nanoparticle concentrations in Composites 2–6, the surfactant is a parasitic factor, and its use can complicate/obscure the matrix–nanoparticle interaction, and the modification of physicochemical parameters of composites may result from the use of the surfactant itself, not nanoparticles. Due to the lack of a coherent and complete description of the influence of surfactants in organometallic composites, we decided to check the effect of oleic acid on the aggregation process and the change in the parameters of the organic matrix in such composites. For this purpose, we used fluorescence imaging of thin films by confocal microscopy. Figure 4 presents the fluorescence of the subsequent slices of the investigated materials.

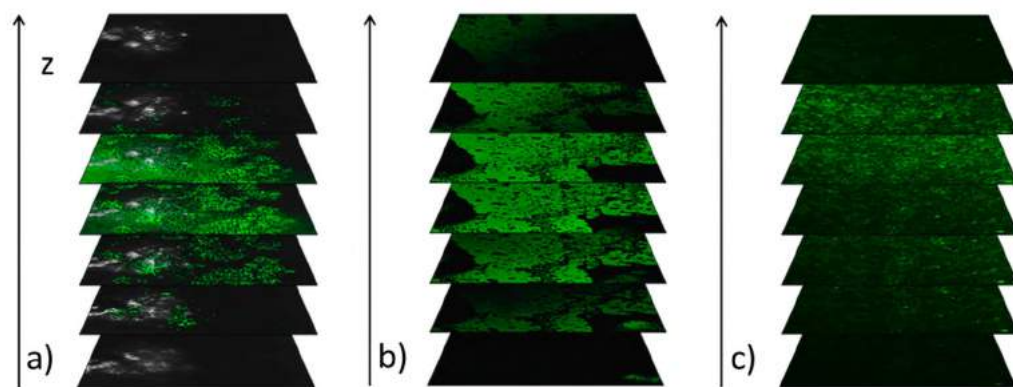


Figure 4. The qualitative representation of the fluorescence intensity in the subsequent slices of Sample 1 (a), oleic acid (b) and Composite 6 (c). The z axis is perpendicular to the x–y plane (parallel to the surface of the microscope slide).

As one can see, both Fe_2O_3 nanoparticles and oleic acid exhibit the fluorescence, while the EHPDB matrix does not. Images of Sample 1 (Fe_2O_3 nanoparticles) present strong centers of fluorescence (intense green spots), which clearly proves the agglomeration, while images of oleic acid show uniform fluorescence over the entire surface and thickness (Figure 4a,b). On the other hand, the images recorded for Composite 6 (Figure 4c) show an intense and multi-site fluorescent signal, which in our opinion, for such a low concentration of nanoparticles (0.3 wt.%), comes mostly from oleic acid, not nanoparticles. However, these images further prove that the nanoparticles are quite well-dispersed in the EHPDB matrix.

3.5. DSC Results

As an example, the DSC curves registered during cooling ($10\text{ }^\circ\text{C}/\text{min}$) for Composites 1–6 are presented in Figure 5a, and as it is clearly seen, the main differences in the phase transitions are for Composite 6 (with oleic acid). Taking into account the transition from isotropic liquid to N^* (Figure 5b), it can be seen that for Composite 1 (pure EHPDB), two close anomalies can be distinguished, corresponding to two phase transitions (two black arrows). We suppose that the blue phase (BP) can exist in a very narrow range (marked by P in Figure 5b), although the characteristic texture of this phase was not observed under a polarizing microscope. It is well-known that blue phases are thermodynamically distinct phases that appear between the helical phase and the isotropic liquid in highly chiral liquid crystals. The EHPDB compound fulfils both conditions—it exhibits an isotropic liquid— N^* phase transition and is a highly chiral compound. For Composites 2 and 4, a subtle anomaly indicates that this BP phase is also present, while for Composites 3 and 5, it is not. However,

this is not sufficient evidence for the presence of BP in the studied composites, so it requires further research, which was not the aim of our study. After addition of nanoparticles to the liquid crystal matrix, the Is–N* phase transition temperature is shifted to lower temperatures (Figure 5b), and the smallest shift is for Composite 5 (0.9 wt.%), which may suggest that for concentrations greater than 0.9 wt.%, the shift will be even smaller, which in turn may indicate the complete nanoparticles' agglomeration and even degradation of liquid crystalline properties. The N* phase for all Composites occurs in a relatively wide temperature range, which was also confirmed by texture observations. In turn, the temperature of the N*–SmA* transition is decreasing with increasing the concentration of nanoparticles to 0.7 wt.% in the Composites. Interestingly, for Composites 1, 3 and 5, in the vicinity of this phase transition, a second weak anomaly can be seen, while for Composites 2 and 4, it cannot (Figure 5b). We suppose that an additional very narrow frustrated smectic A* phase, namely TGBA*, appears [59]. The SmA*–SmC* phase transition is strongly shifted to lower temperatures for Composites 2–5, thus doping broadens the SmA* phase but narrows the SmC* phase range. The drastic narrowing of the SmC* phase due to such small nanoparticle concentrations is not fully understood and requires further research. It is not excluded due to the nanoparticles' mobility in the liquid crystal matrix, and the orthogonal and positional order of the SmA* phase is maintained over the bigger temperature range, which causes the extension of the SmA* phase. At lower temperatures, the viscosity of the liquid crystalline phase increases, movement of nanoparticles is hindered and the transition to the ferroelectric phase begins. In the case of SmC*–Cr transition, the nanoparticles modify not only the onset and peak temperature, but also cause the disappearance of the polymorphism in the range of 57.5–47.5 °C (for Composite 1, the ferroelectric phase changes into a sequence of crystalline phases). Although it is not fully understood and it cannot be explained in a simple way, this proves that nanoparticles in low concentrations can cause the disappearance of not only the liquid crystalline but also the crystal phases (see Figure 5c,d). According to Yadav et al., aggregated nanoparticles act as impurities and decrease the temperature in nanocomposites [24].

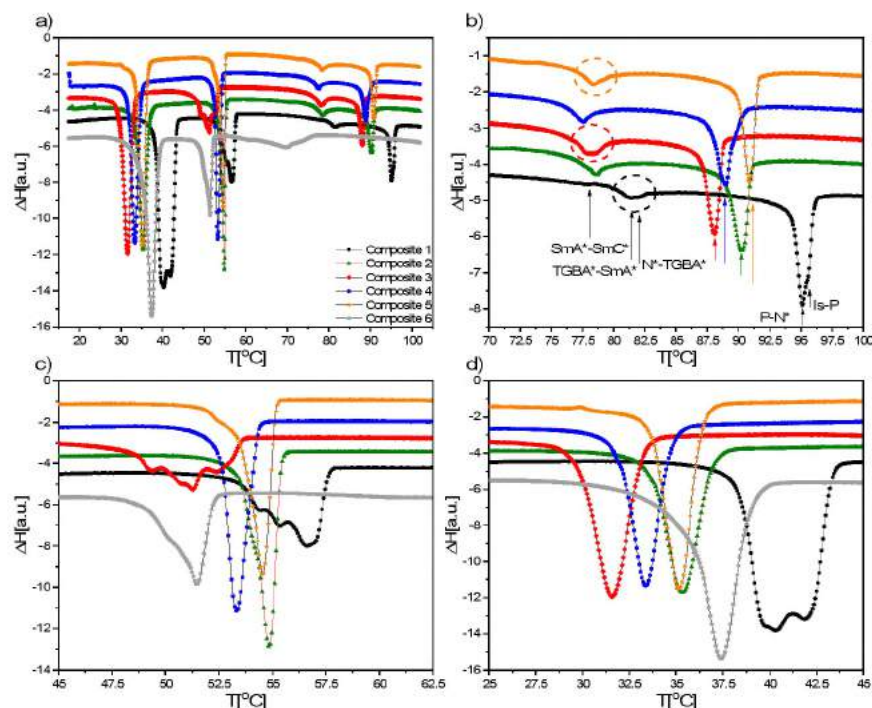


Figure 5. (a) DSC curves registered during cooling at a rate of 10 °C/min for Composites 1–6 and (b) extended temperature ranges of 100.0–70.0 °C, (c) 62.5–45.0 °C and (d) 45.0–25.0 °C.

As it was mentioned above, oleic acid strongly affects the mesophases (only the N* phase exists for Composite 6 during heating) as well as modifies the phase transition

temperature—a very strong shift of the Is–N* phase transition to low temperatures and the narrowing of the mesophases (N* and SmC*) are visible (Figure 5a). On the other hand, the transitions within the crystal phase are not modified much by oleic acid. In the case of Composite 6 (with oleic acid), the Is–N* transition is shoulder-shaped, while the N*–SmA* transition is already visible as a complete anomaly (as in Composition 2 without oleic acid). Under the polarizing microscope, we did not observe uniform transitions as for Composites 1–5, but a drop in formation of the individual phases (only the transition to the crystal covers the entire visible surface). Probably due to the excessive amount of oleic acid used to decorate nanoparticles, it contributes to the destruction of the liquid crystalline properties. Due to the significant influence of oleic acid on the phase sequence of Composite 6, some studies (e.g., electrical, dielectric) were omitted. Interestingly, Da Cruz et al., by doping 5CB with γ -Fe₂O₃, also obtained nanocomposites with strongly reduced N–Iso phase transition temperatures, but finally found that it was caused by a surfactant, not nanoparticles [60]. In our case, we did not use a surfactant for Composites 2–5, so we cannot attribute the temperature shift to anything other than nanoparticles.

During heating, the registered curves were similar for Composites 1–5, however, again, a shift in the phase transition temperatures (particularly in the N*–isotropic liquid phase transition) was observed (see Supplementary Figure S3). A shift of the phase transition temperatures for hybrid materials based on 11OBA and 12OBA liquid crystals doped with Fe₃O₄ nanoparticles (1–3 wt.%) was also observed by Sivasri et al. [61]. In turn, for Composite 6 (with oleic acid), only two anomalies were visible on the heating curve, which is further evidence of the degrading effect of this surfactant.

3.6. TLI Results

Some of the phase transition temperatures were not designated by the DSC method, therefore the complementary method, TLI, was used, mainly to determine the SmA*–SmC* phase transition temperature. This phase transition is strongly shifted to lower temperatures for all doped samples. Thus, doping with Fe₂O₃ nanoparticles widens the SmA* phase range but narrows the SmC* phase range. The normalized transmitted light intensity versus temperatures registered for all composites studied is presented in Figure 6, and as is seen, this transition is a very subtle small hump for Composites 2–5, while for Composite 1 (pure EHPDB), it is quite visible (arrows in Figure 6a). Interestingly, the presence of the TGBA* phase in all composites and an extra phase (probably the BP phase) in Composite 1 were confirmed. Intensity of transmitted light is almost constant within the SmC* for all composites, however it increases to a small extent for the pure matrix. This behavior can be connected with the defected texture of the ferroelectric SmC* phase for Composites 2–5, which was observed by polarizing imaging.

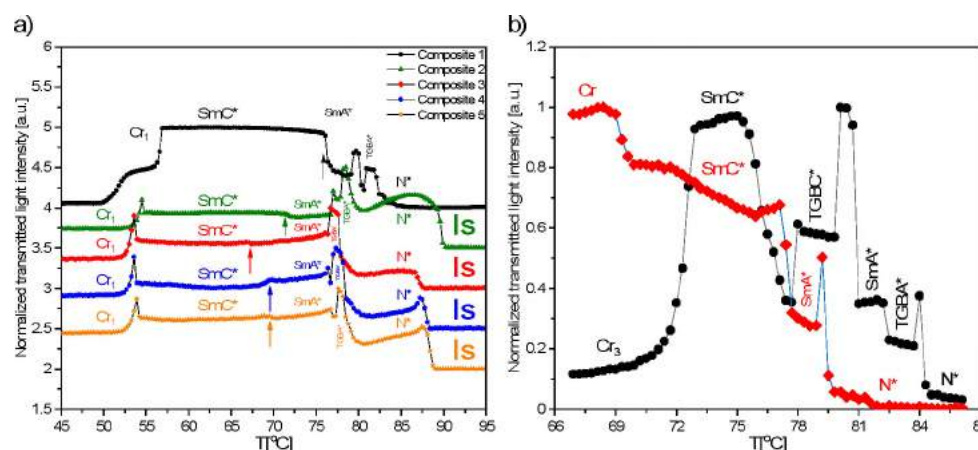


Figure 6. Normalized transmitted light intensity registered during cooling (a) and heating (b), rate = 3 °C/min.

3.7. POM Results

As an example, textures for Composites 1–5 registered for the planar ITO cells during cooling are presented in Figure 7. The admixture of Fe_2O_3 nanoparticles strongly influences the interference image of a thin layer, regardless of the concentration. In the case of N^* phase, the oily-streaks texture was registered for Composite 1, while for Composites 2–5, the fan-shaped texture was registered (see Figure 7, first column). Basically, the nucleation of the N^* phase is in the form of irregular droplets that aggregated very quickly to form a fan-like texture, and with further decreasing temperature, the fan-like texture began to crack and streaks were formed (see Supplementary Figure S4).

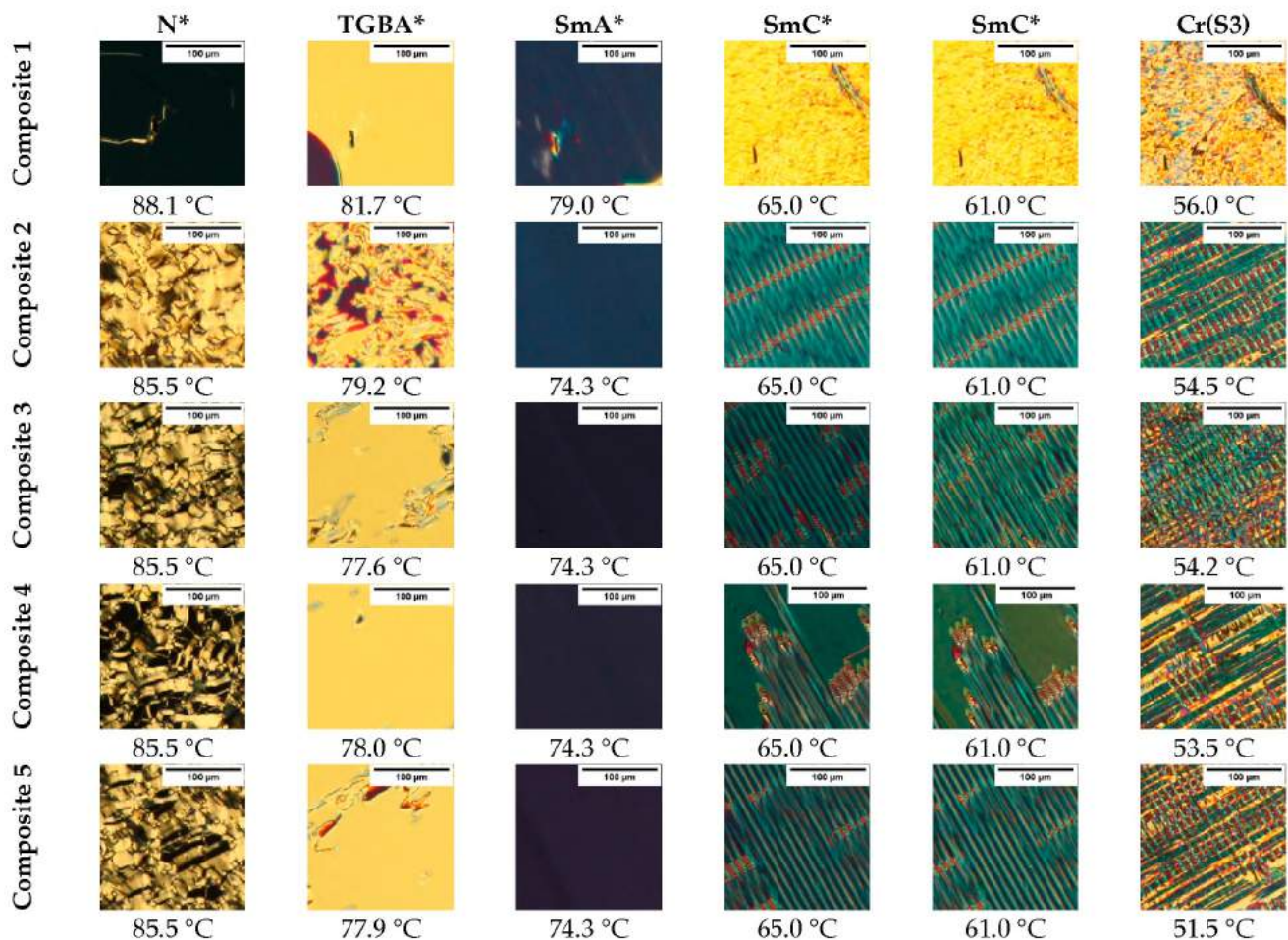


Figure 7. Textures of Composites 1–5 registered during cooling (2 °C/min) at the same light intensity. The last column represents the first observed crystalline phase. The textures within each composite represent the same area.

On further cooling, the frustrated TGBA* phase, as Grandjean texture (uniform in color) with red inclusions, occurred in a very narrow temperature range, and no significant influence of Fe_2O_3 nanoparticles on this texture was observed. A similar texture for the TGBA* phase was observed by Chakraborty et al. for the two-component mixture of 2H6R + H-22.5 [62], although usually, the N^* –TGBA* phase transition is associated only with smudging the texture, e.g., oily-streaks, and it is very often difficult to detect [63]. In turn, the SmA* phase for all composites forms a homogeneous texture [63], while the strong influence of the nanoparticles on the texture of the ferroelectric SmC* phase is clearly visible. Composites 2–5 form a striped texture, not observed for Composite 1 (pure EHPDB) at any temperature. It is very likely that the striation induced by nanoparticles is a certain electrohydrodynamic instability that occurs in nanocomposites in the form of elongated domains (stripes) [64,65] or/and the formation of ferroelectric domains in

nanocomposites [66]. However, this requires further investigation. Misra et al. doped the ferroelectric liquid crystal mixture SCE-13 with spherical Fe_2O_3 nanoparticles (ca. 6–12 nm, 1 wt.%) and observed the emergence of focal-conic domains [67]. Thus, it is not excluded that the size of the nanoparticles determines the texture-striated (larger nanoparticles) and focal-conical domains (smaller nanoparticles). However, this hypothesis requires further research. As the temperature decreases, the linear pattern disappears, and a crystal phase appears (Figure 7). However, in our previous study, we reported on the presence of a metastable S3 phase (unclassified smectic phase) immediately below the SmC^* phase for pure EHPDB [68]. Thus, it is not excluded that the presented texture for the first crystal phase is that for the S3 smectic phase.

The textures registered during cooling for Composite 6 (with oleic acid) are presented in Figure 8, and it is seen that the addition of oleic acid significantly modified the textures (compared with Figure 7). During the transition from the isotropic liquid to the N^* phase, many fine regular droplets of different diameters were visible (Figure 8a), which, on further cooling, coalesced into larger droplets and stripes appeared on them (Figure 8b). This behavior may indicate changes in the N^* phase birefringence and helix pitch. In the SmA^* phase (Figure 8c), some of the drops observed in the N^* phase were visible as color droplets with focal-conic texture, while some of them as dark droplets with a visible border. It seems that droplets with a sufficiently large radius in the N^* phase are also colored in the SmA^* phase, while those with a radius below a certain threshold radius become dark (change the orientation of the molecules from planar to homeotropic). We suppose that in Composite 6 (with oleic acid), from the energetic point of view, the arrangement of molecules in the homeotropic configuration is more favorable, as it was explained by Zakerhamidi et al. that oleic acid (on the surface of nanoparticles) can orient the liquid crystal molecules to a homeotropic state due to the strong coupling between the oleic acid chains and the liquid crystal molecule [69]. However, in our case, the concentration of the nanoparticles was small (0.3 wt.%), but the dark area of the texture was large, and therefore it seems that part of the dark texture does not contain nanoparticles and liquid crystalline molecules (is not homeotropic), but rather oleic acid itself (excessive amount of oleic acid). In turn, if the boundaries are left of the small droplets, it may suggest that there is a homeotropic alignment inside the droplet, while at the edge, the molecules are tilted. As the SmA^* phase is cooling down, the droplets became bigger (Figure 8d), and after transition to the SmC^* phase (recognized by the characteristic fingerprint stripes), they continue to increase (Figure 8e,f). The striation in droplets disappeared with further cooling, and transition to a crystal phase was visible (Figure 8g) as droplets merged. During further cooling, the coexistence of two crystal phases was clearly visible (Figure 8h), while a low-temperature crystal phase is presented in Figure 8i. It is possible that Cr_1 is an unclassified smectic phase (S3), as we mentioned above. XRD studies or the effect of a very strong electric field on the texture of the Cr_1 phase could help identify this phase, but we were not able to perform such studies due to the lack of a sample. However, due to the interpretation difficulties, we consider this as a crystal phase. To sum up, on the one hand, OA inhibits the aggregation of nanoparticles in the LC matrix, but at the same time, it has a strong influence on the phase sequence, and therefore the remaining studies were conducted only for Composites 1–5 (without oleic acid).

Based on the results presented above (POM, DSC, TLI), the phase sequences for Composites 1–6 were determined (see Supplementary Table S1). Figure 9 presents the influence of the Fe_2O_3 nanoparticles on the phase transition during cooling, while Supplementary Figure S5 presents them during heating. Nanoparticles' addition broadens the paraelectric SmA^* phase and narrows the ferroelectric SmC^* one. We suppose that the mobile nanoparticles move quite freely in the organic matrix in the SmA^* phase, which hinders the phase transition to the tilted phase. When the temperature decreases, the mobility of nanoparticles drops, and phase transition follows.

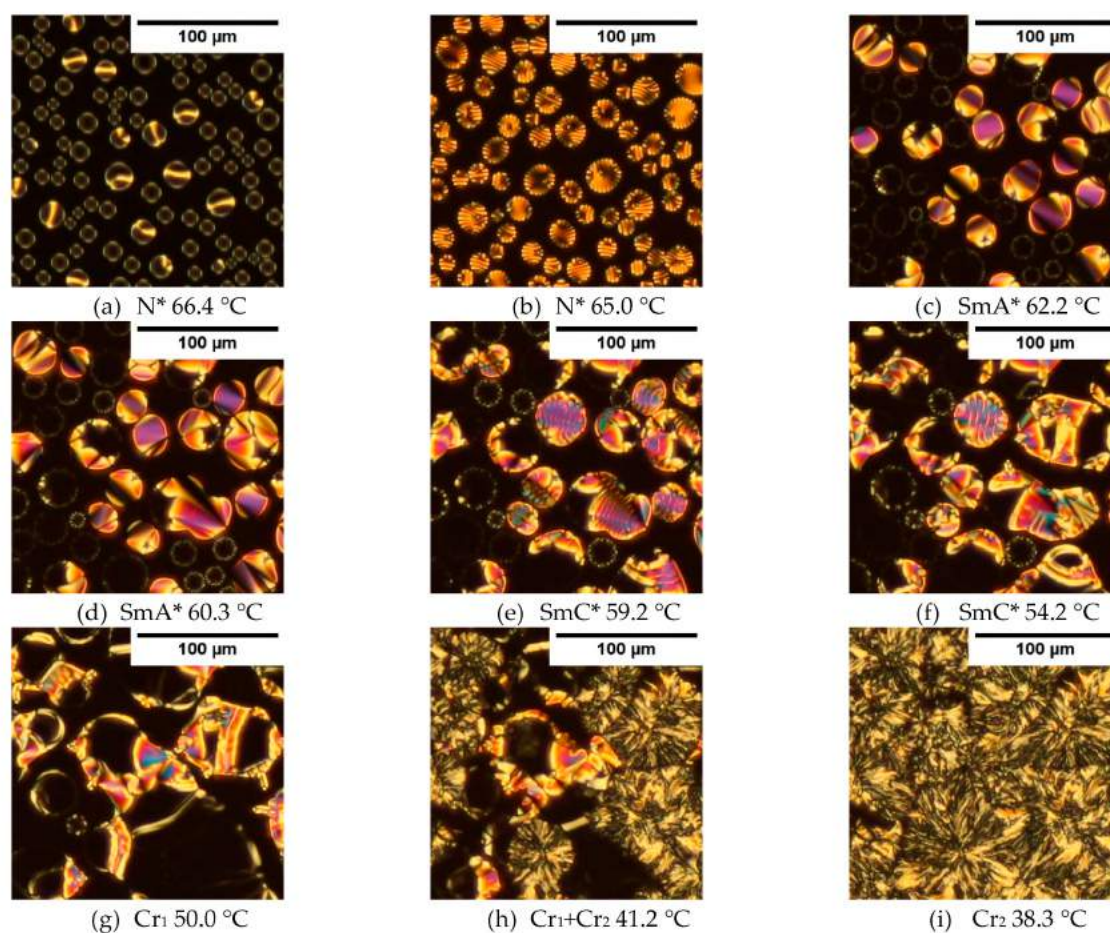


Figure 8. Textures of Composite 6 registered during cooling at a rate of 2 °C/min in the N* (a,b), SmA* (c,d), SmC* (e,f) and crystalline phases (g–i).

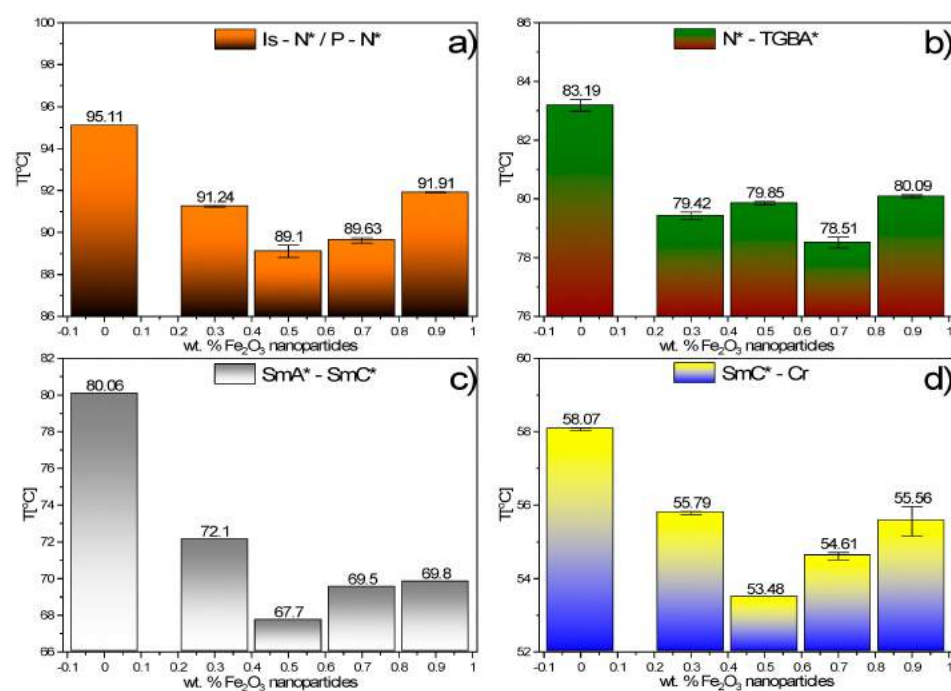


Figure 9. Influence of Fe_2O_3 nanoparticles admixture on the phase transitions during cooling: Is-N*/P-N* (a), N*-TGBA* (b), SmA*-SmC* (c) and SmC*-Cr (d).

3.8. EOM Results

All electro-optic measurements were performed on the uniformly aligned samples. Figure 10 presents, as an example, the alignment process of Composite 5, while Supplementary Figure S6 of Composites 1–5. The ordering conditions were selected experimentally (the rectangular wave, 50 Hz). The textures of doped samples (Composite 2–5) before alignment are quite similar, but different than for pure EHPDB (Composite 1). After applying the electric field, the monodomain of good quality was immediately formed (Figure 10 and Supplementary Figure S6), and after ca. 13 min, the uniformly aligned samples (in the whole area of the electrodes) were obtained. The very good quality of the monodomain proves that the helical pitch is infinite [63].

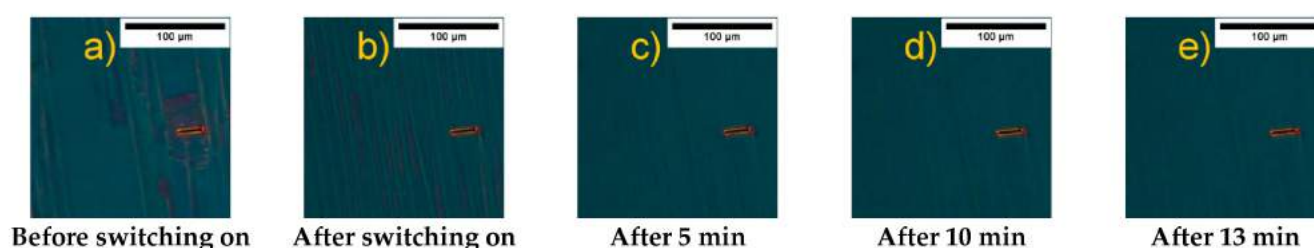


Figure 10. The alignment process of Composite 5 (20 V_{pp}, 50 Hz, rectangular signal).

As can be seen in Figure 11a, a non-zero polarization was observed for each sample already at a voltage of 4.0 V (the voltage threshold associated with the reorientation of molecules is below 4.0 V), while the saturation was observed at different voltages, depending on the Composite. From about 30.0 V, a very slight increase in spontaneous polarization was observed for all Composites. For Composite 1 (pure EHPDB), the spontaneous polarization was saturated at 60.0 V, for Composites 2 and 4, at around 80.0 V, while for Composites 3 and 5, after exceeding 30.0 V, a continuous slow increase in spontaneous polarization was visible. The spontaneous polarization at 100.0 V is equal to 37.22, 18.25, 13.01, 18.82 and 16.90 nC/cm² for Composites 1–5, respectively. It turned out that even the smallest amounts of nanoparticles caused a drastic decrease in spontaneous polarization. Interestingly, there is no close relationship between the concentration of Fe₂O₃ admixture and the decrease in P_s values. For the nanoparticle content of 0.7 and 0.3 wt.%, a two-fold decrease, while for 0.5 wt.%, an almost tripled decrease, in P_s were observed. In turn, for the content of 0.9 wt.%, the P_s was higher than for 0.5 wt.%. Decreasing of the threshold voltage for the reorientation of LC molecules was also obtained with the use of other types of nanoparticles, such as BaTiO₃ and Sn₂P₂S₆ for the compounds Merck 18523 and LC 1550 [70]. In turn, an increase in the threshold voltage after doping with graphene flakes was observed, which was explained by anchoring molecules to the surface of graphene flakes [71].

Temperature dependence of the spontaneous polarization for Composites 1–5 is presented in Figure 11b. Since the SmA*–SmC* phase transition is of the second order, continuous growth of the spontaneous polarization was observed for Composites 2–6. On the other hand, for Composite 1 (pure EHPDB), at the transition temperature (ca. 80 °C), a sudden jump was visible, which is related to the difficulties of measuring the phase transition. The spontaneous polarization does not saturate for any sample, while it decreases after doping, and the maximum value of P_s is equal to 44.99, 31.45, 25.94, 31.85 and 29.67 nC/cm² for Composites 1–5, respectively.

Novotná et al. doped liquid crystal with SmC* phase with Fe₂O₃ nanoparticles (ca. 4 nm) decorated with oleic acid, and also observed a decrease in the spontaneous polarization with increasing the dopant concentration [30]. The same behavior was observed by Khushboo et al. for the ferroelectric W206E mixture doped with NiFe₂O₄ nanoparticles (ca. 45 nm, 0.12, 0.25, 0.50 wt.%) [72]. In turn, Prodanov et al. doped a ferroelectric liquid crystal mixture with CoFe₂O₄ nanoparticles (ca. 7.8 nm, 1 and 3 wt.%) and also observed

a decrease in P_s at lower concentrations, and practically no change at a higher dopant concentration, e.g., similar to the studied composites [73]. Interestingly, Popova et al. doped a ferroelectric liquid crystal with γ - Fe_2O_3 nanoparticles (ca. 15 nm, 0.01–0.02 wt.%) and observed no dopant influences on the spontaneous polarization [74], probably due to the low concentration of the admixture. Therefore, it can be concluded that the admixture of Fe_2O_3 nanoparticles usually reduces the spontaneous polarization. However, it is also not excluded that the spontaneous polarization decreases due to the electrode polarization phenomenon.

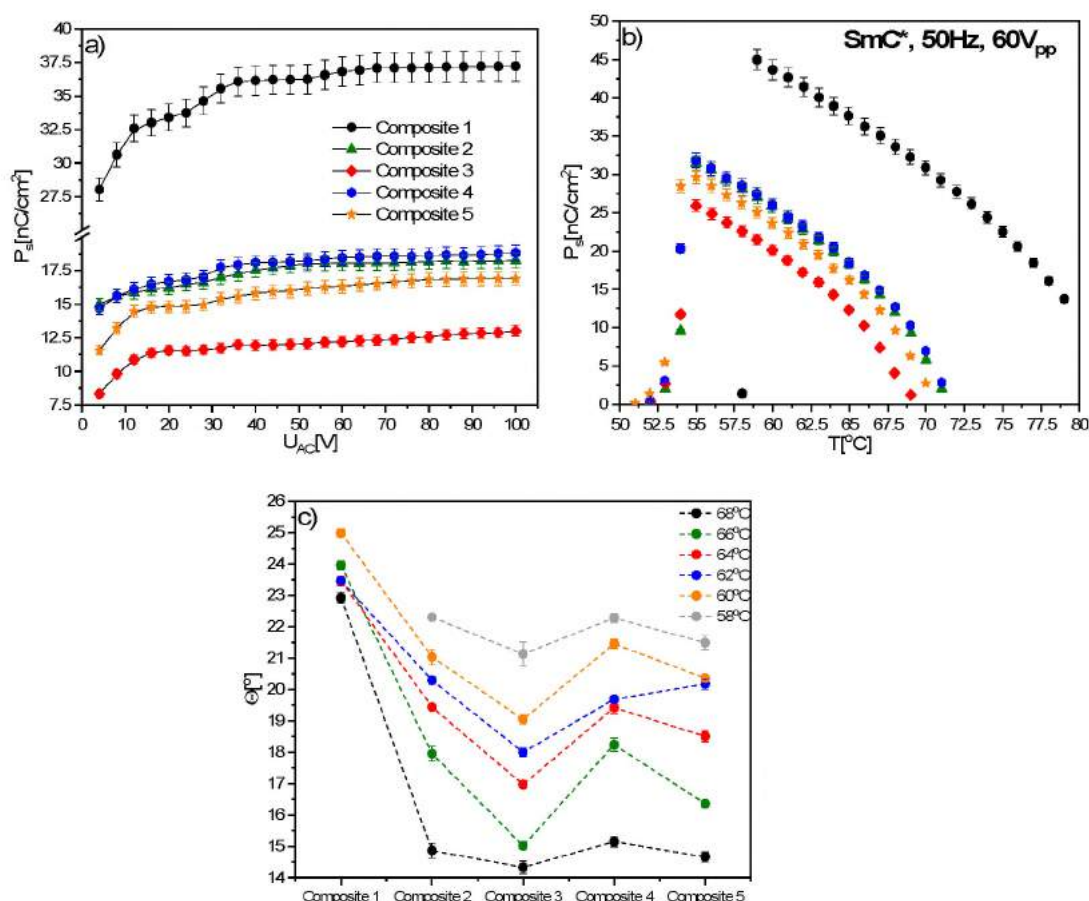


Figure 11. Spontaneous polarization versus applied voltage (50 Hz, triangular wave) in the SmC^* phase (65.0 °C) for Composites 1–5 (a), temperature dependence of spontaneous polarization, the accuracy of the P_s is 3% (b), and tilt angle of Composites 1–5 at several selected temperatures (c). Dashed lines are a guide for the eye.

As an example, the tilt angle for several selected temperatures in the SmC^* phase for Composites 1–5 is presented in Figure 11c. As it is clearly shown, the tilt angle decreases in the same way, with a change of nanoparticle concentration in nanocomposites (Composites 2–5), as spontaneous polarization, and at 68 °C, it is equal to: 22.92°, 14.86°, 14.33°, 15.15° and 14.66° for Composites 1–5, respectively. The greatest decrease, about 8.6°, was found for Composite 3 (0.5 wt.%). Additionally, since the SmA^* – SmC^* transition temperature shifted to about 71 °C in Composites 2–5, it seems that Fe_2O_3 nanoparticles are responsible for the lack of molecular tilt above this temperature. We suppose that the decrease in the tilt angle and spontaneous polarization may be caused by the physical adsorption of organic molecules on the surface of nanoparticles and the strong interaction between nanoparticles in nanocomposites (hindering the reorientation of organic molecules).

In the sample response, during P_s measurements, two anomalies appeared: one related to the reorientation of organic molecules and the second probably related to the ions present in Composites 1–5 (coming from the synthesis). However, this second anomaly

splits into two anomalies for Composites 2–5 (but not for pure EHPDB) when increasing the applied voltage. In our opinion, this third anomaly is related to the introduction of additional ions into the matrix along with the nanoparticles (chemically, other ions than those present in the pure matrix) or to the contamination of Fe_2O_3 nanoparticles with FeO , having a non-zero dipole moment [75]. Another possibility is that a dipole moment is induced in Fe_3O_4 nanoparticles (existing as impurities, see PXRD results) under an external electric field, as was mentioned by Zakerhamidi et al. [69].

The switching time was determined from the sample response to the applied rectangular wave of 20 V_{pp}, and for both the pure matrix and nanocomposites, was much shorter than a millisecond (Figure 12a,b). The ionic response visible for Composites 1–5, after increasing the applied voltage up to 60 V_{pp}, split into two anomalies for nanocomposites: major and minor ionic anomalies, while for Composite 1, it did not (Figure 12c,d), as observed for spontaneous polarization. The reorientation time associated with the minor ion anomaly (τ_{addion}) was determined for several selected temperatures, and it increased with the decreasing temperature for each nanocomposite (Figure 12f). Similarly, the switching time of organic molecules increased with decreasing temperature (Figure 12e), but this increase was much faster for nanocomposites than for the pure matrix. However, at low temperature ranges of the SmC* phase (below 58 °C), a shorter switching time was found for Composite 1 (pure EHPDB) than for nanocomposites (Composites 2–5).

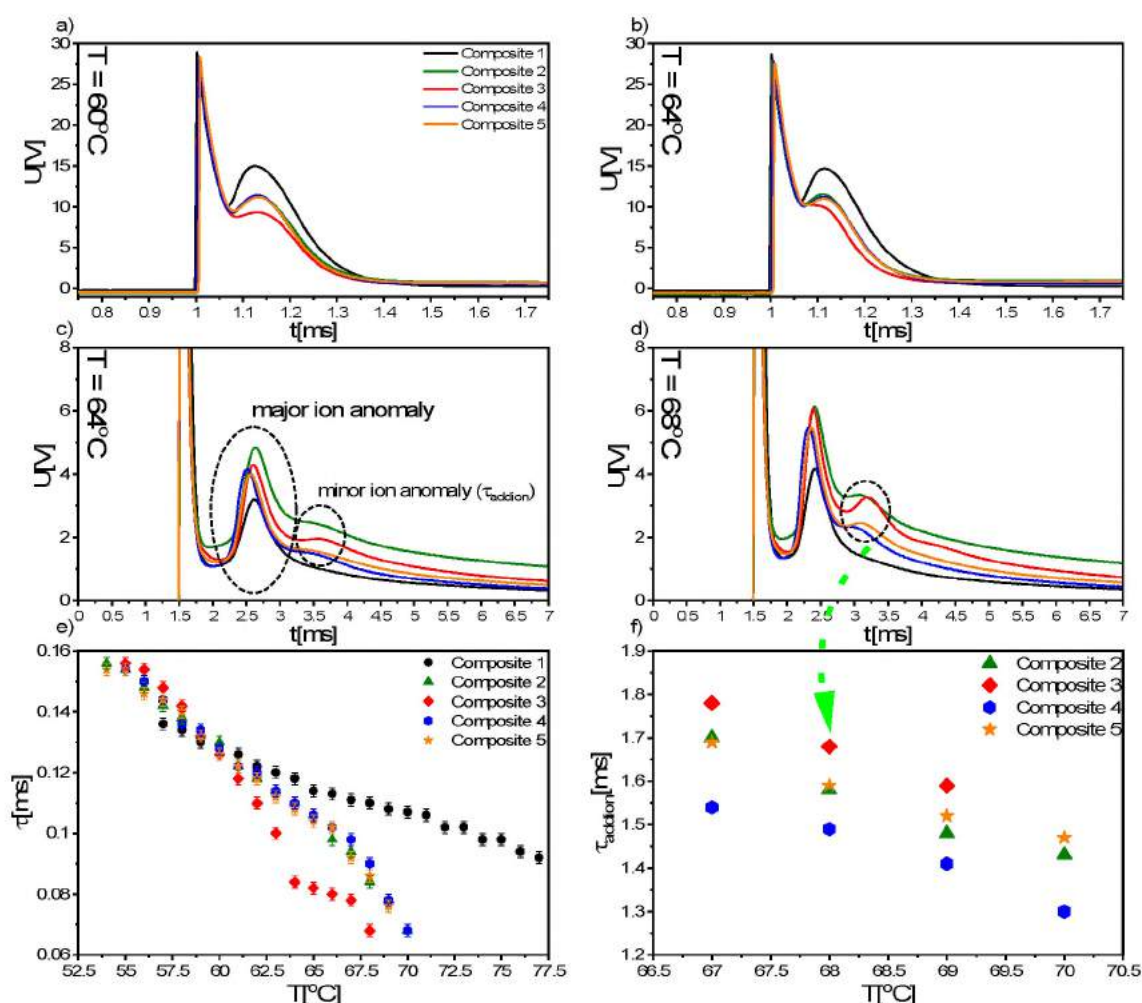


Figure 12. The voltage response of Composites 1–5 on rectangular wave (50 Hz, 20 V_{pp}) at temperatures of 60 °C (a) and 64 °C (b), and on rectangular wave (50 Hz, 60 V_{pp}) at 64 °C (c) and 68 °C (d). Temperature dependence of the switching time for Composites 1–5 (e) and reorientation time of additional ions at several selected temperatures for Composites 2–5 (f). The legend in graph (a) is the same for (a–d) graphs.

Based on the switching time and spontaneous polarization measurements, the rotational viscosity was determined (Equation (1)), and the results are presented in Figure 13.

$$\gamma(T) = \tau(T)P_s(T)E_{\text{applied}} = \tau(T)P_s(T)\frac{U_{\text{applied}}}{d} \quad (1)$$

where γ , τ , P_s , E_{applied} , U_{applied} and d are the rotational viscosity, switching time, spontaneous polarization, the electric field, applied AC voltage and sample thickness, respectively. As expected, the rotational viscosity increased with decreasing temperature for Composites 1–5, but due to the decrease of spontaneous polarization and shorter switching time, the rotational viscosity, γ , drastically decreased after doping (Figure 13). γ values are the same for Composites 2 and 4 (0.3 and 0.7 wt.%, respectively), but for Composites 3 and 5 (0.5 and 0.9 wt.%, respectively), they are smaller, within the measurement uncertainty. Although Goel et al. explained the decrease in the rotational viscosity in studied composites (Ni ca. 34 nm, KCFLC7S matrix) by nanoparticles' adsorption to the ITO surface and modification of anchoring energy of molecules [76], we do not fully understand this behavior and have made an attempt to explain this. We suppose that the aggregation of nanoparticles is either absent or relatively small up to a concentration of 0.5 wt.% (Composite 3), but the agglomeration process becomes important for a higher concentration (0.7 wt.%, Composite 4), and it is even more important in Composite 5 (0.9 wt.%). In addition, Composite 5 can contain significantly more non-agglomerated nanoparticles than Composite 4, which further decreases spontaneous polarization and rotational viscosity.

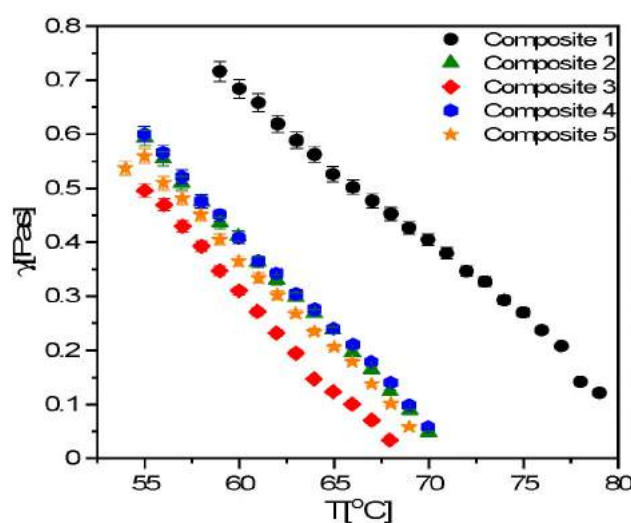


Figure 13. Temperature dependence of the rotational viscosity for Composites 1–5.

The area of electrodes in the ITO cell used is $5 \times 5 \text{ mm}^2$. The width and the length of the LC molecule are ca. $5 \text{ \AA}$ and $40 \text{ \AA}$ [77] respectively, while the thickness of the smectic layer is about $37 \text{ \AA}$ (in tilted SmC^* phase, tilt angle of 20°). Then, the electrode surface will cover about $(5 \text{ mm}/5 \text{ \AA}) \times (5 \text{ mm}/37 \text{ \AA}) = 1.35 \times 10^{13}$ LC molecules, while about $(4.9 \text{ \mu m}/5 \text{ \AA}) \times 1.35 \times 10^{13} = 1.323 \times 10^{17}$ LC molecules will be present in the volume of the electrodes ($4.9 \text{ \mu m}$ —thickness of the ITO planar cell). As it is known, the nanoparticle used is about 12.5 times larger than the liquid crystal molecule (the length of LC molecules $L \approx 40 \text{ \AA}$, the nanoparticle size $d \approx 50 \text{ nm}$, $d/L \approx 12.5$). Therefore, one nanoparticle occupies the volume of 14 LC molecules in one dimension in a single smectic layer of tilted phase (SmC^* , $\theta \approx 20^\circ$), and $14 \times 14 \times 14 = 2744$ LC molecules in three dimensions. We used a very low concentration of nanoparticles for the synthesis of nanocomposites. If 1.323×10^{17} LC molecules will be present in the volume of the electrodes for pure EHPDB, 1.319×10^{17} LC molecules and 9.628×10^9 nanoparticles will be present for Composite 2 (0.3 wt.%). Thus, the admixture of nanoparticles at such a low concentration

eliminates a negligibly small amount of LC molecules and could not be responsible for the significant decrease of spontaneous polarization, tilt angle and rotational viscosity (if the P_s of Composite 3 is practically half of pure EHPDB, the introduced nanoparticles should eliminate half of the LC molecules). The FTIR results do not show that there is a chemical bond between nanoparticles and LC molecules (see below), however strong physical adsorption of molecules to the surface of nanoparticles cannot be ruled out. Besides, in the vicinity of the nanoparticle, the packing of LC molecules can be completely different than in the volume in which there are no nanoparticles.

Figure 14 schematically shows the effect of increasing the concentration of nanoparticles on the arrangement of molecules in a thin layer of composites in measuring the ITO cell. It should be stressed that the drawing is not to scale, i.e., the individual nanoparticle is larger than the liquid crystal molecule. In turn, Vimal et al., by doping ferroelectric liquid crystal Felix 17/100 with ferromagnetic nanoparticles ($\text{ZnO}:\text{Cu}^{2+}$ ions, 1 wt.%), obtained the enhanced spontaneous polarization due to magneto-electric coupling [78]. To summarize, to explain the decrease in electrical parameters, further research is needed, for example, the SQUID method could provide an answer to the question of whether the interaction between nanoparticles (magnetic coupling) may disturb the switching process and cause the spontaneous polarization and the tilt angle of the molecules to decrease. Additionally, the interaction between two types of dipoles (electric for the LC molecules and magnetic for nanoparticles) can strongly modify the electric parameters of nanocomposites, and although the nature of this coupling is not fully understood, its existence cannot be ruled out [79].

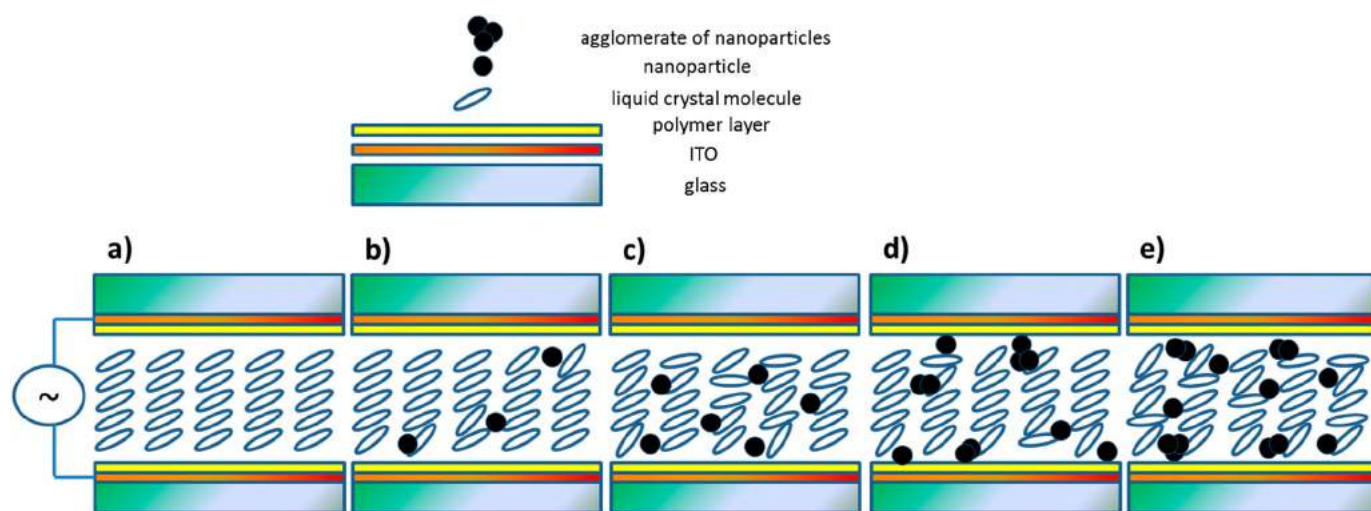


Figure 14. A schematic explanation of the spontaneous polarization behavior in Composites 1–5 with an increase in the concentration of Fe_2O_3 nanoparticles (a–e). Apart from the increase in the amounts of agglomerates in Composite 5 relative to Composite 4, the amount of non-agglomerated nanoparticles increases, which causes a further reduction in spontaneous polarization. The figures are not to scale, in fact the nanoparticles are much larger than the organic molecules. Ions present in the samples, which will reach the properly polarized electrodes under the influence of the AC field, were not taken into account.

Apart from studying the modification by doping the parameters typical for ferroelectric liquid crystals (spontaneous polarization, tilt angle, switching time), the anchoring energy coefficient of molecules to the cell surface and the helical pitch were determined.

The free energy of ferroelectric liquid crystal contains surface-free energy (additional energy derived from unbalanced forces among the molecules on the surface), which is associated with polar and dispersion contributions [80,81]. Polar anchoring is an electrostatic interaction, while dispersive anchoring is London or van der Waals interactions between LC molecules and the anchoring surface (in our case, a polymer layer) [82,83].

Anchoring energy coefficients, dispersion, W_d , and polar, W_p , can be calculated according to the formulas [80,84,85]:

$$W_d(T) = \frac{\gamma(T)d}{4\tau(T)} \quad (2)$$

$$W_p(T) = \sqrt{K(T)P_s(T)E_{th}(T)} \quad (3)$$

where γ , d , τ , K , P_s and E_{th} are rotational viscosity, layer thickness, switching time, mean elastic constant, spontaneous polarization and threshold field for molecular reorientation, respectively. Due to the lack of the K value, it was not possible to determine the polar anchoring coefficient, W_p . In turn, as shown in Figure 15 the admixture decreases the dispersion coefficient, W_d (mainly due to γ and τ modification), and its temperature dependence is very similar to the spontaneous polarization (see Figure 11b). Decreasing the W_d coefficient should decrease the threshold voltage for switching between on and off states, which is consistent with the data presented in Figure 11a.

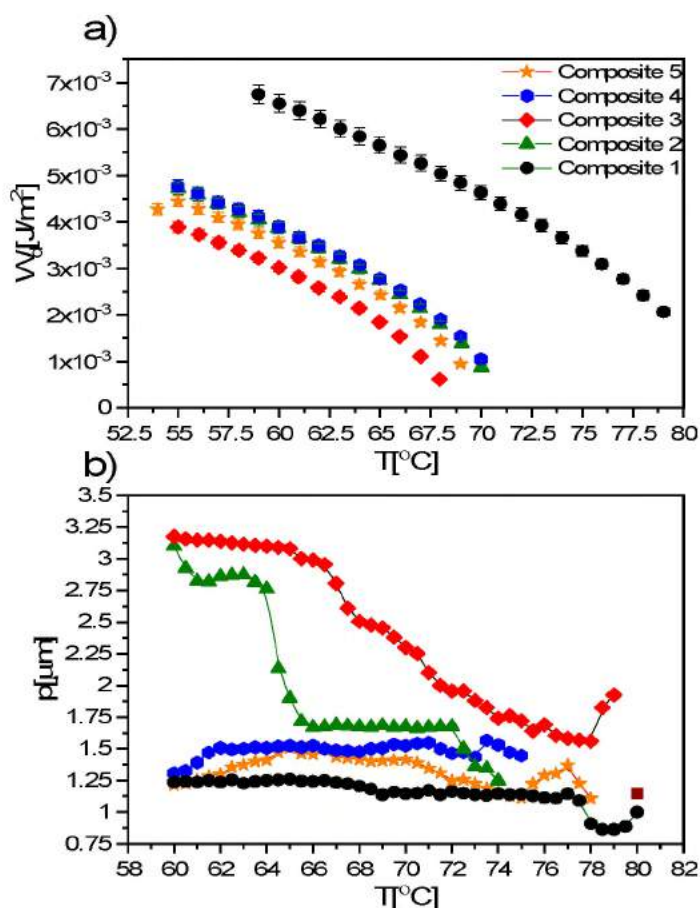


Figure 15. Temperature dependence of the dispersion anchoring coefficient of LC molecules to the surface of the polymer layer (a) and temperature dependence of the helix pitch (b) for Composites 1–5.

The helix pitch in the SmC^* phase is modified by an addition of nanoparticles, as it is shown in Figure 15b. This modification strongly depends on the concentration of nanoparticles used—the lowest is for the highest Fe_2O_3 concentration (0.9 wt.%, Composite 5), while the highest is for the lowest concentrations (0.3 and 0.5 wt.%, Composites 2 and 3, respectively). Moreover, deep in the SmC^* phase, a continuous increase in the helix pitch was observed for Composite 3, which leads to an increase in the thickness of the smectic layers. It seems that different behavior for lower (0.3 and 0.5 wt.%) and higher (0.7 and 0.9 wt.%) concentrations may arise from the aggregation process. The modification by doping the helix pitch is in good agreement with the tilt angle data for Composites 2 and 3,

in contrast to Composite 5 with negligible modification of the helix pitch and significant modification of the tilt angle. The incomprehensible modification of the helix pitch in the case of Composites 4 and 5 (0.7 and 0.9 wt.%) is probably related to poor texture quality, and thus low quality of the fringes, which resulted in underestimating the helix pitch in these nanocomposites. Middha et al. doped cholesteric liquid crystal ZLI-4151 + CB15 using MWCNTs (ca. 110–170 nm, length 5–9 μm , 0.01, 0.1, 0.5, 1.0 wt.%) and obtained materials with shorter helix pitches [86]. Due to hardware limitations, we were unable to determine the helix pitch in the N^* phase. It is not excluded that the influence of the admixture (nanoparticles or nanotubes) is quite different for various liquid crystalline phases.

Textures registered for the free drop of Composite 1 (pure EHPDB) in various phases are presented in Supplementary Figure S7. The textures of isotropic liquid and the SmA^* phase are completely black (Figure S7a,d), while characteristic textures of cholesteric N^* phase are visible in Supplementary Figure S7b. In turn, the common fingerprint texture of the TGBA^* phase is clearly visible in Supplementary Figure S7c. Interestingly, the other fingerprint texture (Supplementary Figure S7e,f) was also registered below the SmA^* phase, and we suppose that it is another frustrated phase in a very narrow temperature range, e.g., TGBC^* (not registered by other methods). Characteristic textures of a chiral ferroelectric SmC^* phase with an equidistant line pattern are presented in Supplementary Figure S7f,g. We suppose that detection of the frustrated TGBC^* phase was possible in this study due to the very slow cooling rate (0.1 $^{\circ}\text{C}/\text{min}$) not used in other methods (5 $^{\circ}\text{C}/\text{min}$ in DSC or 3 $^{\circ}\text{C}/\text{min}$ in TLI), but a thorough investigation of the presence of this phase in nanocomposites is not the aim of this study.

3.9. FTIR Results

The comparison of FTIR spectra obtained at 20 $^{\circ}\text{C}$ for Composites 1–6 and oleic acid is presented in Figure 16. For better visibility, two spectral ranges: 450–2000 and 2700–3200 cm^{-1} , where all fundamental bands occur, are exposed. The IR spectrum of Composite 1 (pure EHPDB) fully confirms its proper chemical and molecular composition—all the expected essential bands are present in the spectrum. Most prominent bands are connected to $\nu(\text{C}-\text{O})$ and $\nu(\text{C}=\text{O})$ stretching modes in aromatic ester. The first occurred in the spectral range of 1050–1300 cm^{-1} and the second one was placed at 1724 cm^{-1} . Additionally, very intensive bands connected to stretching $\nu(\text{CH})_{\text{ar}}$ and bending $\delta_{\text{oop}}(\text{CH})_{\text{ar}}$ vibrations within para-substituted aromatic rings appeared at 1607, 1510 and 850 cm^{-1} , respectively. The band characteristic for the epoxy ring appeared at 902 cm^{-1} and is connected to $\nu(\text{C}-\text{O})_{\text{epoxy}}$. The spectrum also contains stretching and bending vibrations of methyl and methylene groups of aliphatic chain, which occurred in the spectral ranges of 2800–3000 and 1300–1480 cm^{-1} , respectively.

Comparing the spectra of Composite 1 and nanocomposites (Composites 2–5), it can be seen that they are basically identical taking into consideration positions and intensities of all bands. Additionally, no new bands were observed in the spectra of all composites, which suggests that there are no molecular interactions between Fe_2O_3 nanoparticles and EHPDB that would lead to modification of the chemical structure of the liquid crystal matrix. However, it has to be noted that the amount of Fe_2O_3 nanoparticles in the investigated materials is below 1 wt.%, and at such a low concentration, the IR method may not be sensitive enough to see it. In case of Composites 2 and 4, one additional band with a maximum at 1638 cm^{-1} can be seen, which is connected to a small amount of water impurity in these samples. On heating the samples up to 100 $^{\circ}\text{C}$, the band disappeared due to its evaporation (see Supplementary Figure S8). Comparing the spectra of Composite 2 and Composite 6, one can see that they are also basically the same, except for the region between 1670 and 1710 cm^{-1} , where some broadening is clearly visible in case of the Composite with oleic acid. It comes from the band connected to the stretching vibration of the carbonyl group, which is most prominent in the spectrum of oleic acid. It proves that oleic acid is present in this sample, but it does not change the molecular structure of the investigated composite as we did not observe any changes in bands' positions or

intensities. In turn, the spectra of Composites 1–6 obviously changed upon heating to 100 °C, but again, there were no differences between them (see Supplementary Figure S8a), while the spectra obtained at 10 °C, after the heating–cooling cycle (see Supplementary Figure S8b), are comparable to the ones obtained for the samples without thermal history and being in the ordered crystalline phase (Figure 16).

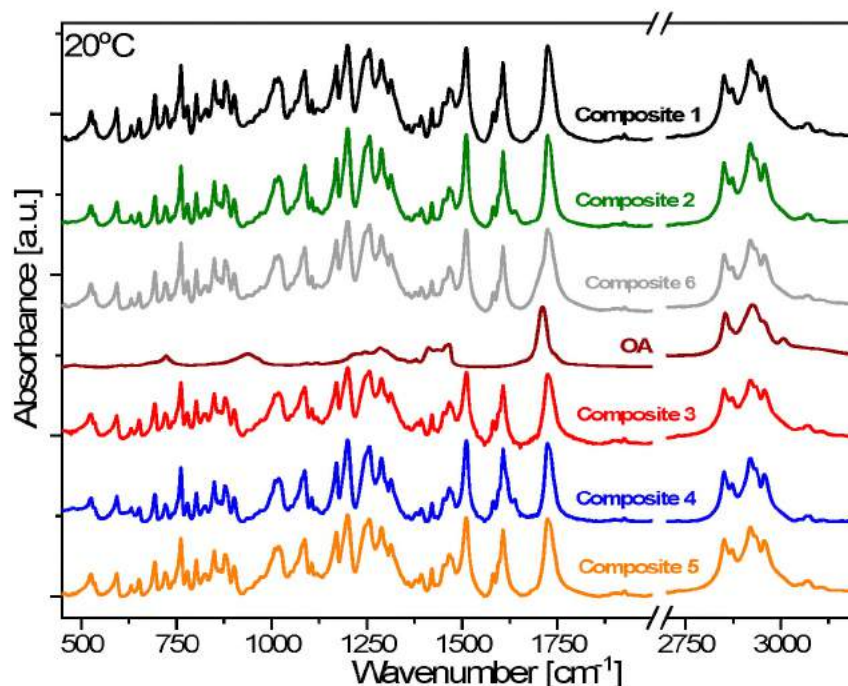


Figure 16. FTIR spectra of Composites 1–6 and oleic acid obtained at 20 °C.

4. Conclusions

In this paper, we presented the effect of low concentrations of a γ -Fe₂O₃ nanoparticles admixture (containing small amounts of hematite and magnetite) on the physical properties of the EHPDB ferroelectric liquid crystal, especially in the SmC* phase. The influence of the addition of oleic acid to the nanocomposites was also studied. A number of complementary methods were used, and based on the obtained results, the following conclusions can be drawn:

- The structure of the EHPDB matrix did not change after doping. The diffraction patterns of the nanocomposites are practically the same as in the case of pure EHPDB, only the low-intensity reflections coming from Fe₂O₃ nanoparticles exist in addition. The surface morphology of the nanocomposites also did not change after doping (without oleic acid).
- The following phases during cooling were registered for studied composites: BP, N*, TGBA*, SmA*, TGBC* and SmC*. The shift of the phase transition temperatures to lower values, the disappearance of BP and the polymorphism of crystal phases, as well as the broadening of the SmA* versus the narrowing of the SmC* phase after the addition of Fe₂O₃ nanoparticles, were observed. What is interesting is that a very narrow TGBA* phase existed in all nanocomposites. The broadening of the SmA* phase in favor of SmC* was explained by modifying the mobility of nanoparticles. A very strong influence of the admixture on the texture of the SmC* phase in nanocomposites was observed as a strong striation.
- A very strong influence of the admixture on the electrical parameters was noted. The spontaneous polarization, tilt angle, switching time and rotational viscosity decreased after doping. The additional voltage response registered for nanocomposites was assigned to the additional ions introduced with nanoparticles into the EHPDB matrix.

A slightly different modification of the SmC* phase parameters for nanocomposites with higher concentrations of nanoparticles (0.7 and 0.9 wt.%) was explained by the strong influence of Fe₂O₃ aggregation.

- The addition of oleic acid greatly narrowed the range of the mesophases with cooling and practically caused the disappearance of the liquid crystal polymorphism during heating. It was also responsible for the formation of ripples on the surface and changing the orientation of organic molecules from planar to homeotropic in a quite specific way (depending on the diameter of cholesteric droplets).

To summarize, the aim of our work was to show that materials with precisely defined parameters can be obtained by controlling the concentration of a nanoparticle admixture. As we have shown, modification of the electrical parameters of the LC matrix by the nanoparticles (at very small concentrations) is significant, however the explanation is not easy; very often, several effects may modify a given property of the matrix. It should be kept in mind that the interactions: LC molecule–LC molecule, LC molecule–nanoparticle, nanoparticle–nanoparticle and nanoparticle–electrode, should also be considered. Therefore, the issue is complex and requires further experimental research or advanced computer simulations.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/ma14164722/s1>, Figure S1: Digital optical images of Sample 1, Sample 2 and Composite 1. The magnification is shown in the images, where colored dotted squares correspond to the enlarged areas, Figure S2: SEM images of Samples 1–2 and Composites 1–6. The magnification is shown in the images, where colored dotted squares correspond to the enlarged areas, Figure S3: DSC curves registered during heating at a rate of 10 °C/min for Composites 1–6 (a) and extended temperature range of 75.0–100.0 °C (b), Figure S4: Textures of the N* phase registered for Composite 3 during cooling down from isotropic phase (2 °C/min). Formation of N* phase droplets immediately after the Is–N* phase transition with visible focal-conic inclusions (a). Typical fan-like texture (b). Cracking of fan-like structure (c). Beginning of forming stripes on a cracked fan-shape structure (d). The formation process of streaks characteristic of the oily-streaks texture (e). Typical oily-streaks texture from which a transition to the TGBA* frustrated phase was observed at lower temperatures (f). All images show the same sample area as the temperature is lowered, Figure S5: Influence of Fe₂O₃ nanoparticles admixture on the phase transitions during heating: Cr–SmC*, SmC*–SmA*, N*–Is/P–N*, Figure S6: The alignment process of Composites 1–5 (20 V_{pp}, 50 Hz, rectangular wave), Figure S7: Textures registered for the free drop of Composite 1 (pure EHPDB) in: isotropic phase, 96.1 °C (a), cholesteric phase, 90.5 °C (b), TGBA* phase, 84.0 °C (c), SmA* phase, 82.5 °C (d), TGBC* phase, 80.0 °C (e), TGBC* phase, 79.50 °C (f), SmC* phase, 78.5 °C (g), SmC* phase, 60.0 °C (h), Figure S8: FTIR spectra of Composites 1–6 and oleic acid obtained at 100 °C (a) and 10 °C, after the heating–cooling cycle (b), Table S1: The phase sequences on heating and cooling for Composites 1–6. The TGBA*–SmA* phase transition temperature was omitted here due to the large uncertainties in determination.

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Modifications of FLC Physical Properties through Doping with Fe_2O_3 Nanoparticles (Part I)

1. Sample preparation

The Composite 6 was prepared according to the scheme:

1. The adequate amounts of pure EHPDB and Fe_2O_3 nanoparticles were weighed into separate vials (see Table 1).
2. Oleic acid of 0.5 μL was added to vial with nanoparticles at room temperature (a small drop of oleic acid was spread on the bottom of vial to cover the nanoparticles) and the vial was left at room temperature for several hours.
3. 1.5 mL of chloroform was added to the nanoparticles + oleic acid at room temperature and the solution was sonicated in 50 s(on)/10 s(off) mode for 45 min ($A = 30\%$, ice blanket).
4. Steps like for Composites 1–5.

Two samples of Fe_2O_3 nanoparticles was prepared to check the influence of oleic acid on the properties of nanoparticles: pure nanoparticles (Sample 1) and nanoparticles decorated with oleic acid (Sample 2):

Sample 1: The appropriate amount of nanoparticles was weighed.

Sample 2: The appropriate amount of nanoparticles was weighed into vial and oleic acid of 150.0 μL was spread on the bottom of vial to cover the nanoparticles. The vial was left for several hours. Next, the steps 3–9 of the synthesis route of Composite 6 (without the steps related to EHPDB) were done, except the time in step 6 was 225 min in order to obtain about 1mL of solution.

2. Results

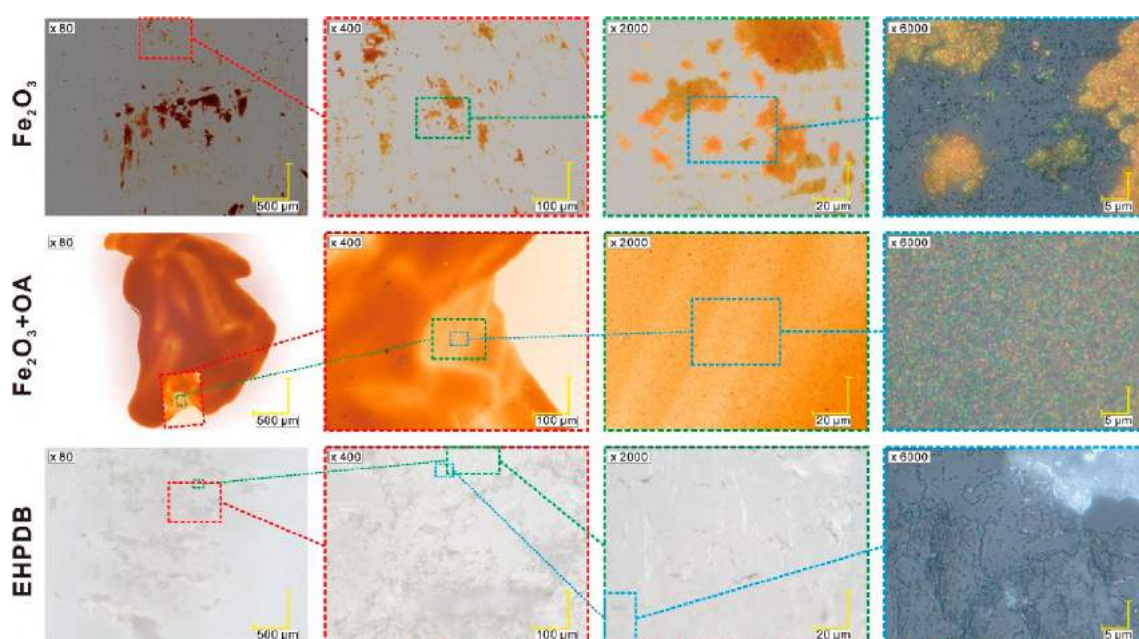


Figure S1. Digital optical images of Sample 1, Sample 2 and Composite 1. The magnification is shown in the images, coloured dotted squares correspond to the enlarged areas.

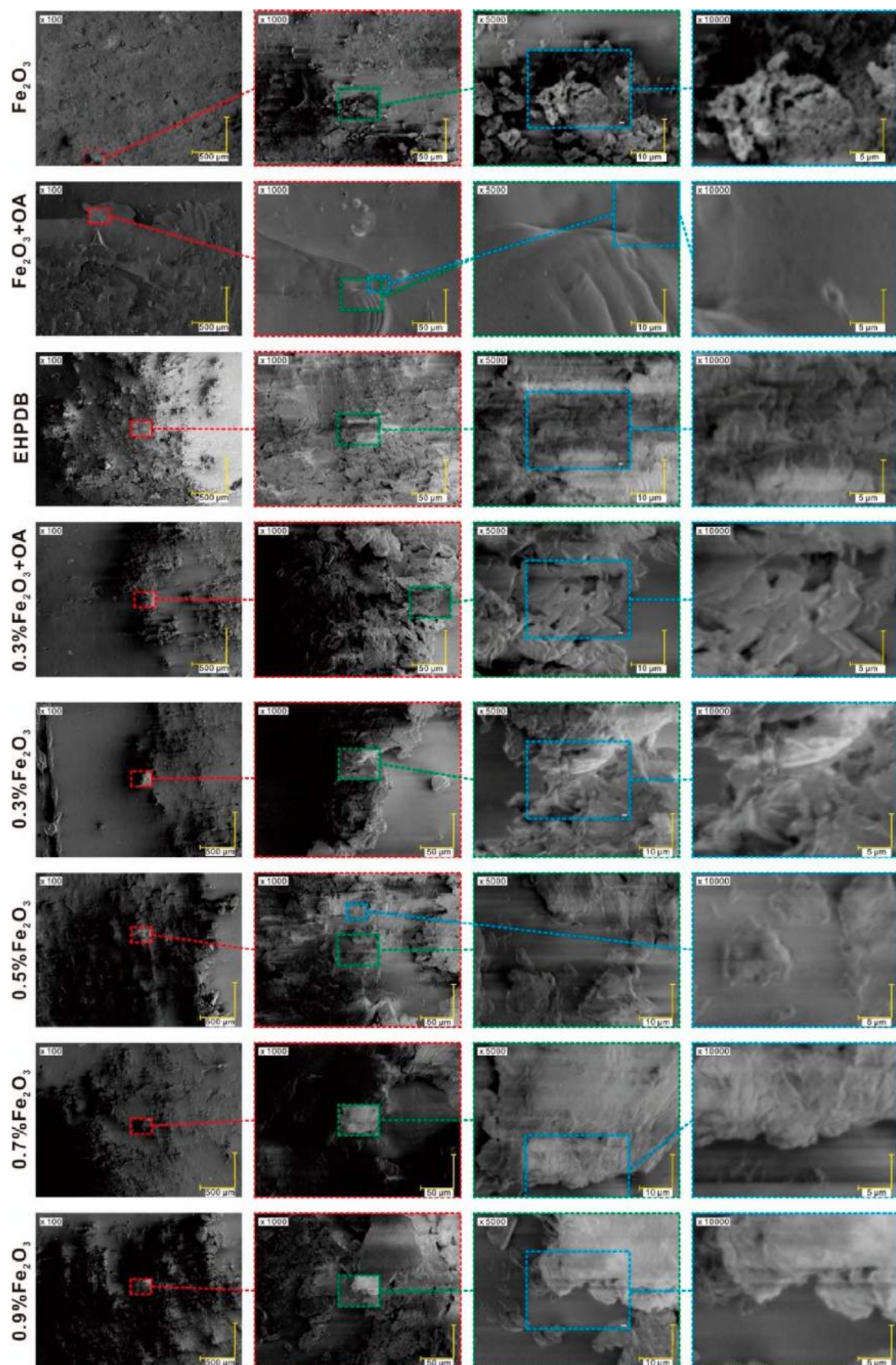


Figure S2. SEM images of Samples 1–2 and Composites 1–6. The magnification is given in the images, coloured dotted squares correspond to the enlarged areas.

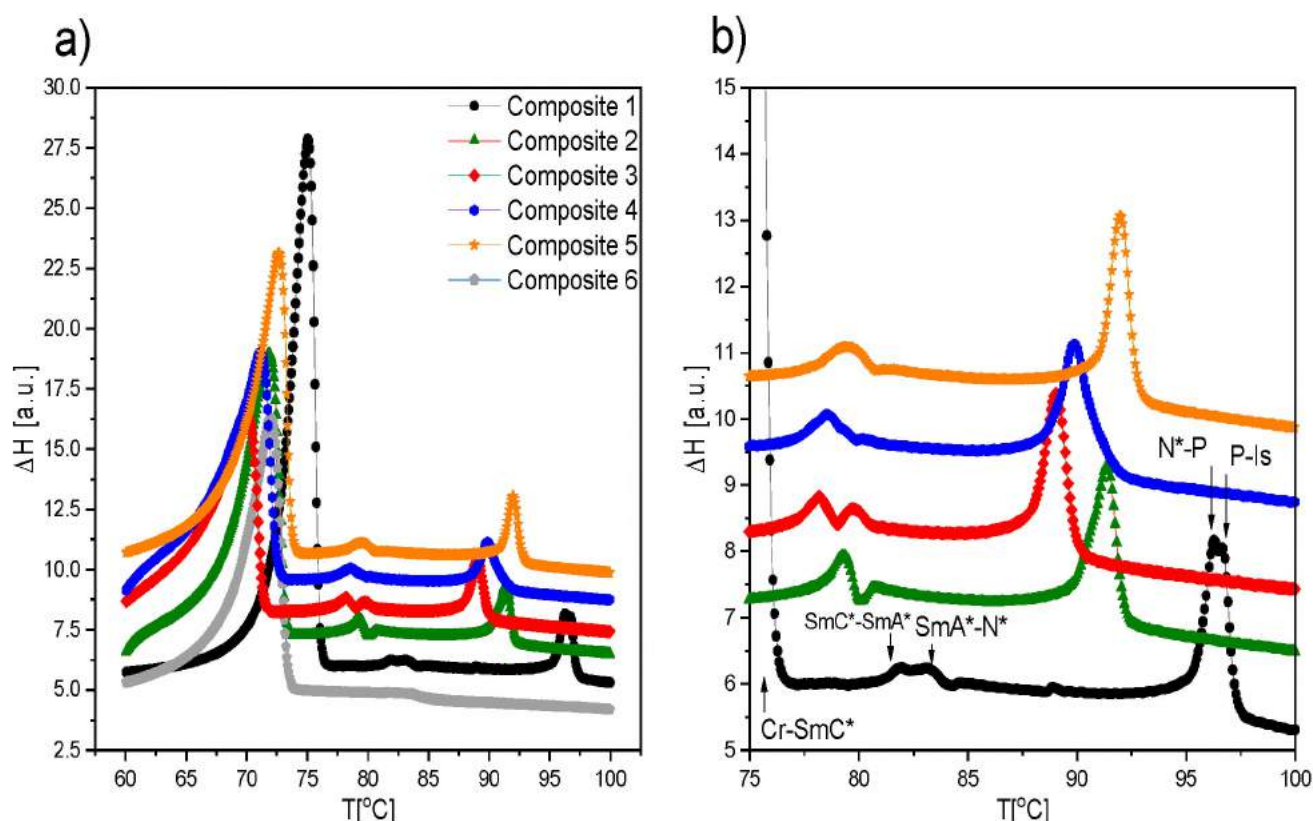


Figure S3. DSC curves registered during heating at 10 °C/min rate for Composites 1–6 (a) and extended temperature range 75.0–100.0 °C (b).

In Figure S3 the first anomaly represents the transition to the ferroelectric phase, the second transition between SmC*–SmA*, the third paraelectric–cholesteric phase transition and the last one N*–isotropic liquid phase transition. As can be seen the transition SmA*–N* for the Composite 4 is visible in the form of a shoulder while for the Composite 5 we observe two connected transitions into one with a wide width–half. In the case of a Composite 1 the last phase transition is double, which indicates a narrow range of the extra phase which was also mentioned in cooling cycle. A small hump visible around 89.0 °C for Composite 1 it is an artefact, not observed for measurements at other rates. The admixture used in a concentration of 0.5 wt.% causes a significant narrowing of the cholesteric phase, which was also weakened during cooling.

One of the most commonly observed textures for the N* phase is the oily–streaks texture. For planar conditions, in N* phase the long molecular axis lies within the smectic plane which is perpendicular to the plates. This implies that the cholesteric axis of the helix is oriented parallel to the glass plates. In the case of the Composite 1, the cholesteric phase was immediately formed into an oily–streaks texture. The oily–streaks texture represents a network of defect lines immersed in homogeneously helical regions. The structure of oily–streaks depends, inter alia, on surface anchoring. In general, the oily–streaks network is not static, but it can grow or fade, resulting, for example, in a uniformly oriented sample. This behavior was observed for the pure matrix (the oily–streaks texture changes relatively quickly to a uniform color—the Grandjean texture due to lowering the temperature). Moreover, the observed streaks in the pure matrix were single. Completely different behavior was observed in the case of all composites. Another natural texture seen in the cholesteric phase is fan-shaped texture. From this texture, the N* phase began to form in all nanocomposites.

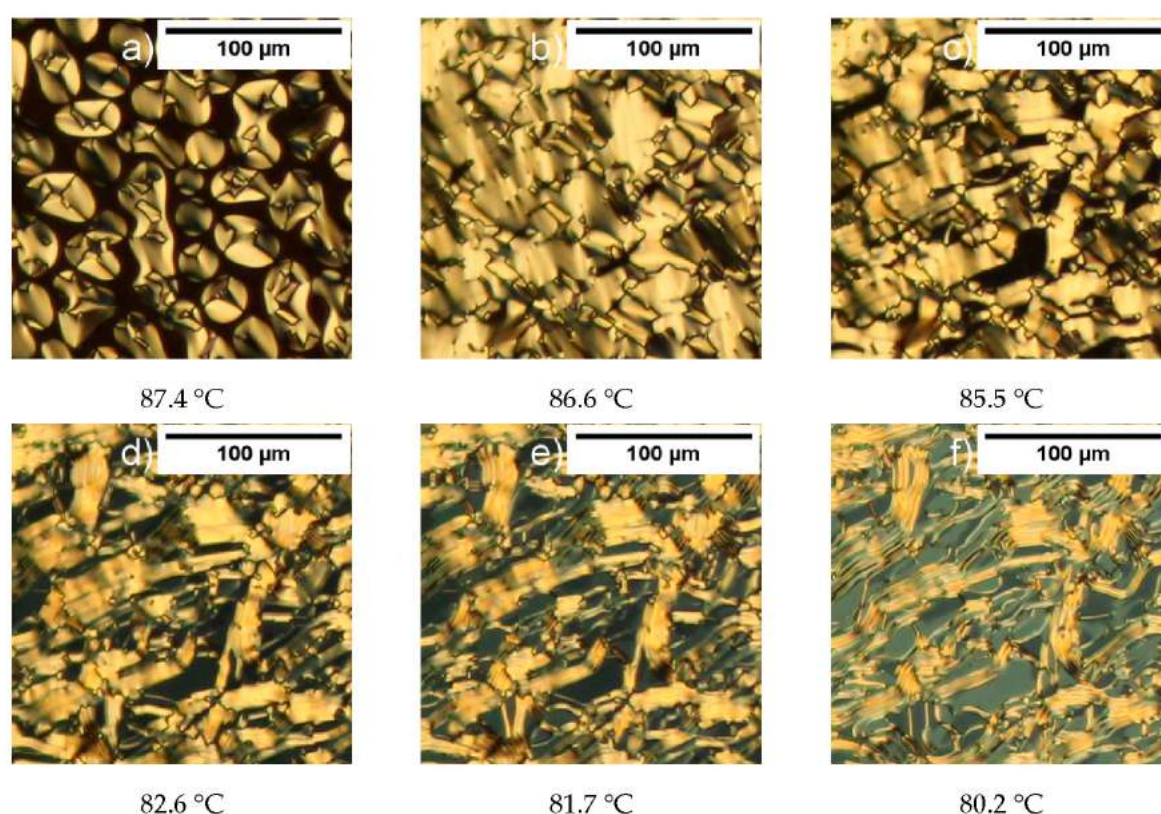


Figure S4. Textures of the N^* phase registered for Composite 3 during cooling down from isotropic phase ($2^\circ\text{C}/\text{min}$). Formation of N^* phase droplets immediately after the $Is-N^*$ phase transition with visible focal-conic inclusions (a). Typical fan-like texture (b). Cracking of fan-like structure (c). Beginning of forming stripes on a cracked fan-shape structure (d). The formation process of streaks characteristic for the texture oily-streaks (e). Typical oily-streaks texture from which a transition to the $TGBA^*$ frustrated phase was observed at lower temperatures (f). All images show the same sample area as the temperature is lowered.

Table S1. The phase sequences on heating and cooling for Composites 1–6. The $TGBA^*-SmA^*$ phase transition temperature was omitted here due to the large uncertainties in determining.

Composites	The Phase Sequence (Cooling)
Composite 1	$Is \xrightarrow{96.29^\circ\text{C}(0.01^\circ\text{C})} P \xrightarrow{95.11^\circ\text{C}} N^* \xrightarrow{83.19^\circ\text{C}(0.20^\circ\text{C})} TGBA^* \xrightarrow{\sim 80.06^\circ\text{C}} SmA^* \xrightarrow{\sim 79.00^\circ\text{C}} SmC^* \xrightarrow{58.07^\circ\text{C}(0.04^\circ\text{C})} Cr_1$ $\xrightarrow{56.93^\circ\text{C}} Cr_2 \xrightarrow{55.69^\circ\text{C}} Cr_3 \xrightarrow{54.73^\circ\text{C}} Cr_4 \xrightarrow{44.64^\circ\text{C}(0.18^\circ\text{C})} Cr_5 \xrightarrow{41.25^\circ\text{C}} Cr_6 \xrightarrow{40.43^\circ\text{C}} Cr_7$
Composite 2	$Is \xrightarrow{91.24^\circ\text{C}(0.03^\circ\text{C})} (P)N^* \xrightarrow{79.42^\circ\text{C}(0.13^\circ\text{C})} (TGBA^*)SmA^* \xrightarrow{72.20^\circ\text{C}} SmC^* \xrightarrow{55.79^\circ\text{C}(0.04^\circ\text{C})} Cr_1 \xrightarrow{54.58^\circ\text{C}} Cr_2 \xrightarrow{38.31^\circ\text{C}(0.13^\circ\text{C})} Cr_3$ $Is \xrightarrow{89.10^\circ\text{C}(0.30^\circ\text{C})} N^* \xrightarrow{79.85^\circ\text{C}(0.06^\circ\text{C})} (TGBA^*)SmA^* \xrightarrow{67.70^\circ\text{C}} SmC^* \xrightarrow{52.75^\circ\text{C}} Cr_1 \xrightarrow{51.65^\circ\text{C}} Cr_2 \xrightarrow{50.77^\circ\text{C}} Cr_3 \xrightarrow{50.18^\circ\text{C}} Cr_4 \xrightarrow{50.18^\circ\text{C}} Cr_5$
Composite 3	$Is \xrightarrow{49.45^\circ\text{C}} N^* \xrightarrow{34.63^\circ\text{C}(0.14^\circ\text{C})} Cr_6 \xrightarrow{34.63^\circ\text{C}(0.14^\circ\text{C})} Cr_7$ $Is \xrightarrow{89.63^\circ\text{C}(0.13^\circ\text{C})} (P)N^* \xrightarrow{78.51^\circ\text{C}(0.19^\circ\text{C})} (TGBA^*)SmA^* \xrightarrow{69.50^\circ\text{C}} SmC^* \xrightarrow{54.61^\circ\text{C}(0.10^\circ\text{C})} Cr_1 \xrightarrow{36.10^\circ\text{C}(0.15^\circ\text{C})} Cr_2$
Composite 4	$Is \xrightarrow{91.91^\circ\text{C}(0.02^\circ\text{C})} N^* \xrightarrow{80.09^\circ\text{C}(0.06^\circ\text{C})} (TGBA^*)SmA^* \xrightarrow{69.80^\circ\text{C}} SmC^* \xrightarrow{55.56^\circ\text{C}(0.40^\circ\text{C})} Cr_1 \xrightarrow{52.52^\circ\text{C}} Cr_2 \xrightarrow{37.95^\circ\text{C}(0.20^\circ\text{C})} Cr_3$ $Is \xrightarrow{73.21^\circ\text{C}} X \xrightarrow{72.09^\circ\text{C}(0.36^\circ\text{C})} N^* \xrightarrow{62.64^\circ\text{C}(0.83^\circ\text{C})} SmA^* \xrightarrow{52.36^\circ\text{C}(0.05^\circ\text{C})} SmC^* \xrightarrow{50.76^\circ\text{C}} Cr_1 \xrightarrow{39.84^\circ\text{C}(0.19^\circ\text{C})} Cr_2$
Composite 5	
Composite 6	
Composites	The Phase Sequence (Heating)
Composite 1	$Cr_1 \rightarrow Cr_2 \rightarrow Cr_3 \xrightarrow{72.51^\circ\text{C}(0.11^\circ\text{C})} SmC^* \xrightarrow{\sim 78.00^\circ\text{C}} TGBA^* \xrightarrow{80.76^\circ\text{C}(0.10^\circ\text{C})} SmA^* \xrightarrow{82.04^\circ\text{C}(0.20^\circ\text{C})} TGBA^* \xrightarrow{\sim 84.00^\circ\text{C}} N^* \xrightarrow{94.92^\circ\text{C}(0.04^\circ\text{C})} P$ $\xrightarrow{96.63^\circ\text{C}} Is$
Composite 2	$Cr \xrightarrow{68.28^\circ\text{C}(0.12^\circ\text{C})} SmC^* \xrightarrow{\sim 76.00^\circ\text{C}} TGBA^* \xrightarrow{77.72^\circ\text{C}(0.05^\circ\text{C})} SmA^* \xrightarrow{79.34^\circ\text{C}(0.14^\circ\text{C})} N^* \xrightarrow{89.67^\circ\text{C}(0.09^\circ\text{C})} Is$
Composite 3	$Cr \xrightarrow{65.62^\circ\text{C}(0.65^\circ\text{C})} SmC^* \xrightarrow{76.38^\circ\text{C}(0.13^\circ\text{C})} SmA^* \xrightarrow{78.69^\circ\text{C}(0.10^\circ\text{C})} N^* \xrightarrow{87.45^\circ\text{C}(0.07^\circ\text{C})} Is$
Composite 4	$Cr \xrightarrow{66.84^\circ\text{C}(0.35^\circ\text{C})} SmC^* \xrightarrow{76.97^\circ\text{C}(0.26^\circ\text{C})} SmA^* \xrightarrow{\sim 79.00^\circ\text{C}} N^* \xrightarrow{88.22^\circ\text{C}(0.12^\circ\text{C})} Is$
Composite 5	$Cr \xrightarrow{69.06^\circ\text{C}(0.14^\circ\text{C})} SmC^* \xrightarrow{77.73^\circ\text{C}(0.07^\circ\text{C})} SmA^* \xrightarrow{\sim 79.00^\circ\text{C}} N^* \xrightarrow{90.78^\circ\text{C}(0.02^\circ\text{C})} Is$
Composite 6	$Cr_2 \xrightarrow{69.48^\circ\text{C}(0.11^\circ\text{C})} Cr_2 + N^* \xrightarrow{75.57^\circ\text{C}(7.77^\circ\text{C})} Is$

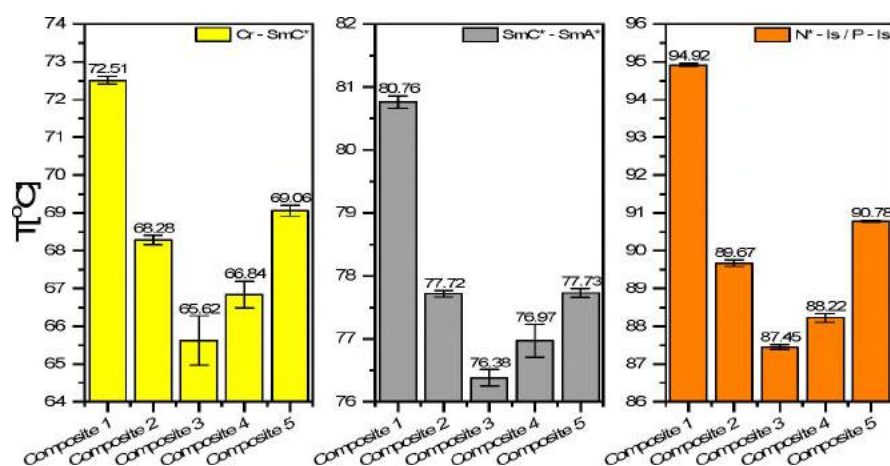


Figure S5. Influence of Fe_2O_3 nanoparticles admixture on the phase transitions during heating: Cr-SmC*, SmC*-SmA*, N*-Is/P-Is.

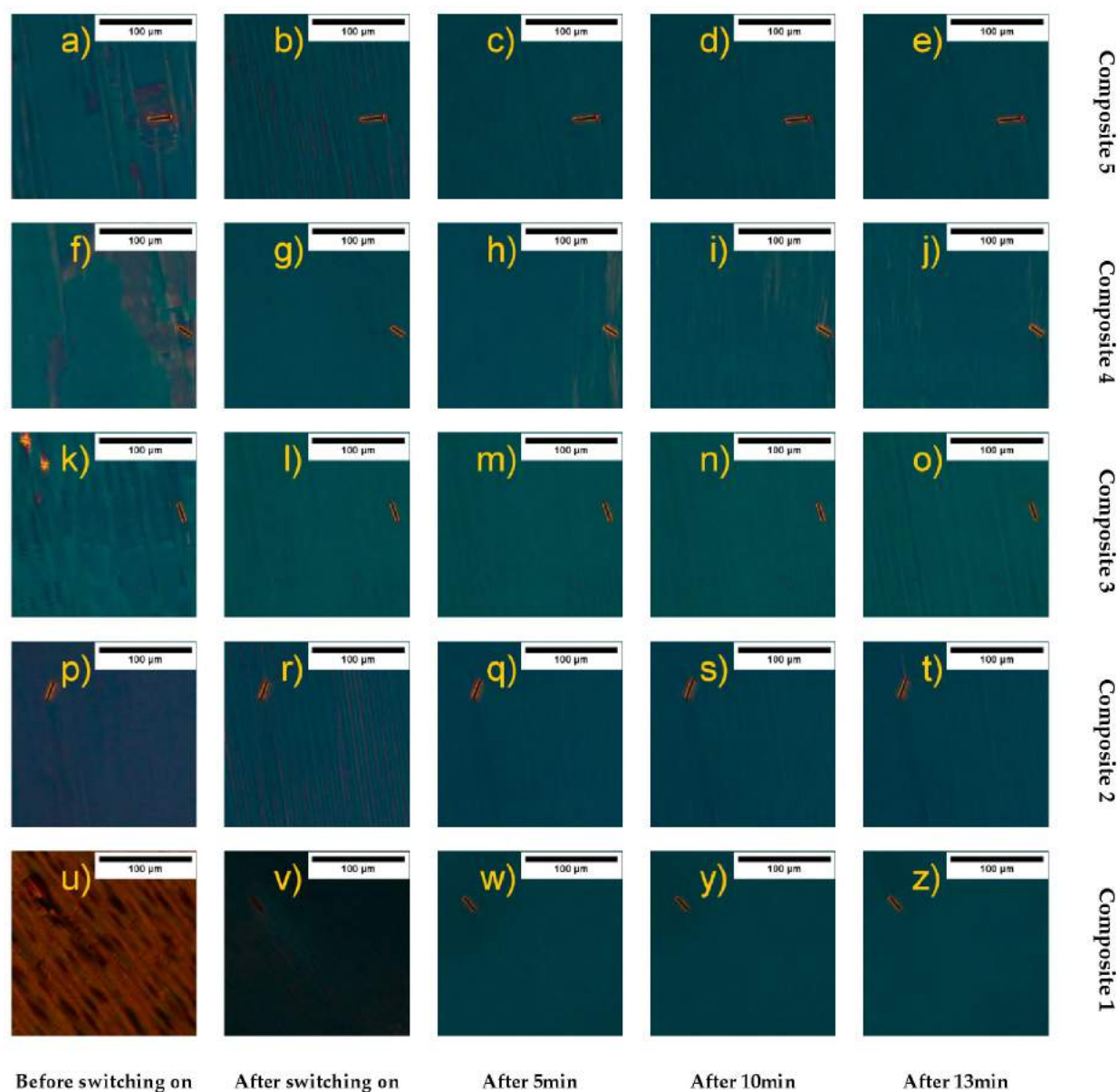


Figure S6. The alignment process of Composites 1–5 (20V_{pp}, 50 Hz, rectangular wave).

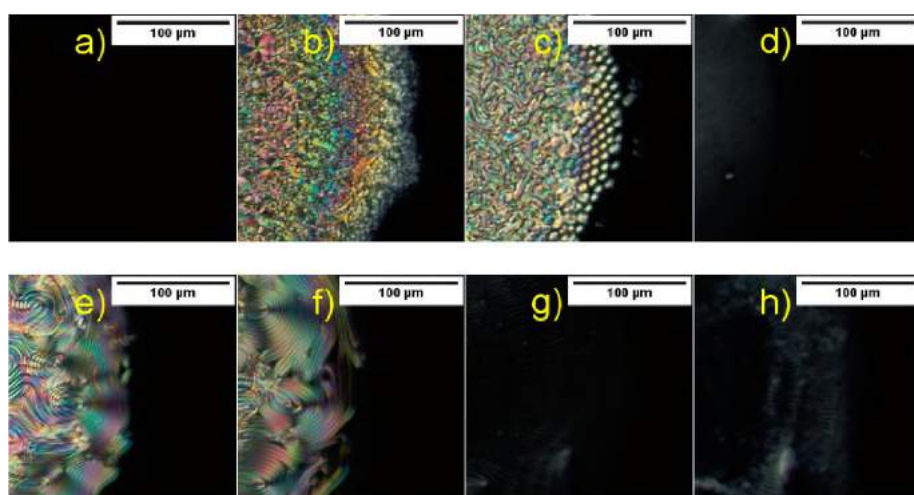


Figure S7. Textures registered for the free drop of Composite 1 (pure EHPDB) in: isotropic phase, 96.1 °C (a); cholesteric phase, 90.5 °C (b); TGBA* phase, 84.0 °C (c); SmA* phase, 82.5 °C (d); TGBC* phase, 80.0 °C (e); and TGBC* phase, 79.50 °C (f); SmC* phase, 78.5 °C (g); SmC* phase, 60.0 °C (h).

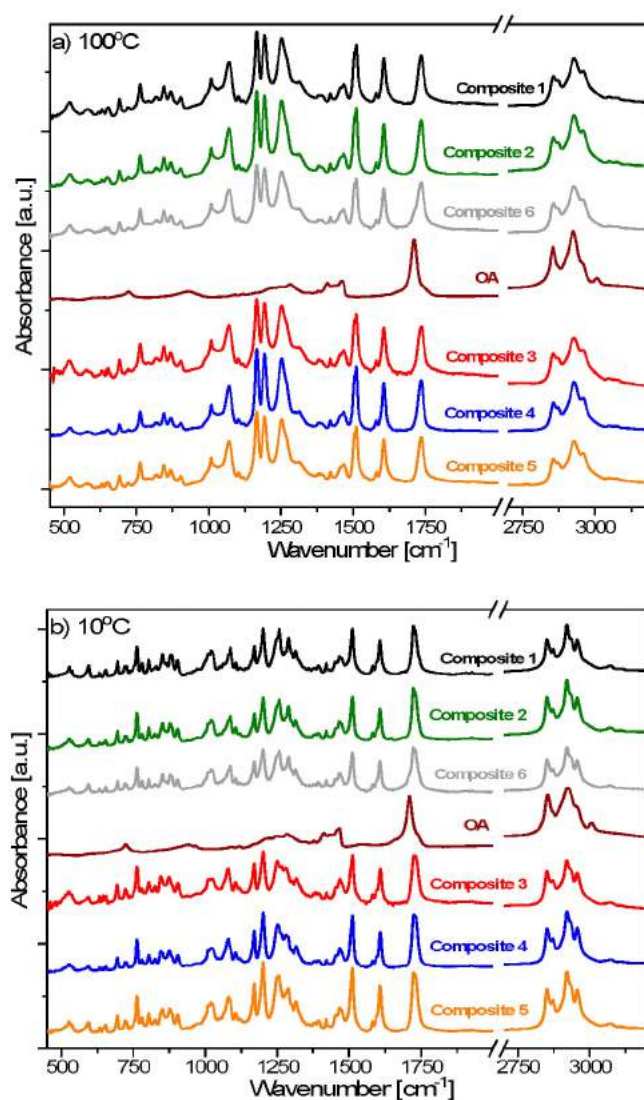


Figure 8. FTIR spectra of Composite 1–6 and oleic acid obtained at 100 °C (a) and 10 °C, after the heating–cooling cycle (b).

The comparison of the spectra of Composites 1–6 obtained after heating to 100°C, thus in the isotropic phase, is presented in Figure S8a. Additionally, the spectrum of oleic acid is shown at this temperature for comparison. The spectra of all Composites 1–6 obviously change upon heating but again there are no differences between them. The broadening of the band connected to vibration of carbonyl group in the spectrum of the composite with oleic acid is still visible. In turn, in Figure S8b the spectra obtained for all Composites 1–6 and pure oleic acid at 10 °C (after heating–cooling cycle) are shown. They are comparable to the ones obtained for the samples without thermal history and being in the ordered crystalline phase (Figure 16). Some discrepancies between the spectra obtained at 10 °C can be noticed in the spectral ranges of: 835–893, 1050–1100 and 1220–1340 cm^{-1} . This may be due to the fact that the transition from the liquid crystal to ordered crystalline phase does not occur in its entirety.



Article

Modifications of EHPDB Physical Properties through Doping with Fe₂O₃ Nanoparticles (Part II)

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Abstract: The aim of our study was to analyze the influence of various concentrations of γ -Fe₂O₃ nanoparticles on the physical properties of the liquid crystalline ferroelectric SmC* phase, as well as to check the effect of introducing nanoparticles in the LC matrix on their properties in the prepared five nanocomposites. UV-vis spectroscopy showed that the admixture reduced the absorption of nanocomposites in the UV range, additional absorption bands appeared, and all nanocomposites were transparent in the range of 500–850 nm. The molecular dynamics in particular phases of the nanocomposites were investigated by the dielectric spectroscopy method, and it was found that nanoparticles caused a significant increase in the dielectric constant at low frequencies, a strong modification of the dielectric processes in the SmC* phase, and the emergence of new relaxation processes for the highest dopant concentrations. SQUID magnetometry allowed us to determine the magnetic nature of the nanoparticles used, and to show that the blocked state of nanoparticles was preserved in nanocomposites (hysteresis loops were also registered in the ferroelectric SmC* phase). The dependence of the coercive field on the admixture concentration and the widening of the hysteresis loop in nanocomposites in relation to pure nanoparticles were also found. In turn, the FT-MIR spectroscopy method was used to check the influence of the impurity concentration on the formation/disappearance or modification of the absorption bands, and the modification of both the FWHM and the maximum positions for the four selected vibrations in the MIR range, as well as the discontinuous behavior of these parameters at the phase transitions, were found.

Keywords: ferroelectric liquid crystal; γ -Fe₂O₃ nanoparticles; light absorption; dielectric relaxation; magnetization; metal-organic nanocomposite



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1. Introduction

Hybrid materials are of great interest in the modern world because they can simultaneously exhibit many interesting properties. Typically, hybrid materials are materials that result from the combination of inorganic and organic chemical objects. In the soft matter field, hybrid materials can be created based on the combination of, e.g., a liquid crystal (compound or binary, three or more component mixture) and nanomaterial (nanoparticles, nanotubes, quantum dots, or nanorods). The huge variety of both liquid crystal materials and nanomaterials allows the creation of a number of hybrid materials with interesting properties. However, liquid crystals have been known since 1888, and only recent nanotechnology development has opened up new research opportunities. Generally, the synthesis of liquid crystals from a chemical point of view is very complex, multistep, costly, and time-consuming, even within one homologue series, and the parameters of synthesized materials are usually not adjusted to a specific application. Thus, in order to tune the parameters (phase transition temperatures, spontaneous polarization, threshold voltage,

switching time, molecular tilt angle, extent of light transmission, light absorption range, dielectric permittivity, impedance and conductivity, layer roughness, stiffness, etc.), scientists modify the molecular structure. Such modifications cover, for example: adding more aromatic parts to the rigid core, increasing the number of methylene groups, fluorination of the side chain and/or aromatic parts, and introduction of heteroatoms or polymerization reactions in order to obtain polymer dispersed liquid crystals (PDLCs) [1–10].

It turns out that many interesting parameters of liquid crystalline materials can be modified by doping with nanomaterials. This path is quite simple, because by changing the concentration of the nanomaterial, it is possible to obtain modified properties of the final nanocomposite, and at the same time, such a hybrid material combines the features of both constituent materials. Additionally, nanomaterials are easily available on the market, and their low cost favors this method. Despite many advantages, nanocomposites based on liquid crystals are still not very popular, and so far, most of the published articles have focused on nanocomposites based on nematics. Huang et al. observed an increase in photoluminescence for the concentration of Ag nanoparticles (ca. 88 nm) up to 1 wt %, then its decrease (up to 4 wt %) in the nanocomposite based on the liquid crystal 5CB, which was explained by the surface plasmon resonance for nanoparticles [11]. Magnetic needles were used to enriched nematic liquid crystal, and as a result, the planar alignment from the homeotropic one was obtained in low magnetic fields (10–30 G) [12]. Zadoina et al. showed that after doping liquid crystal polymer by nanomagnets (cobalt nanorods, ca. 5.5 nm, length 83 nm, 4 wt %) the liquid crystal order was preserved, T_g decreased, and the magnetic properties and the nanorods' orientation were improved [13]. In turn, the decrease in the threshold voltage was observed after doping 6OCB by Fe nanoparticles (ca. 35–45 nm, 0.25 wt %) [14], as well as after addition of BaTiO₃ nanoparticles (ca. 50 nm, 0.5 wt %) into a polymer-dispersed liquid crystal based on E7 [15]. Interestingly, Hasegawa et al., after doping nematic liquid crystal by BaTiO₃ nanoparticles (ca. 80 nm, 0.25 wt %), decreased the T_{NI} transition temperature without modification of the threshold voltage [16]. It turned out that after addition of γ -Fe₂O₃ nanoparticles (needles, diameter ca. 25 nm, length 175 nm, 0.05 wt %, decorated by various surfactants) into 5CB liquid crystal, the molecular structure of the surfactant affected the nematic order, as well as nanoparticles' aggregation process [17]. By doping nematic liquid crystal EBBA with metallic multiwalled carbon nanotubes (MWCNT, diameter ca. 12–20 nm, length several micrometers, up to 1.0 wt %), a conductive network was formed in an organic matrix, and for a nanocomposite with 0.15 wt % MWCNT, the electric conductivity increased by about two orders of magnitude [18]. Shriyan et al. also used MWCNT as dopant into PDLC, and observed decreasing of the resistivity and increasing of the capacitance, especially for high admixture concentrations; while for small concentrations, the rise and fall times were improved, which was explained by smaller liquid crystal droplets in the polymer matrix [19]. In turn, by doping 8OCB with Fe₂O₃ nanoparticles (ca. 6–12 nm, 0.5 and 1.0 wt %), better alignment of molecules, fewer defects, an increase in dielectric dispersion and in V_{th} , as well as a decrease in the dielectric anisotropy, was obtained. The shift of the relaxation process towards a lower frequency was explained by the different surface potentials and interactions between LC molecules and nanoparticles [20].

Despite many promising features of smectic liquid crystals, in the literature there are only a few articles about doping them. This is what motivated our research. The most interesting of the smectic phases is the ferroelectric SmC* phase built of chiral molecules. In this phase, the organic molecules are arranged in layers and tilted (in a different direction at each layer, forming a helix of the resultant dipole moments). It is known that the spontaneous polarization appears under the external electric/magnetic field in this phase [21]. The strong-enough external field causes the reorientation of the dipole moments along the field lines, and thus unwinding of the helix (all dipoles are aligned with the external field, and the spontaneous polarization reaches its maximum) [22]. The use of an alternate electric field changes the orientation of the macroscopic polarization, in what is known as electro-optic switching (one of the most important utility parameters of these

materials) [23,24]. If there is more than one polar group in the structure of an organic molecule and their distance from the chiral center is small, then the dipole moment of such a molecule is greater, and therefore the spontaneous polarization is higher. Three years after the discovery of ferroelectric liquid crystal (FLC), the existence of a periodic structure (helix) in the SmC^* phase was confirmed by Yoshino et al., who observed a periodic pattern in polarized light, and a change in the intensity of light passing through a thin FLC layer as the applied voltage changed. For the unwound helix, a decrease in light scattering and thus an increase in its transmission was observed [25]. Prakash et al. showed that spontaneous polarization and rotational viscosity increased, while dielectric loss factor was an order of magnitude larger after doping the ferroelectric liquid crystal LAHS18 with MWCNTs (ca. 30–50 nm, length > 0.3 μm , 0.1 wt %). This behavior was explained by the increase in electric conductivity and the formation of a conducting network through nanotubes. Interestingly, a nonzero P_s was observed in the SmA^* phase, which was attributed to the possible existence of a short-range orientational order, caused by, inter alia, surface anchoring organic molecules to MWCNTs and ionic impurities in the doped sample [26]. Two ferroelectric liquid crystals (Felix 17/000, Felix 16/100) were doped with quantum dots of $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{ZnS}$ (ca. 8.7 nm, 1.0 wt %) and CdSe (ca. 3.5 nm, 1.0 wt %), and it was found that the tilt angle was smaller by about 8° (as an attraction effect between quantum dots surrounding the molecules), and P_s decreased (as the secondary order parameter coupling with the tilt angle) for the doped Felix 17/000. Moreover, a new relaxation process around 10^5 Hz was revealed for the doped Felix 16/100 [27]. Das et al., after addition of Au nanoparticles (ca. 6–8 nm) to nonchiral liquid crystal with an SmC phase, observed a decrease in all phase transition temperatures, a strong increase in light absorption for two bands below 300 nm, and a 4-fold increase in electric conductivity in the crystal phase [28]. Dey et al. used the antiferroelectric liquid crystal DM1 as a host for MWCNTs (ca. 8–15 nm, length 0.5–2.0 μm , 0.12 wt %) and obtained better alignment (more homogeneous textures), while the primary order parameter was not disturbed and the rotational viscosity and switching time decreased by about 50%, and the electric conductivity decreased (as a result of trapping ions). Interestingly, the PL (in-phase fluctuations of the director's phase in adjacent layers) relaxation mode was not observed, while the relaxation frequency of the PH (anti-phase fluctuations of the director's phase in adjacent layers) mode drastically decreased in the SmC^*_A of the doped sample. Moreover, the Goldstone mode in the antiferroelectric SmC^*_A was hereditary from the SmC^* phase, and a new relaxation process was revealed after suppression of the Goldstone mode, but only for the doped sample [29]. Chaudhary et al. doped an FLC W206E mixture with ZnO nanoparticles (ca. 10 nm, 0.1–1.0 wt %) and observed the memory effect (explained by charge transfer from the organic molecule to the ZnO nanoparticle) and more centers to the charge transfer for higher concentrations [30]. In turn, after doping the ferroelectric mixture ZLI-4851 with Ni nanoparticles (ca. 20 and 40 nm, 0.5 wt %) an increase in the spontaneous polarization and a shortening of the switching times of about 200 μs were observed [31]. In turn, the influence of carbon nanomaterials on the nematic and smectic liquid crystals can be found in review papers [32,33]. Joshi et al. showed that Al_2O_3 (ca. 4–7, 20–30, 30–50 nm) admixed with KCFLC 7S and 10S caused the adsorption of impurities to their surfaces [34]. Such adsorption of impurities to the nanoparticle surface was also observed by Chandran et al. when doping KCFLC 10S with ZrO_2 nanoparticles (ca. 30 nm, 4 wt %) [35]. Singh et al. doped Felix 16/100 with a $\text{ZnO}_{1-x}\text{S}_x$ nanomaterial (ca. 10–15 nm, 0.25, 0.50, 1.0 and 1.5 wt %), and explained that the observed influence of nanoparticles on the dielectric increment and relaxation frequency was related to the formation (by agglomerates) of zigzag defects or a chevron structure [36]. Singh et al. reported that one of the effects of doping CdSe quantum dots (QDs, ca. 3.5 nm, 0.5, 1.0 and 2.0 wt %) onto Felix 16/100 was the emergence of a new relaxation mode (attributed to dipolar interactions between FLC molecules and quantum dots) depending on their concentration, as well as the modification of the GM relaxation frequency [37]. In turn, the new relaxation process observed by doping Felix 17/100 with ZnS QDs was attributed to the flexoelectric tilt fluctuations in the FLC next to QDs [38].

Finally, it should be noted that the excess of nanoparticles in the created nanocomposites may destroy or strongly disturb the liquid crystal order, which in turn may lead to the uselessness of the created hybrid materials.

The aim of our work was to show how $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles affected the physical properties of the EHPDB liquid crystal. The created nanocomposites consisted of an organic matrix (liquid crystal EHPDB) exhibiting ferroelectric properties, and an inorganic guest ($\gamma\text{-Fe}_2\text{O}_3$ nanoparticles) exhibiting a paramagnetic and blocked state. In our previous paper, we presented in detail the synthesis of studied nanocomposites and results of diffraction, microscopic, calorimetric, electric and FT-MIR spectroscopy methods, and showed that modification of the electric parameters of the EHPDB liquid crystal by nanoparticles was significant; however, to explain this further, research is needed [39]. Therefore, in this paper we decided to examine how interactions between components of the composites were revealed in their properties by using light absorption in the UV-vis and MIR (FT-MIR) range, frequency domain dielectric spectroscopy (FDDS), and magnetic superconducting quantum interference device magnetometry (SQUID) methods. Influence of the temperature and nanoparticle concentration, as well as oleic acid (used to nanoparticles decoration), on the intensities of the chosen absorption bands were carefully analyzed. The modification of the specific electric conductivity by nanoparticles and their influence on the parameters of relaxation processes ($\Delta\epsilon$, ν_r , τ_r , α , σ_{DC}) were also investigated. In turn, SQUID was used to determine the blocking temperature, T_B , of nanoparticles based on ZFC (zero field cooled) and FC (field cooled) curves, and to examine the influence of nanoparticles on the magnetization, hysteresis loops, the coercive field, and the remanence. A detailed analysis of the absorption bands in the middle infrared region was also performed. We believe that by easily modifying the parameters of the SmC* phase with small nanoparticle concentrations, such nanocomposites will find application in industry or medicine, where nematic materials currently dominate [40], or will be a good alternative to orthoconic liquid crystals by obtaining good dark states for a smaller voltage threshold [41].

2. Results and Discussion

2.1. Samples Studied

All created nanocomposites were metal–organic hybrid systems with ferroelectric liquid crystal EHPDB as the matrix (host) and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles as an admixture (guest). Properties of six nanocomposites denoted as Composites 1–6 (Composite 1 (0.0 wt %), Composite 2 (0.3 wt %), Composite 3 (0.5 wt %), Composite 4 (0.7 wt %), Composite 5 (0.9 wt %) and Composite 6 (0.3 wt % + oleic acid)), as well as pure nanoparticles of $\gamma\text{-Fe}_2\text{O}_3$ (Sample 1) and nanoparticles decorated with oleic acid (Sample 2), were studied. A detailed description of the sample preparation can be found in our recent paper [39], while phase sequence during cooling of the prepared composites was as follows (phase transition temperatures in parentheses are in Celsius):

Composite 1: Is(96.29)P(95.11)N*(83.19)TGBA*(~80.06)SmA*(~79.00)SmC*(58.07)Cr₁

Composite 2: Is(91.24)P(?)N*(79.42)TGBA*(?)SmA*(72.20)SmC*(55.79)Cr₁

Composite 3: Is(89.10)N*(79.85)TGBA*(?)SmA*(67.70)SmC*(53.48)Cr₁

Composite 4: Is(89.63)P(?)N*(78.51)TGBA*(?)SmA*(69.50)SmC*(54.61)Cr₁

Composite 5: Is(91.91)N*(80.09)TGBA*(?)SmA*(69.80)SmC*(55.56)Cr₁

Composite 6: Is(73.21)X(72.09)N*(62.64)SmA*(52.36)SmC*(50.76)Cr₁(39.84)Cr₂

A question mark in parentheses means that the transition temperature could not be determined (or was subject to a very large error), while P denotes the blue phase.

2.2. Ultraviolet-Visible Spectroscopy (UV-Vis) Results

2.2.1. UV-Vis Results for Samples 1–2

Both Sample 1 and Sample 2 absorbed in the 200–700 nm range (brown color of maghemite $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles [42]) with clear absorption bands around 220, 370, 500, and 650 nm (Figure 1a,c). Intensity of absorption was much lower for Sample 2 than for Sample 1 (between 250 nm and ca. 600 nm). In our opinion, this could be due to the fact that

Sample 2 contained fewer $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, which in addition were immersed in oleic acid. It is possible that oleic acid, in measuring the wavelength range, was transparent, so it did not absorb. It was noteworthy that absorption of indicated wavelengths (e.g., 225, 240, and 290 nm, marked by arrows in Figure 1a) behaved the same for both samples (oscillated), and did not change significantly upon cooling from 120 °C down to 0 °C (Figure 1b,d), although the absorbance at the wavelengths under consideration was much lower after the addition of oleic acid. Interestingly, at 225 nm, Sample 1 (pure nanoparticles), as well as Sample 2 (with oleic acid), absorbed almost all the incident radiation, while the absorption band width with a maximum of around 220 nm was narrower for Sample 2. In summary, the oleic acid significantly modified the optical properties of the nanoparticles used.

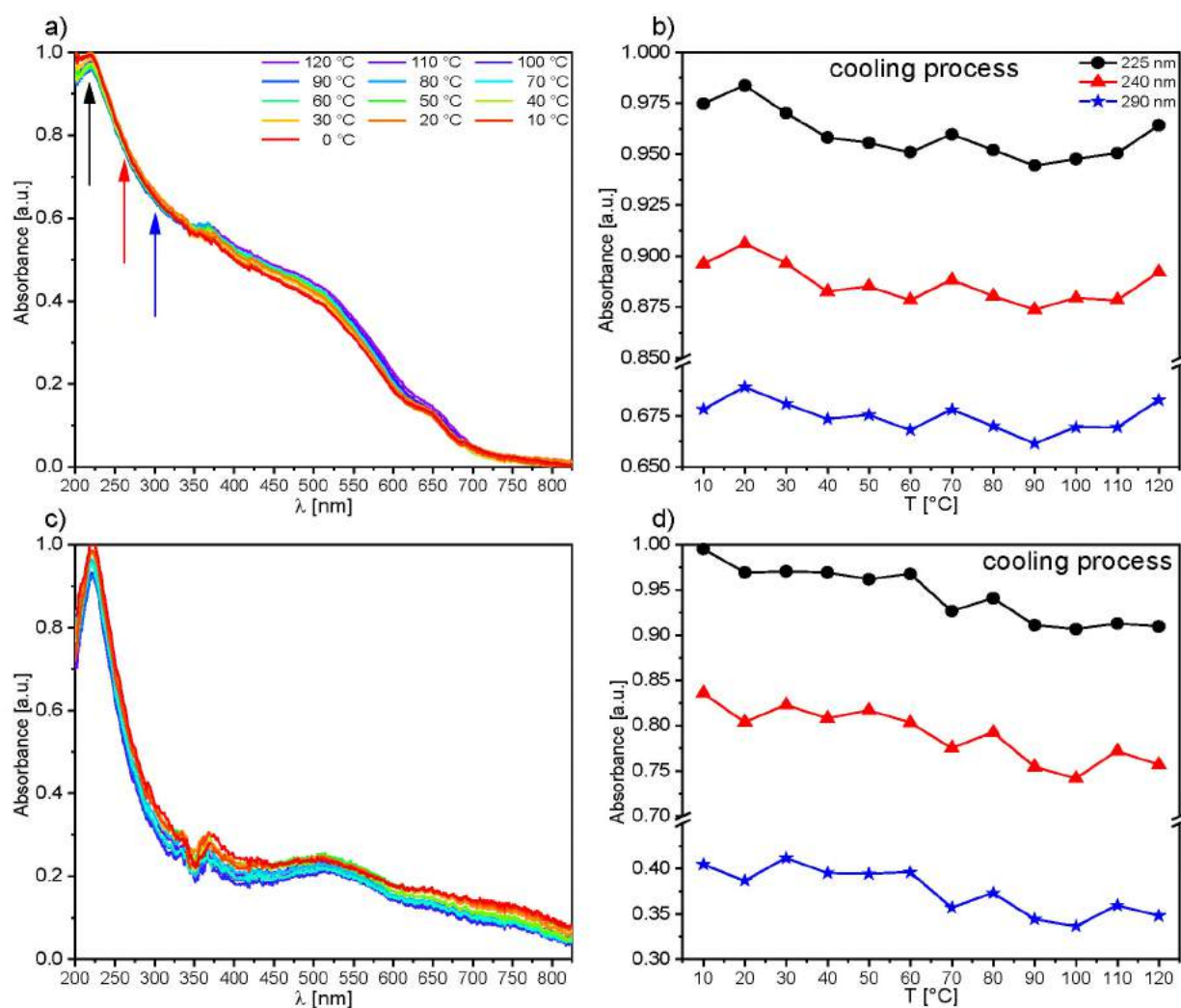


Figure 1. The solid state UV-vis absorption spectra for Sample 1 (a) and Sample 2 (c) in the 200–850 nm range, as well as the temperature influence on the chosen wavelengths for Sample 1 (b) and Sample 2 (d). The legend in graph (a) is the same for (c), while that in graph (b) is the same for graph (d).

2.2.2. UV-Vis Results for Composite 1

Temperature's influence on the absorbance of a pure ferroelectric liquid crystal EHPDB (Composite 1) was investigated during heating and subsequent cooling (23 °C–120 °C–23 °C). As is seen in Figure 2a, one absorption band in the UV region with a maximum around 225 nm was well visible for Composite 1 at room temperature. Figure S1 presents the absorption spectra registered for several chosen temperatures during heating of Composite 1, and for better clarity, the temperature dependence of the first derivative of the absorbance for selected wavelengths. After heating above 70 °C (see Figure 2b and Figure S1), for

wavelengths of 225 nm, 240 nm, and 290 nm, the absorbance slightly decreased, which was related to the phase transition of crystal to liquid crystalline state, and was in good agreement with the DSC results [39]. Upon further heating, the absorbance increased for wavelengths of 225 nm and 240 nm exponentially up to about 95 °C, above which the absorbance stabilized up to at least 120 °C (Figure 2b). This behavior was related to the phase transition from the liquid crystalline state to an isotropic liquid, and was also in agreement with the DSC results [39]. Interestingly, the absorbance for the wavelength of 290 nm behaved quite differently during further heating; from the phase transition to the SmC* phase, it monotonically decreases. Upon subsequent cooling, the spectra remain unchanged down to 95 °C, while below this value the absorbance for 225 nm and 240 nm decreased with decreasing temperature, down to ca. 50 °C. In turn, for the wavelength of 290 nm, there was an increase in the absorbance up to the crystal phase. A clear jump at the phase transition to crystal phase was well visible in the absorbance for all mentioned wavelengths. As is seen in Figure 2a, the sample became a nonabsorbent material from ca. 425 nm, and only at ca. 575 nm and 750 nm did the absorbance begin to slight increase, but it was still at a level of 5%.

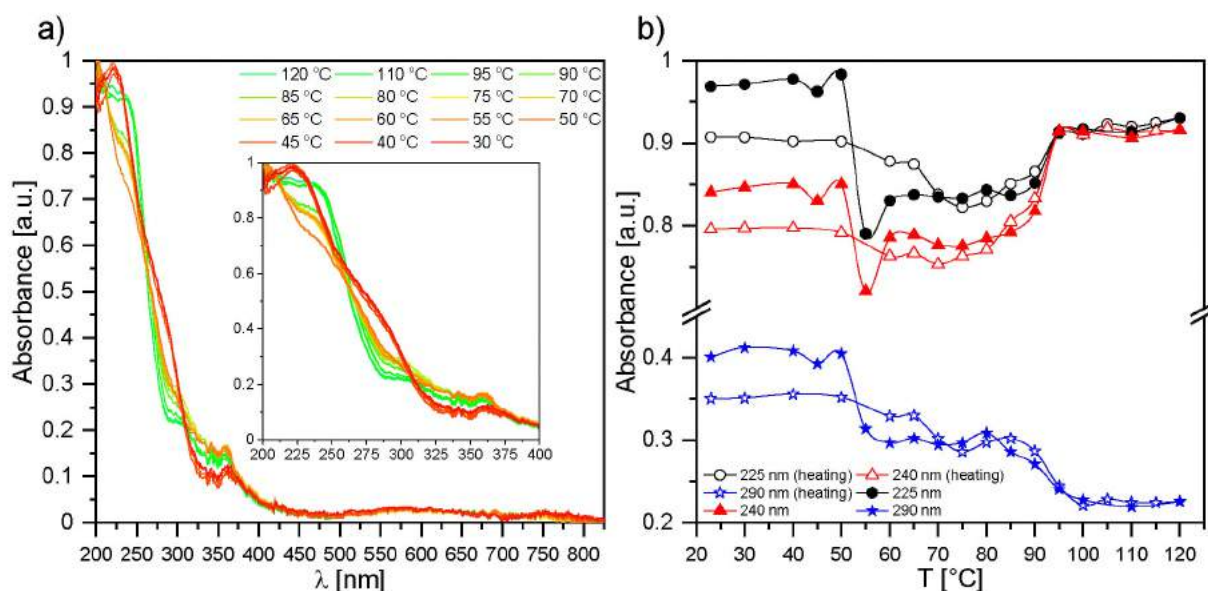


Figure 2. Solid state UV-vis absorption spectra of Composite 1 (pure EHPDB) at several chosen temperatures in the 200–850 nm range during cooling (a), and temperature dependence of the absorbance at around 225, 240 and 290 nm (b). The inset in graph (a) presents an enlarged region of 200–400 nm.

2.2.3. UV-Vis Results for Composites 2–5

The main difference in the spectra of Composites 2–5 (Figure S2) and pure EHPDB—Composite 1 (Figure 2a) was the presence of additional bands (in the range of 350–600 nm) with small intensities corresponding to the absorption of pure nanoparticles (Figure 1a). The temperature evolutions of absorption spectra for Composites 2–5 (see Figures 3, 4 and S3) were very similar to that of pure EHPDB. The monotonous decrease in absorbance in the visible region upon heating can be explained by the reorientation of the nanoparticles and liquid crystal molecules at the phase transition from solid to liquid crystalline phase. After this phase transition, the absorbance for the wavelengths 225 nm and 240 nm slightly increased and stabilized at the temperature of the phase transition to the isotropic liquid. Such behavior was observed for all nanocomposites. Interestingly, for the 290 nm wavelength, the situation was completely different for all nanocomposites; there was a continuous decrease in the absorbance from the crystal–liquid crystalline phase transition, with a distinct jump at the liquid crystal–isotropic phase transition, and stabilization above this temperature. On the other hand, during cooling just below the isotropic liquid–cholesteric

phase transition, the absorbance for the wavelengths 225 nm and 240 nm slightly decreased and reached a plateau throughout the SmC* phase, and at the transition to the crystal phase, a jump was clear visible. However, a decrease in absorbance only for Composite 3, while an almost 50% increase in absorbance for Composite 5, was visible for these wavelengths. In the case of the wavelength at 290 nm, a plateau within the SmC* phase and an increase in the absorbance during crystallization were registered. It is worth noting that the absorbances at 225 nm, 240 nm, and 290 nm were much lower (even by about 30%) for Composite 5 both during heating and cooling as compared to the other nanocomposites (particularly in the isotropic liquid phase and to a smaller extent in the SmC* phase).

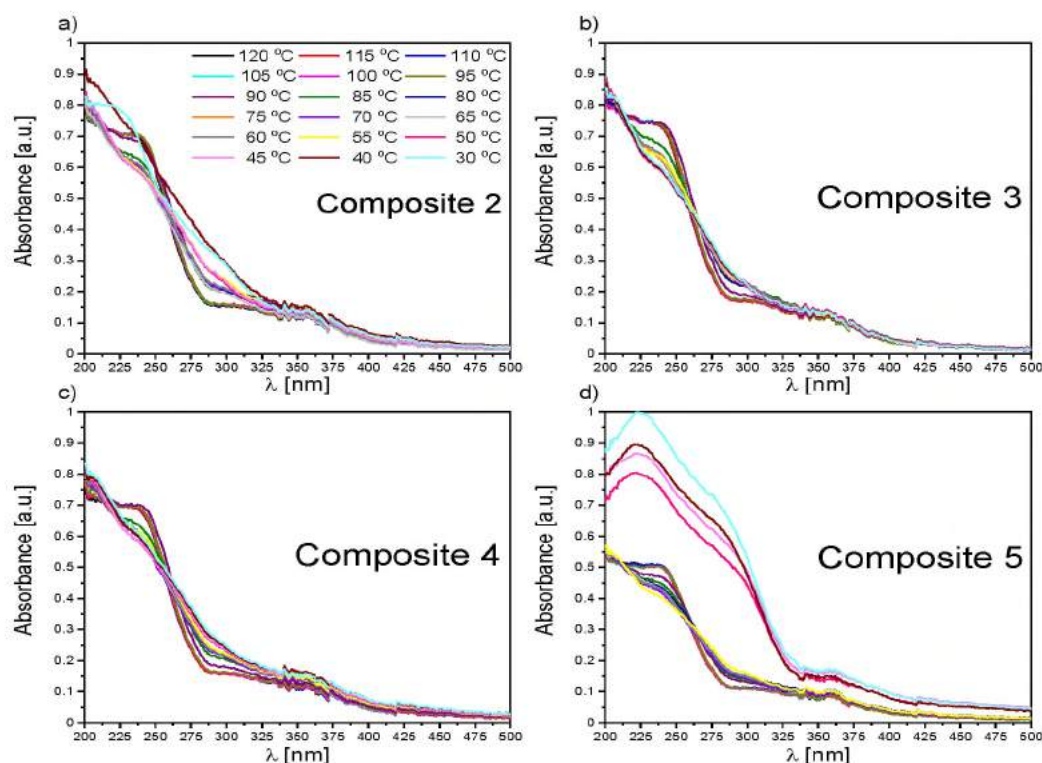


Figure 3. Solid state UV-vis absorption spectra of Composite 2 (a), Composite 3 (b), Composite 4 (c), and Composite 5 (d) at several chosen temperatures during cooling. The legend in graph (a) is the same for all graphs.

Both the undoped sample (Composite 1) and doped samples (Composites 2–5) showed no absorption of incident light in the 500–850 nm range (the absorbance was below 5%; however, this spectral range had a low signal-to-noise ratio, regardless of temperature), which means that Composites 1–5 were transparent in this range. Figure 3 presents the spectral range of 200–500 nm and a high absorbance of the created nanocomposites (Composites 2–5) in the UV region, indicating almost complete absorption of incident radiation. However, a decrease in absorbance with an increase in the γ -Fe₂O₃ admixture concentration was visible. The nanoparticles in the organic matrix most likely acted as a scattering agent in the UV region. As is seen in Figure S3, the temperatures at which the absorbance changed corresponded to the phase transition temperatures obtained by the DSC method [39].

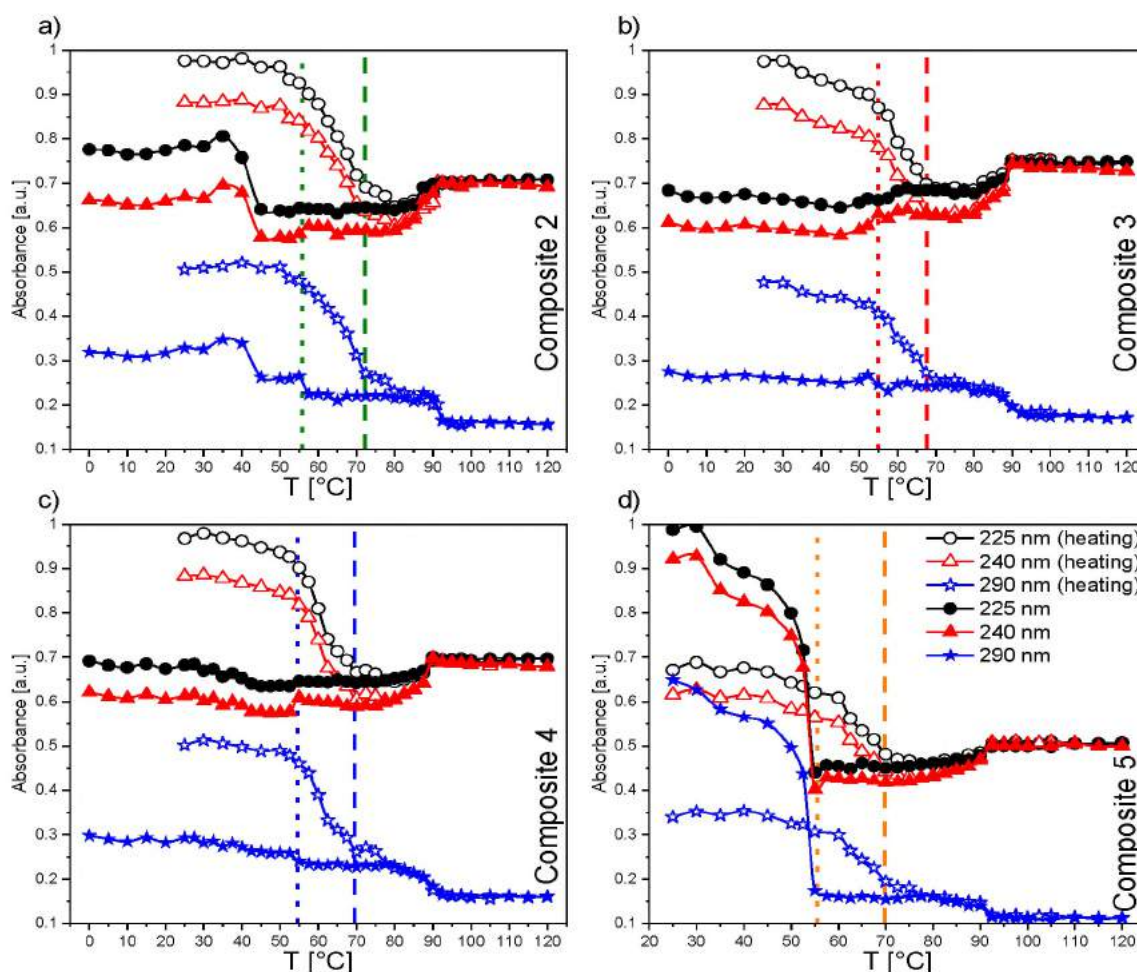


Figure 4. Influence of heating and cooling on the absorbance at 225, 240, and 290 nm for Composite 2 (a), Composite 3 (b), Composite 4 (c), and Composite 5 (d). The legend in graph (d) is the same for all graphs. The vertical dashed and dotted lines represent the SmA*–SmC* and SmC*–Cr₁ phase transition temperatures (during cooling), respectively.

Figure 5 presents the spectra recorded during cooling in the N* and SmC* phases for Composites 1–5. In both the N* and SmC* phases, the highest absorbance was observed for Composite 1, and the lowest for Composite 5. Only for Composite 3 was an increase in absorbance in the SmC* phase compared to the N* phase clearly visible, while similar absorbance in these phases was shown for Composites 2 and 4. For Composite 5, a decrease in absorbance by as much as 45% relative to the pure matrix was observed, and this difference for each temperature became smaller for longer wavelengths. To the best of our knowledge, no γ -Fe₂O₃ nanoparticles showed plasmon resonance, which could explain the changes in absorbance for Composites 2–5 relative to pure EHPDB. Except for Composite 2, there was a well-observed trend: a decrease in the absorbance with an increase in the nanoparticle concentration. Interestingly, the difference in absorbance for Composites 4 and 5 even reached about 20%. Such observations led to the conclusion that the nanoparticles acted as scattering centers for the incident light in the EHPDB matrix. It seemed that single nanoparticles and small aggregates in the matrix reacted differently to the incident radiation. The highest nanoparticle concentration and the presence of aggregates (Composite 5) were responsible for the scattering of the incident light to the highest extent. On the other hand, the qualitative nature of the spectra recorded in the N* phase was very similar to those recorded in the SmC* phase, except for Composite 2.

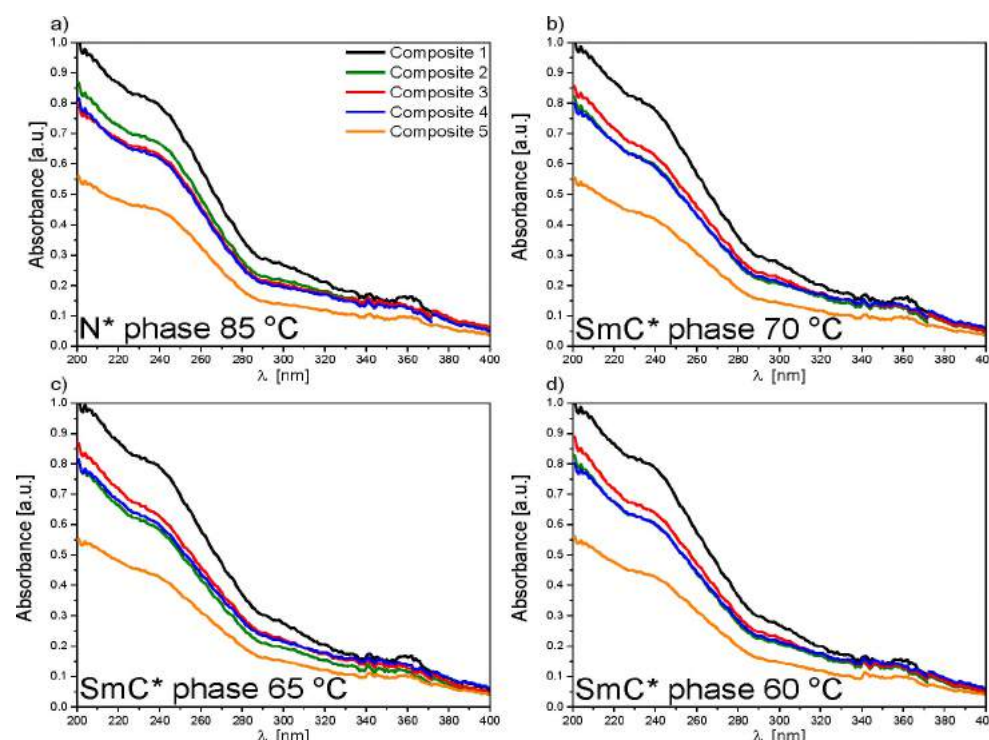


Figure 5. The UV-vis absorption spectra (200–400 nm) for all studied nanocomposites registered during cooling in the N* phase at 85.0 °C (a) and the SmC* phase at 70.0 °C (b), 65.0 °C (c), and 60.0 °C (d). The legend in graph (a) is the same for all graphs.

2.2.4. UV-Vis Results for Composite 6

The temperature evolution of the UV-vis absorption spectrum of Composite 6 (Figure 6a) was not significantly different from that of Composites 2–5. The differences that were worth paying attention to were higher absorbance (especially in the UV region during cooling) and lower during heating (Figure S4a) in comparison to Composite 2 (the same concentration of γ -Fe₂O₃, but without oleic acid). Similarly to other nanocomposites, Composite 6 was transparent from about 400 nm, and no plateau was observed for 225 nm and 240 nm in the isotropic liquid. A slight decrease in the melting point in relation to Composite 2 (Figure S4) was visible.

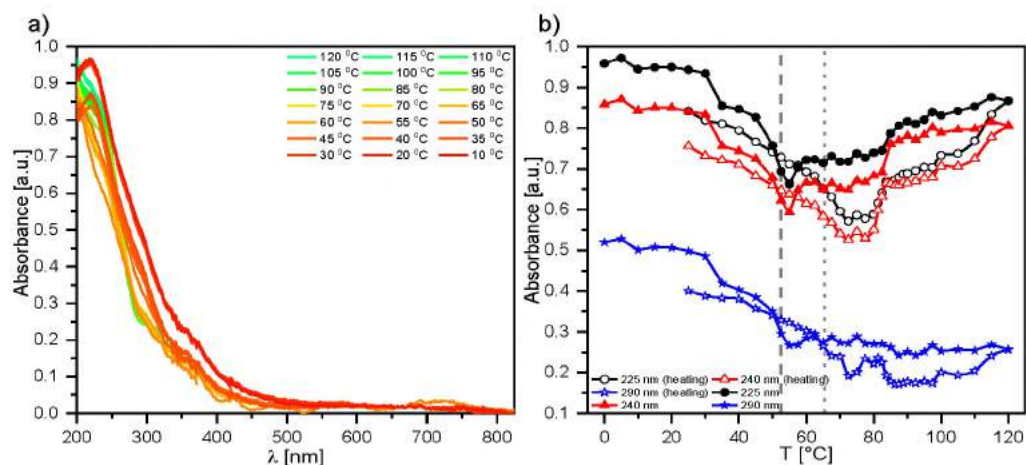


Figure 6. Solid state UV-vis absorption spectra of Composite 6 (γ -Fe₂O₃, 0.3 wt % + oleic acid) at several chosen temperatures in the 200–850 nm range (a), and the influence of heating and cooling on the absorbance at 225, 240, and 290 nm (b). The vertical dashed and dotted lines represent the SmA*–SmC* and N*–SmA* phase transition temperatures (during cooling), respectively.

2.2.5. Theoretical Calculations of UV-Vis and Energy Level Diagram

The structural parameters and energy level diagrams of an organic liquid crystal can be strongly influenced by the electronic nature and position of chemical groups, as well as the relative position of the molecules in the solid state [43]. Geometrical optimization of an EHPDB molecule was performed in the gas phase using the B3LYP method for the basis set cc-pVDZ embedded in the Gaussian16 software (Figure S5 and Table S1) [44,45]. Consequently, the nonplanar character of this molecule was confirmed, with a dihedral angle of 46° between the aromatic rings of parts 'B' and 'C' (Figure S5). Moreover, the energy level diagram for EHPDB was determined, resulting in a HOMO (the highest occupied molecular orbital)-LUMO (the lowest unoccupied molecular orbital) gap equal to 4.67192 eV, which indicated the very high kinetic stability and low chemical reactivity of EHPDB, as well as a high value of global chemical hardness ($\eta = 2.33596$ eV) compared to other liquid crystals [43]. Additional time-dependent density functional theory (TD-DFT) calculations were performed for the lowest 100 electronic transitions, yielding the oscillator strength and corresponding molecular orbitals (Table S2). The analysis of these data confirmed that electronic transitions occurred exclusively in the UV region (Figure S5): ~ 300 nm (123:HOMO $\rightarrow$ 124:LUMO transition involving π -electron transfer from 'B' to 'C' part of EHPDB), ~ 255 nm (122:HOMO-1 $\rightarrow$ 124:LUMO and 123:HOMO $\rightarrow$ 125:LUMO + 1/126:LUMO + 2 transition involving the transfer of π -electrons within the 'C' part, and from the 'B' part to the 'B' or 'C' parts, respectively), ~ 215 nm (123:HOMO $\rightarrow$ 127:LUMO + 3 and 120:HOMO-3 $\rightarrow$ 124:LUMO and transition involving the transfer of π -electrons within the 'B' part, and from the 'B' to 'C' part, respectively), and ~ 190 nm (121:HOMO-2 $\rightarrow$ 126:LUMO + 2 and 120:HOMO-3 $\rightarrow$ 125:LUMO + 1 transition of π -electrons from the 'A' to 'C' part, and within the 'B' part). Moreover, the calculated spectrum was shifted to a higher energy by approximately 30 nm compared to the experimental spectra, due to the applied single-point DFT calculation method, which, despite omitting the periodicity of the structure in the liquid crystal phases, still accurately reflected the experimental spectra of Composites 1–6.

In order to determine the possible origin of the shift of the UV-vis absorption spectra of Composites 1–6 towards lower energies after cooling, a similar calculation for the second model ('planar' EHPDB molecule) with a dihedral angle close to 0° between the aromatic rings of the 'B' and 'C' parts was performed (Tables S3 and S4 and Figure S6). This approach showed that the decrease in the dihedral angle did not affect the electronic structure of the frontier molecular orbitals, but significantly decreased the HOMO-LUMO energy gap (4.22293 eV) [46]. Consequently, the calculated UV-vis spectrum for the 'planar' EHPDB molecule was shifted to higher wavelengths in the UV region. These results suggested a potential explanation for changes in the UV-vis spectra as a result of the mutual orientation of the aromatic rings within the liquid crystal molecule caused by phase transitions. In the crystalline phase, π -stacking between the aromatic rings and hydrogen bonds was expected to stabilize the planar structure. Next, during heating, thermal motions overcame weak interactions and led to an augment of the dihedral angle and the energy gap values, as well as a shift of the absorption spectrum towards lower energies. Finally, the cooling process led to the reverse behavior.

2.3. Frequency Domain Dielectric Spectroscopy (FDDS) Results

The analysis of the dielectric spectroscopy results was limited to the liquid crystalline and crystal phases, as they were the most interesting. Particular emphasis was placed on the temperature range of the ferroelectric SmC* phase to determine how the γ -Fe₂O₃ nanoparticle admixture affected the relaxation processes present in the LC matrix, and whether they extinguished them or whether new ones appeared. Because the range of the SmC* phase was very narrow, and it was impossible to obtain a uniformly planar orientation for Composite 6, the dielectric properties of this composite were not studied [39].

Starting with the first liquid crystalline phase during cooling, two relaxation processes were registered for Composites 2–5 in the N* phase. The mode with a very large dielectric

increment in the low frequency range was interpreted as the Maxwell–Wagner–Sillars (MWS) relaxation process; while in the higher frequency range, as the molecular s-process (reorientation around a short molecular axis). However, due to the limited measuring range (up to 10^6 Hz), the molecular process was partially observed only for Composites 2–5, although we reported in our previous paper on the molecular s-process for pure EHPDB in the range of 10^6 – 10^7 Hz [47]. The relaxation frequency of this molecular process for Composites 2–5 was lower than for Composite 1 (pure matrix), which meant that nanoparticles hindered reorientation around the short molecular axis. In the TGBA* and SmA* phases, apart from the low-frequency MWS process, the soft mode (SM) was registered for Composite 1 and Composites 3–5, while for Composite 2, it was not. Figure 7 presents the dielectric dispersion and absorption, the loss tangent ($\text{tg}\delta = \epsilon''/\epsilon'$), and the Cole–Cole plots for Composites 3–5 in the TGBA*/SmA* phase. It was seen that the MWS process was dominant in the low-frequency range; while at higher frequencies, the soft mode was visible (in the insets). As is known, the relaxation frequency for this process is temperature-dependent, especially in the vicinity of the SmA*–SmC* phase transition, where the V-shaped behavior is usually observed [48–50]. For Composites 3–5, the full V-shape behavior of the relaxation frequency was not visible (see Figure 8b), as the SM disappeared completely after phase transition to the SmC* phase.

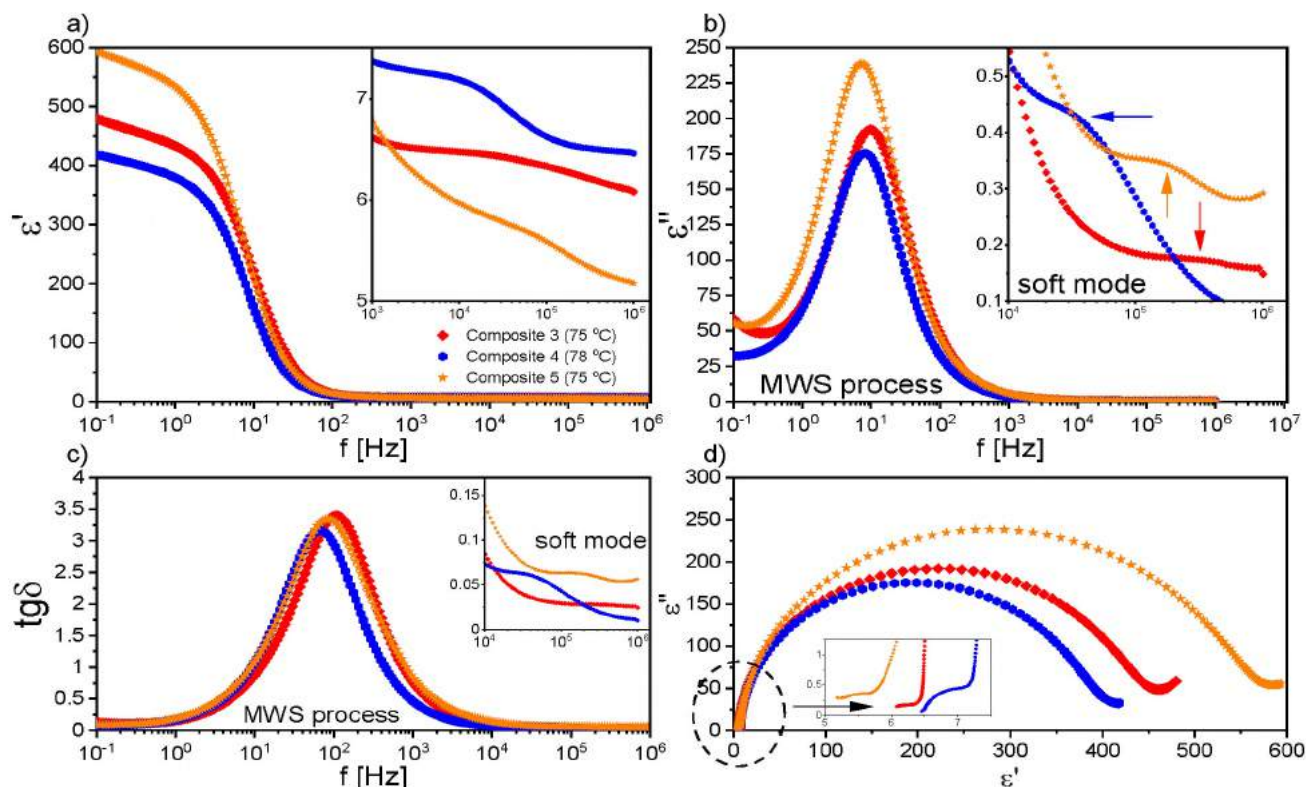


Figure 7. Dielectric dispersion (a) and absorption (b), loss tangent versus frequency (c), and Cole–Cole plot (d) for Composites 3–5 in the TGBA*/SmA* phase. Insets present the high-frequency range. The legend in graph (a) is the same for all graphs.

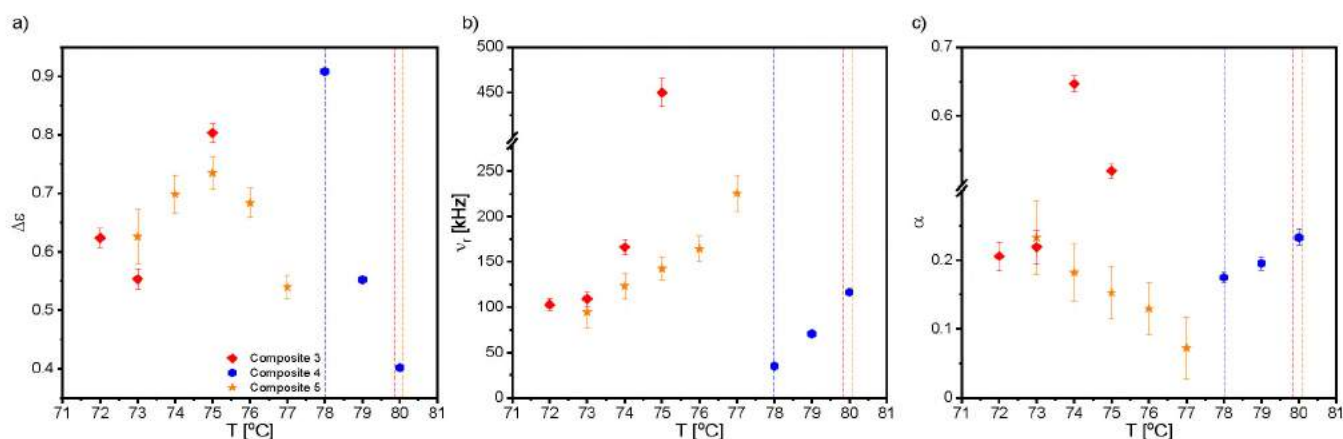


Figure 8. Temperature dependence of the dielectric increment, $\Delta\epsilon$ (a); the relaxation frequency, ν_r (b); and the α distribution parameter of the relaxation time (c) of the SM for Composites 3–5. The legend in graph (a) is the same for all graphs. The vertical dashed lines represent the N*–TGBA*–SmA* phase transition temperature (during cooling), respectively.

Temperature dependence of the dielectric increment, $\Delta\epsilon$; the relaxation frequency, ν_r ; and the distribution parameter of the relaxation time, α , obtained by fitting the Cole–Cole model [51] to the registered dielectric spectra in the TGBA*/SmA* phases are presented in Figure 8. The α parameter for SM was mostly in the range of 0.1–0.2, and only for Composite 3 was above 0.5 (Figure 7c). The small dielectric increment and strongly temperature-dependent relaxation frequency were characteristic of the soft mode, and was reported in the literature, e.g., for ferroelectric liquid crystal 10.OPOSMH [52].

Figure 9a,b present the dielectric spectra registered in the ferroelectric SmC* phase for Composites 1–5, while Cole–Cole plots are presented in Figure 9c,d. The dominant MWS process in the low-frequency range was well visible. In the SmC* phase, in addition to the MWS process, the Goldstone mode (GM) was registered in the nanocomposites (except for Composite 2), which was related to the phase fluctuation of the director in the smectic layer [53]. It seemed that the GM was strongly suppressed and covered by the MWS process in Composite 2 (see Figure 9d); therefore, the determination of its dielectric parameters was not possible. For Composite 1, up to 60 $^{\circ}\text{C}$, the MWS and GM processes were observed. At lower temperatures, the MWS relaxation frequency strongly depended on temperature, and shifted to lower frequencies (while simultaneously, the dielectric increment decreased). For Composite 2 in the SmC* phase, the MWS process was observed, and a very weak dielectric process (most likely a molecular one) in a higher frequency range. In turn, for Composites 4–5, apart from the MWS and the GM processes, a weak dielectric process (most likely a molecular one) in a higher frequency range was registered in the SmC* phase (marked as new high-frequency mode in Figure 9c). In the case of Composite 4, in the vicinity of 63 $^{\circ}\text{C}$, another relaxation process was revealed between the MWS and the GM processes (surrounded by the dashed circle in Figure 9c). As is seen in Figure 9a, the dielectric constant increased significantly after doping, while Khushboo et al. observed its decrease by more than half in the ferroelectric liquid crystal mixture W206E doped with Fe nanoparticles (0.1 wt %) [54].

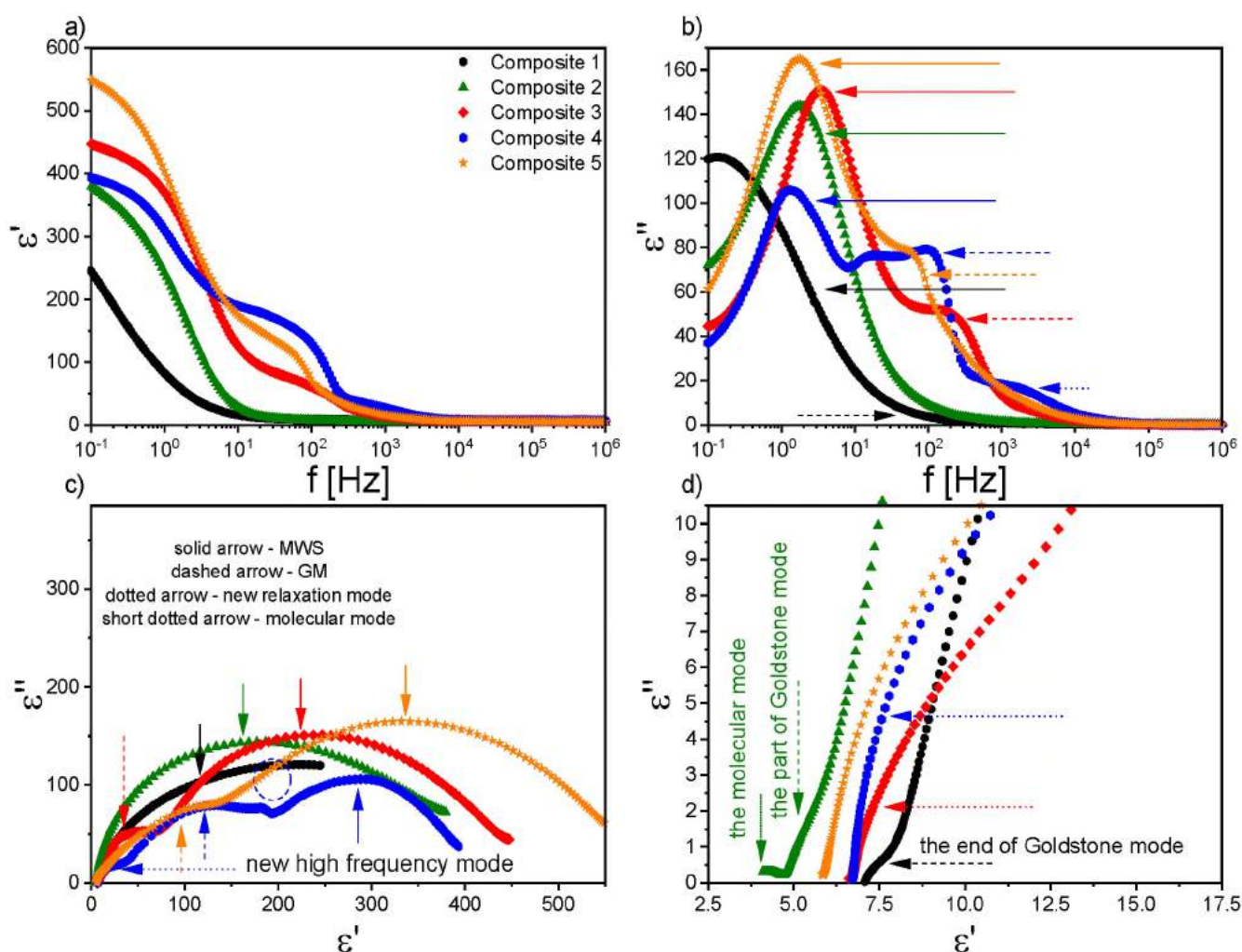


Figure 9. Dielectric spectra of Composites 1–5 in the ferroelectric SmC* phase (60 °C): dispersion (a); absorption (b); Cole–Cole plot (c); enlarged high-frequency part of Cole–Cole plot (d). Continuous colored arrows indicate the MWS process, dashed—the GM, dotted—a new relaxation process, and short-dotted—a molecular process. The legend in graph (a) is the same for all graphs. The dashed blue circle in graph (c) indicates an additional relaxation process present between the MWS and the Goldstone processes for Composite 4.

The influence of nanodopants in the liquid crystal matrix on relaxation processes is reported in the literature; for example, Singh et al., by doping the ferroelectric liquid crystalline mixture Felix 16/100 with quantum dots of CdSe (ca. 3.5 nm, 1 and 2 wt %), registered a new temperature-dependent relaxation process for a nanocomposite with 1 wt % CdSe, but for 2 wt % CdSe, did not. This process was explained by quantum fluctuations, which were suppressed at higher concentrations. In turn, after doping, the GM process became broader, and shifted towards lower frequencies, while the dielectric increment and the specific electrical conductivity decreased, which was explained by the trapping of ion impurities by QDs with strong adsorption abilities [55]. On the other hand, the nanocomposites based on Felix 17/100 doped with CdSe (ca. 3.5 nm, 1 and 2 wt %) showed a decrease in P_s , W_D , and W_P ; an increase in rotational viscosity; homeotropic alignment of FLC molecules; and a new ionic relaxation process around 300 Hz, which was interpreted as the adsorption phenomenon or accumulation of ion carriers on the QDs' surface [56]. In our case, for Composite 4, the relaxation process between MWS and GM at a frequency around 20 Hz (60 °C) may have a similar origin, e.g., accumulation of ion carriers on the γ -Fe₂O₃ nanoparticles' surfaces. It cannot be ruled out that this process

was related to certain movements of nanoparticle aggregates or the joint movement of LC molecules with the surrounding nanoparticles (or their aggregates). In turn, the relaxation frequency of the new high-frequency mode in Composite 4 (Figure 9c) was higher than that of GM, as it was observed for the relaxation process in Felix 17/100 doped with a higher concentration of ZnS QDs [38]. This relaxation process was attributed to the flexoelectric tilt fluctuations in the host in the vicinity of QDs, and it may be possible that for Composite 4, the origin of the new high-frequency relaxation mode was the same.

The temperature dependencies of the dielectric increment and relaxation times of the GM for Composites 1 and 3–5 are presented in Figure 10. The dielectric increment, as well as the relaxation time for Composite 1, was temperature independent, which was characteristic of the Goldstone mode. Moreover, the relaxation time was the same order as that of another pure ferroelectric liquid crystal, 3FO6C1 [57]. In contrast, the relaxation frequency of the Goldstone mode in nanocomposites was at the level of a pure C8 compound over a wide temperature range [58]. Different behaviors in the temperature dependence of both the dielectric increment and relaxation times took place for Composites 3–5—they were strongly temperature-dependent, and higher than for Composite 1. The dielectric increment after admixture increased 4-fold (up to ca. 180); however, there is a known GM with an even higher $\Delta\epsilon$ in pure material [59]. Importantly, as the nanoparticle concentration increased, the relaxation time for the GM also increased. Extending the GM relaxation time in Composites 3–5 compared to Composite 1 was associated with difficulties in movement at the molecular level after doping with nanoparticles. The higher the concentration of nanoparticles in the matrix, the more difficult or inhibited the movement of LC molecules in the vicinity of the nanoparticles was. Ibragimov et al. doped 5CB and H37 liquid crystals with BaTiO₃ particles (ca. 600 nm) and also observed the increase in the relaxation times after doping [60]. This was explained by a strong interaction existing between organic molecules and the BaTiO₃ particles (most likely permanent dipole—permanent dipole). Due to interacting organic molecules and dispersed particles, the rotation of molecules was hindered in the vicinity of the particles. As a result, the frequency was shifted to lower values. A similar explanation for the longer relaxation time of the GM after doping with γ -Fe₂O₃ nanoparticles can be adapted in our case; however, the interaction's nature could be different (e.g., permanent dipole—induced dipole). A similar behavior of the GM's parameters was observed in pure compounds from the homologous series 3FnHBM6(S), as well as in pure K1, K2, and K3 compounds [61,62]. In turn, Gathania et al. doped the ferroelectric mixture FLC-6980 with a dichroic dye (2wt %) and obtained ca. 3- and 5-fold increases in the SM and GM dielectric increments, respectively [63]. It is also known that the relaxation time is directly proportional to the rotational viscosity, γ , and helix pitch, p , while inversely proportional to the elastic constant, K_3 . Thus, the observed change in the GM relaxation time with the temperature for Composites 3–5 may have resulted from the competition between the temperature dependence of K_3 , p , and γ in the SmC* phase. The temperature dependencies of p and γ for different admixture concentrations were determined by us (see our last article [39]); however, due to the lack of K_3 temperature dependence, we were not able to confirm this estimate.

It should also be noted here that the existence of a domain mode (DM) in Composites 2–5 could not be ruled out, as we observed striped textures of the SmC* phase for these composites [39]. Haase et al. reported on the possibility of observing ferroelectric domains under a polarizing microscope in the form of a striped texture [64], while DM appeared for an already partially unwound helix under an external electric field, and was associated with the formation of ferroelectric domains (dipole moments from several adjacent smectic layers were directed in one direction) [65].

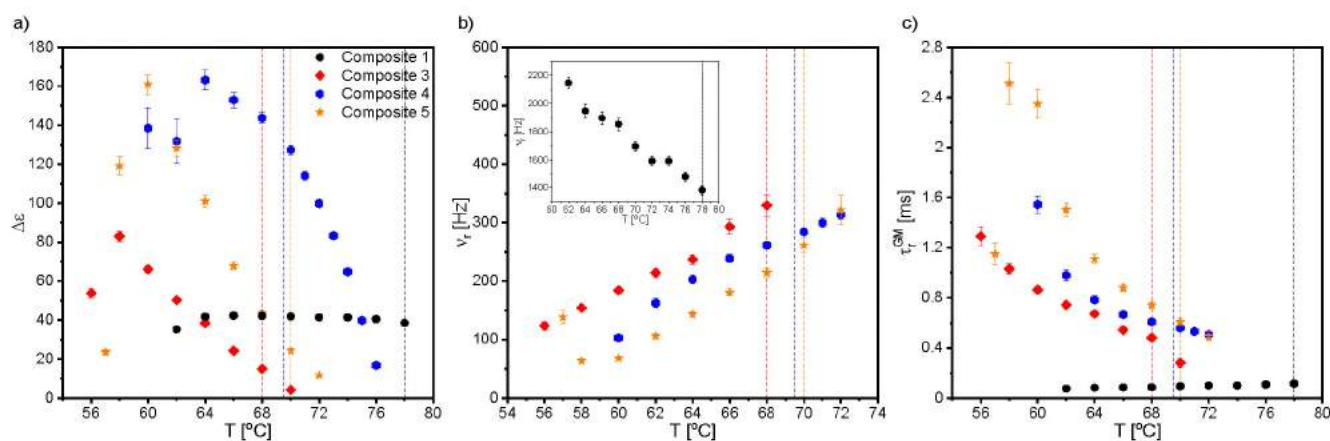


Figure 10. Temperature dependencies of the dielectric increment, $\Delta\epsilon$ (a), relaxation time (b) and relaxation time (c) of the Goldstone mode in nanocomposites. The legend in graph (a) is the same for all graphs. The vertical dashed lines represent the SmA*–SmC* phase transition temperature (during cooling).

During further cooling, in the vicinity of the transition to the crystal phase, the MWS process disappeared for all nanocomposites, while another relaxation process (at ca. 10^4 Hz) was registered in the crystal phase down to 25 $^{\circ}\text{C}$. Figure 11 presents the dielectric spectra and the real component of the specific electric conductivity registered for all nanocomposites in the crystal phase. As is seen in Figure 11b, the relaxation frequency of this process weakly depended on the nanoparticles concentration, while its intensity increased after doping. This process could not be attributed to the presence of nanoparticles in the LC matrix, as it was also observed for Composite 1 (pure matrix). Its relatively high relaxation frequency instead suggested that it may have been associated with the impurities (not ions) existing in the EHPDB (purity ca. 98%, according to the manufacturer).

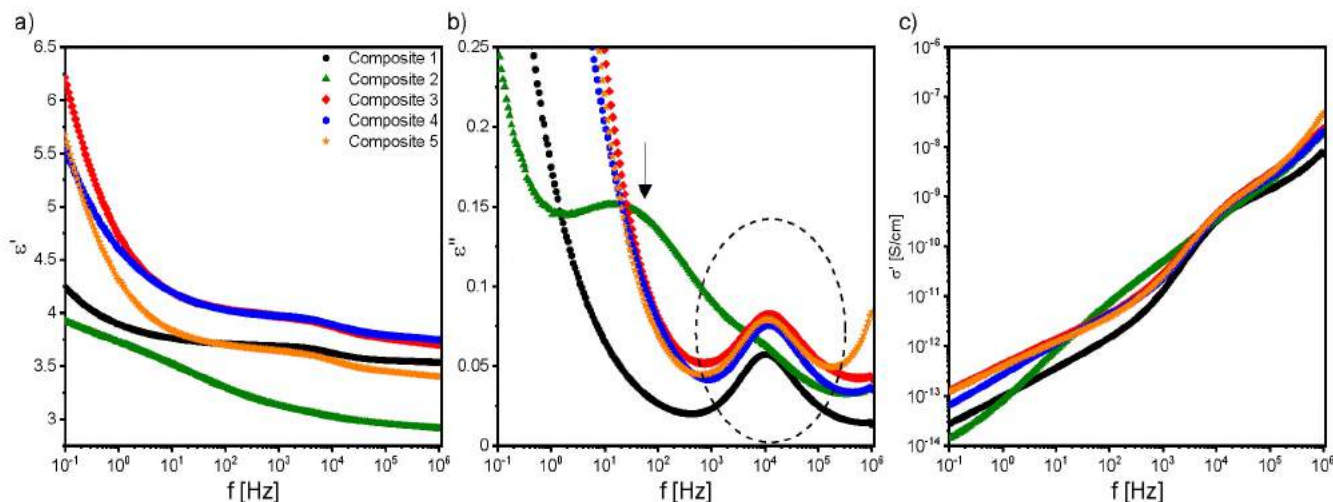


Figure 11. Dielectric dispersion (a) and absorption (b), as well as real component of the specific electric conductivity (c) for Composites 1–5 in the crystal phase (30 $^{\circ}\text{C}$). The vertical arrow in (b) indicates the additional process registered for Composite 2. The legend in graph (a) is the same for all graphs. The dashed ellipse in (b) surrounds the high-frequency process present for all nanocomposites in the crystal phase.

An additional strong relaxation process, strongly temperature-dependent, was registered only for Composite 2 in the crystal phase (indicated by the arrow in Figure 11b). This process covered the high-frequency process (see the dashed ellipse in Figure 11b) present for all nanocomposites in the crystal phase. Its relaxation frequency decreased with

decreasing temperature by almost three orders of magnitude. The nature of this process is still unknown. Similarly, the additional relaxation process was observed by Goel et al. after doping an LC matrix with Ni nanoparticles, and was explained by exchange interactions for higher nanoparticle concentrations [66]. The specific electric conductivity in the crystal phase changes was quite irregular with frequency for Composites 1–5 (Figure 11c); however, an admixture effect on its increase was visible (except at a few points at the low-frequency limit for Composite 2, which could have been due to the existence of the strong low-frequency process in this nanocomposite).

Figure 12 presents temperature dependencies of the $\Delta\epsilon$, ν_r , and α parameters of the high-frequency relaxation process observed in the crystal phase for all nanocomposites (in the case of Composite 2, the double Cole–Cole function was fitted). As is seen, this relaxation process was visible at cooling just from the SmC^*-Cr phase transition for Composite 1, while it appeared a few degrees below this transition for Composites 2–5. Its dielectric parameters ($\Delta\epsilon$, ν_r , and α) increased after doping the LC matrix with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, except for Composite 2 (due to the overlapping of the low- and high-frequency processes, they were subjected to large uncertainties). The strong modifications of the α parameter were due to the distortion of the long-range order in the crystal phase.

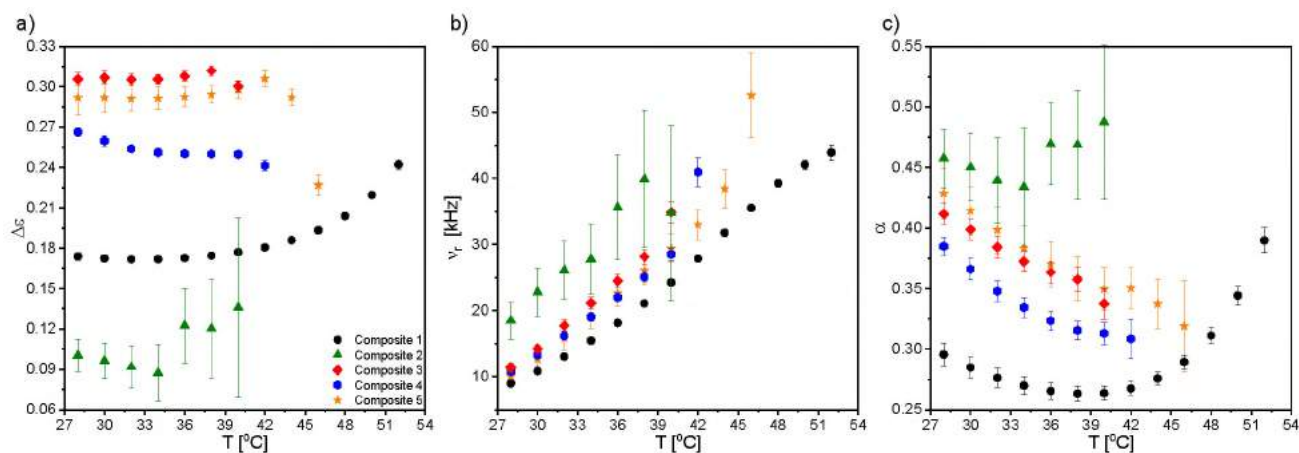


Figure 12. Temperature dependencies of the dielectric increment, $\Delta\epsilon$ (a); relaxation frequency, ν_r (b); and distribution parameter of relaxation time, α (c) of the relaxation process registered in the crystal phase. Due to the overlapping of two processes for Composite 2, the parameters were subject to large uncertainties. The legend in graph (a) is the same for all graphs.

As mentioned above, a very strong Maxwell–Wagner–Sillars (MWS) process was registered in the low-frequency range in the isotropic liquid, as well as in all liquid crystalline phases. Charge carriers in the samples (e.g., ionic impurities) could be blocked on the internal dielectric boundary layers on the mesoscopic scale, which was manifested in the dielectric spectrum as the Maxwell–Wagner–Sillars process [67]. The MWS process must be considered, especially in heterogeneous materials such as colloids, biological materials, blends, liquid crystal polymers, and composite systems [68]. In addition, charge carriers in contact with the nanocomposites can accumulate on the outer electrodes, which in turn is manifested by a strong increase in, among others, dielectric dispersion, and is called electrode polarization (EP, on a macroscopic scale) [67]. In the case of MWS and EP, the charge carriers were separated and made separate contributions to the polarization. In both cases, the contribution to the dielectric losses was high. It is also well known that ions present in organic materials modify the various physical properties, including the conductivity. After applying an electric field to the sample, mobile ions (coming from LC matrix or nanoparticles) moved to the electrodes of the measuring cell, and the local field acting on LC molecules was smaller than applied field. Moreover, this ion separation (electrode polarization) caused a continuous increase in dielectric dispersion, ϵ'' , which could reach enormous values, especially in the low-frequency range. However, in Composites

1–5, in the low-frequency range the EP contribution was quite small, and it could be seen as a nonplateau region (see Figures 7 and 9). A contribution to the MWS process also was made by the polarization relaxation taking place at the interface between two various materials with different dielectric constants. A characteristic feature of the MWS process is the increase in the dielectric dispersion in the low-frequency range.

As mentioned above, the MWS relaxation process originated from the relaxation of the polarization at the interface between different dielectric materials [67]. In the case of created nanocomposites, this interface was between (1) liquid crystal and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and (2) liquid crystal and polymer alignment layer on the sample electrodes. After applying the electric field to the measuring cell, the surface charges accumulated at these interfaces, and the Debye-type MWS relaxation process could be registered [67]. In turn, the interface between the liquid crystal and electrode was related to the electrode polarization phenomenon at the low-frequency limit. Interfaces acted as capacitors (with small plate distances), so finally the formation of a super capacitor at low frequencies (ca. 1 Hz) and hence rapid increase in the dielectric dispersion (parasitic effect) were observed. Usually, two or more relaxation processes and conductivity contributions are observed in the dielectric spectrum. If the conductivity is of electronic origin, it does not influence the dielectric dispersion, ϵ' [67], but does affect the dielectric absorption, ϵ'' ($\epsilon'' = \sigma_0 / (2\pi f \epsilon_0)$; σ_0 is the DC conductivity). In the case of ionic charge carriers, the dielectric absorption satisfied the relationship $\epsilon'' \sim \nu^{-s}$ ($s < 1$, ν is frequency). These ionic charge carriers were responsible for electrode polarization or Maxwell–Wagner–Sillars relaxation. For the electronic conductivity contribution (ohmic conductivity), the slope of ϵ'' in the low-frequency range was equal to -1 , while in the case of nonohmic conductivity or polarization effects (MWS and/or EP), the slope was greater than -1 (at higher frequencies, the conductivity contribution slope is equal to -1) [67]. Of course, the electrode polarization was also associated with an increase in the dielectric dispersion. Taking all of the above into account, the Cole–Cole model with the DC conductivity contribution was fitted to the experimental data, and the results obtained for the MWS process are presented in Figure 13. As is seen, the dielectric increment was temperature independent in the high-temperature range for all Composites, except for Composite 2. The change in the temperature dependence of $\Delta\epsilon$, at different temperatures, for Composites 1 and 3–5 was related to the $\text{SmA}^* \text{--} \text{SmC}^*$ phase transition, while a monotonous decrease was observed for Composite 2.

Additionally, both the dielectric increment and ϵ_s were higher for nanocomposites than for pure EHPDB (Composite 1), which was due to the interfacial polarization (at the liquid crystal–nanoparticles interface). However, Katiyar et al. obtained a decrease in relative permittivity while doping nematic liquid crystal NLC 2020 with TiO_2 nanoparticles (ca. 20–24 nm, anatase), which was explained by the ion trapping phenomenon by nanoparticles [69]. The relaxation frequency of the MWS process increased with increasing temperature for all composites, and the highest was for Composite 3. Such behavior was also observed earlier [70]. As mentioned above, the MWS process was a Debye type, therefore the α parameter should be equal to 0, and the Cole–Cole plot should be in the form of a semicircle with the center on the ϵ' axis [71]. For Composites 1 and 3–5, the α parameter was small (especially at 75–100 °C); while for Composite 2, it was much higher (due to, inter alia, the overlapping of the MWS and Goldstone processes). Goswami et al., as well as Czerwicz et al., showed that for the ferroelectric liquid crystals 6F3R and 6F6BbiOC8, the relaxation frequency of the MWS process was very weakly dependent on temperature, and the dielectric increment was greater than for the Goldstone process [72,73]. In Figure 13e, it is well visible that the DC conductivity decreased with decreasing temperature. Within the measurement uncertainty, the electronic conductivity was the same for Composites 3 and 5. However, for Composite 4 up to 82 °C was the smallest. Throughout the temperature range of the SmC^* phase, the DC conductivity was higher for Composites 2–5 compared to the pure matrix (Composite 1).

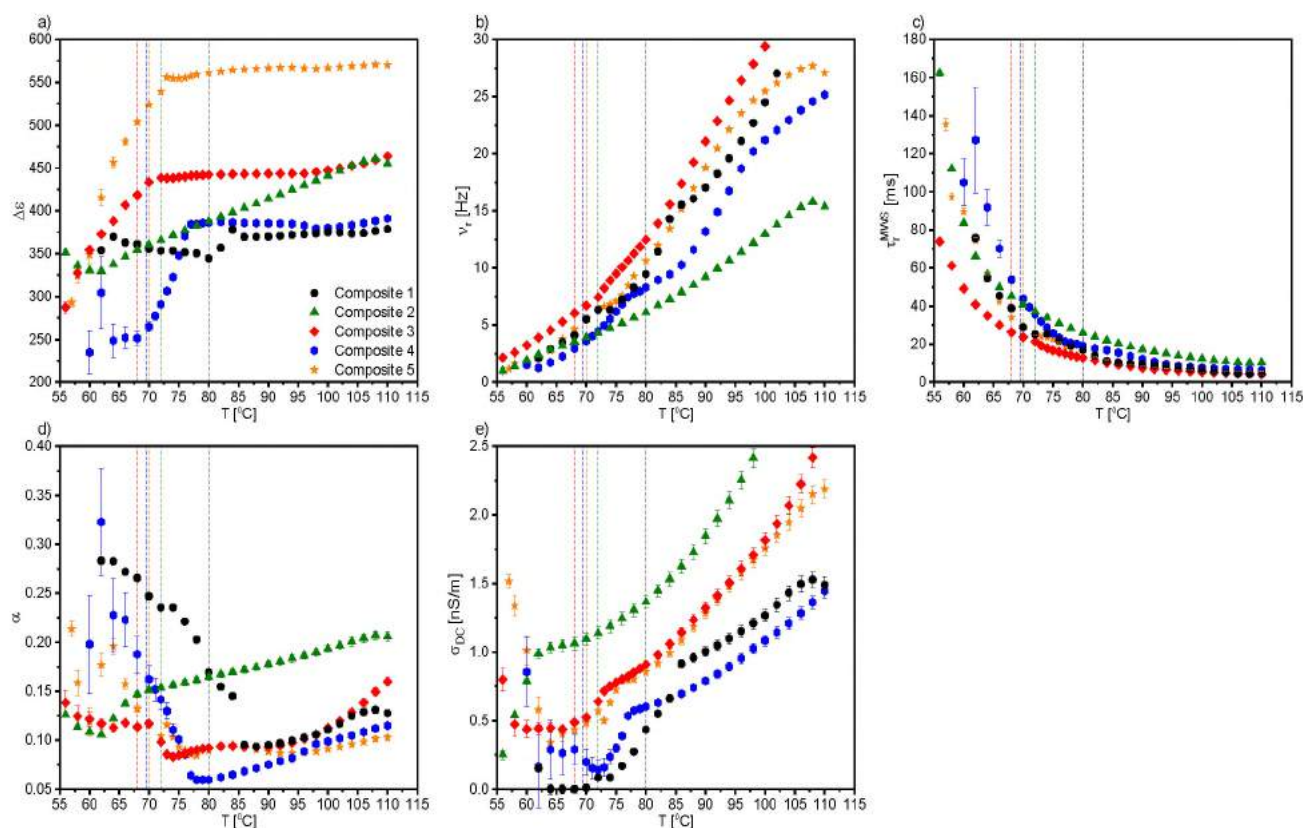


Figure 13. Temperature dependencies of the dielectric increment, $\Delta\epsilon$ (a); relaxation frequency, ν_r (b); relaxation time (c); the distribution parameter of relaxation time, α (d) of the Maxwell–Wagner–Sillars process; as well as DC conductivity (e) for Composites 1–5. The legend in graph (a) is the same for all graphs. The vertical dashed lines represent the SmA*–SmC* phase transition temperature (during cooling).

Another interesting issue from the application point of view was the specific electric conductivity, σ^* . As is seen in Figure 14, the real part of σ^* ($\sigma^* = \sigma' - i\sigma''$ [74]) for nanocomposites was higher than for the pure matrix. It should also be kept in mind that the conductivity could also be affected by ionic impurities adsorbed on nanoparticles and introduced into the matrix at the synthesis stage. At higher temperatures, they desorbed from the nanoparticles' surfaces and become parasitic ions in the matrix [75]. It is very interesting that σ' was much higher in mesophases than in the crystal phase, and the differences were enormous. For example, for Composite 5, the difference in σ' between the crystal and liquid crystalline phases was around 1500 pS/cm. Within mesophases, the highest specific electric conductivity was for Composite 5, as was expected for the nanocomposite with the highest amount of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Kumar et al. also observed an increase in conductivity after doping the ferroelectric liquid crystals 5F6T and 6F6T with TiO_2 nanoparticles (ca. 18–23 nm, 0.1 and 1.0 wt %) [76], as did Naser, after doping liquid crystal with Fe_3O_4 nanoparticles (up to 1 wt %) [77].

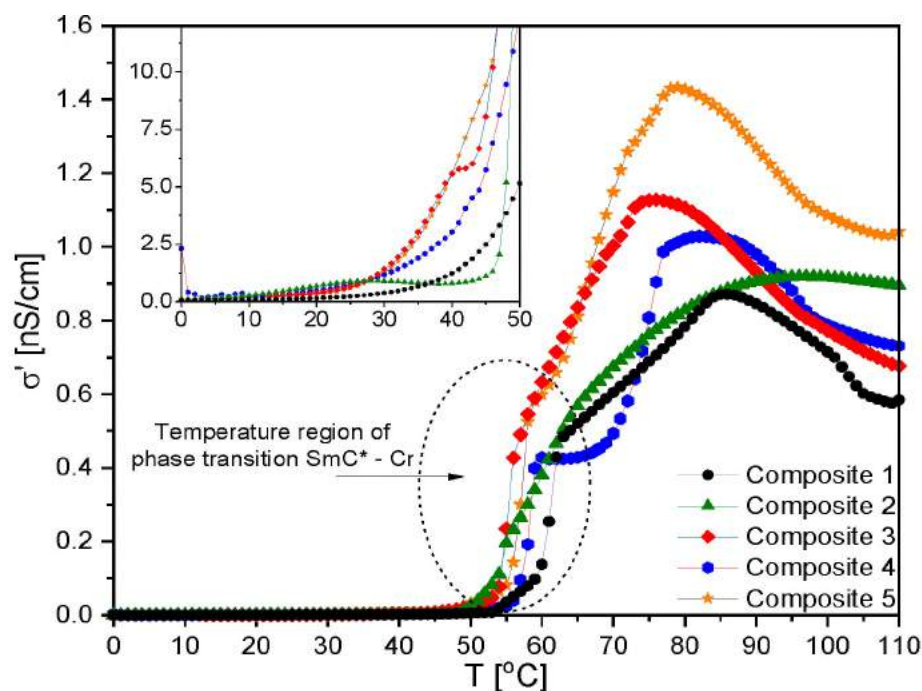


Figure 14. Temperature dependencies of the real part of specific electric conductivity for Composites 1–5 registered at 10.5 Hz.

2.4. Superconducting Quantum Interference Device (SQUID) Magnetometry Results

It is known that liquid crystal molecules are usually diamagnets, and in a sufficiently strong magnetic field (3–4 T), they align in the direction of the field forces. The introduction of non-diamagnetic inorganic nanoparticles decreased the magnetic field needed for the reorientation of LC molecules [78]. However, the aim of our study was to find out how the properties of nanoparticles would change after they were introduced into an LC matrix.

Measurements of magnetic properties were used to check whether the synthesized nanocomposites (with small γ -Fe₂O₃ nanoparticle concentration) exhibited a hysteresis loop present for pure nanoparticles in a wide temperature range (in a blocked state), and how the concentration of γ -Fe₂O₃ nanoparticles affected the characteristic parameters of the hysteresis loop, such as: saturation magnetization, M_S ; residual magnetization in the zero magnetic field, M_R ; and the coercive field, H_C . Additionally, we wanted to determine how an admixture modified the magnetization in the ferroelectric SmC* phase of the studied nanocomposites.

Because γ -Fe₂O₃ nanoparticles were studied, the blocking temperature, T_B (phase transition temperature between superparamagnetic and blocked state), existed. In the blocked state (below T_B), the magnetic moments of the nanoparticles were frozen, and the value of thermal energy was not sufficient to reorient them. Below a certain critical size of γ -Fe₂O₃ nanoparticles, their magnetic properties changed from ferromagnetic to superparamagnetic (size effect). However, the critical size of nanoparticles depended, inter alia, on the conditions of synthesis. In the superparamagnetic state, the magnetization curve was not a hysteresis loop, magnetization saturation was not observed (even in a high magnetic field), and irreversibility below T_B occurred [79].

The magnetic properties of Samples 1–2 and Composites 2–6 were investigated by measuring the temperature dependence of magnetization in a DC magnetic field of 200 Oe (ZFC and FC curves; the external magnetic field dependence of magnetization and the magnetic hysteresis (at 10, 100, 200, and 300 K)). As an example, ZFC and FC curves for Sample 1 and Composite 3 are presented in Figure 15. The fluctuations visible in the FC curve for the Composite 3 were probably caused by an excessive temperature rate. Both the ZFC and FC curves for Sample 1 were similar to those of Composite 3 and other nanocomposites, respectively. As is seen, the FC curve reached saturation in

a low-temperature range for both samples, which was previously observed for smaller $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles [79] and was associated with dipolar interactions. Moreover, the convergence of the ZFC and FC curves was not visible up to 380 K; therefore, both Sample 1 and the nanocomposites were in the blocked state (T_B corresponded to the convergence point of both the ZFC and FC curves). It seemed that T_B was outside of the measuring range, because we did not use any surfactant to decorate the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, in opposition to Kataby et al., who observed significant T_B modifications depending on the surfactant used (e.g., stearic acid shifted T_B to 280 K in relation to sulfonic acids, where T_B was around 120 K) [79], as well as Tanwar et al., who showed that decoration of nanoparticles with oleic acid changed T_B (from 95 K up to 15 K in the 0.5 T magnetic field) [80]. It should also be noted that in the case of surfactant-functionalized nanoparticles, the T_B depends on the strength of the magnetic field. Moreover, the T_B for the same type of nanoparticles may differ depending on the size of the nanoparticles, their decoration or not with a surfactant, as well as possible impurities. Wu et al. showed that the T_B for $\gamma\text{-Fe}_2\text{O}_3$ short nanotubes very strongly depended on the DC magnetic field used to register the ZFC/FC curves (T_B decreased from 275 K to 40 K when the applied magnetic field changed from 500 Oe to 5000 Oe) [81]. Summarizing the above, apart from the modification of the phase transition temperatures and the degradation of mesophases [39], this was another reason not to use any surfactant in the preparation of composites.

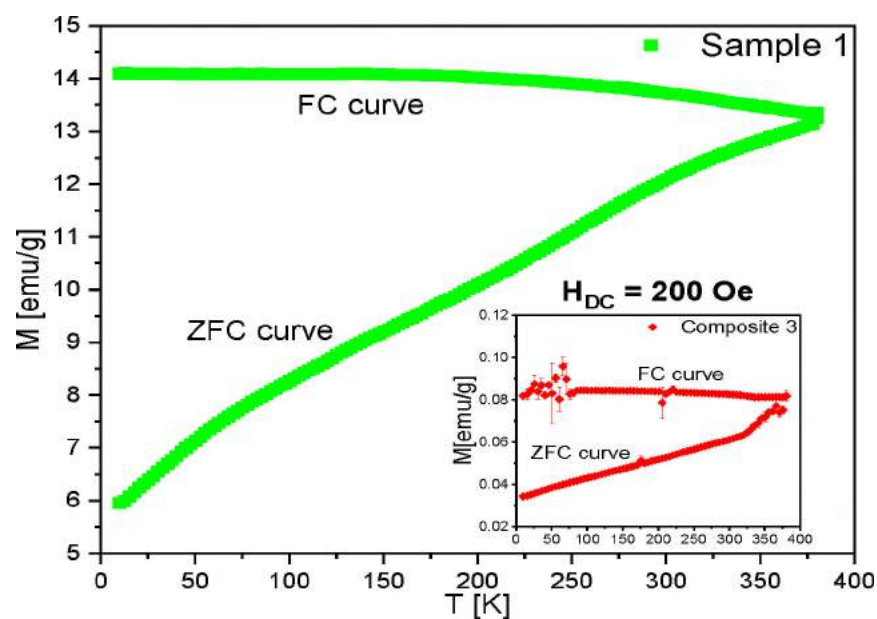


Figure 15. The qualitative temperature dependence of magnetization in the external magnetic field (200 Oe) for Sample 1 (pure $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles) and Composite 3 (in the inset).

Since all samples consisted of the same $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (confirmed by XRD measurements [39]), all experimental data were scaled to the average value of magnetic properties from three independent measurements for pure $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. This approach allowed the determination of the estimated weight concentration of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles used for the preparation of mixtures with EHPDB and/or oleic acid, as well as a direct comparison of the magnetic properties. The predicted and estimated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle content in Samples 1–2 and Composites 2–6 are gathered in Table 1 and plotted in Figure 16. Analysis of these data led to the observation that the estimated concentrations of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in Composites 2–6 were slightly lower than predicted. Such a deviation was a consequence of the partial miscibility of the low-concentrated nanoparticles in the liquid crystal matrix, which led to the deposition of a small amount of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles on the glassware surface during the evaporation of the mother solution in chloroform, which, in the last stage of a mechanical collection of the product, resulted

in a reduction in the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle content. One of the most probable reasons was the formation of nanoparticle aggregates that could no longer be considered as single domains with one super spin, as well as different sizes of nanoparticles in the composites (<50 nm). As mentioned above, the same behavior of ZFC/FC curves was observed for all the samples, so even a small concentration of $\gamma\text{-Fe}_2\text{O}_3$ in the liquid crystal matrix retained its properties and made the entire nanocomposite form a blocked state up to 380 K. Therefore, it was possible to obtain both a ferroelectric material (because EHPDB exhibited the liquid crystalline SmC* ferroelectric phase) and a magnetically blocked material. In turn, Novotná et al. obtained a ferroelectric–superparamagnetic material with a T_B equal to ca. 15 K [82].

Table 1. Predicted and estimated weight percentages of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in the samples.

Sample/Composite	Predicted wt % of $\gamma\text{-Fe}_2\text{O}_3$	Estimated wt % of $\gamma\text{-Fe}_2\text{O}_3$
Sample 1	100	100
Sample 2	100	11.9(1)
Composite 2	0.3	0.13(6)
Composite 3	0.5	0.37(5)
Composite 4	0.7	0.60(5)
Composite 5	0.9	0.75(4)
Composite 6	0.3	0.16(5)

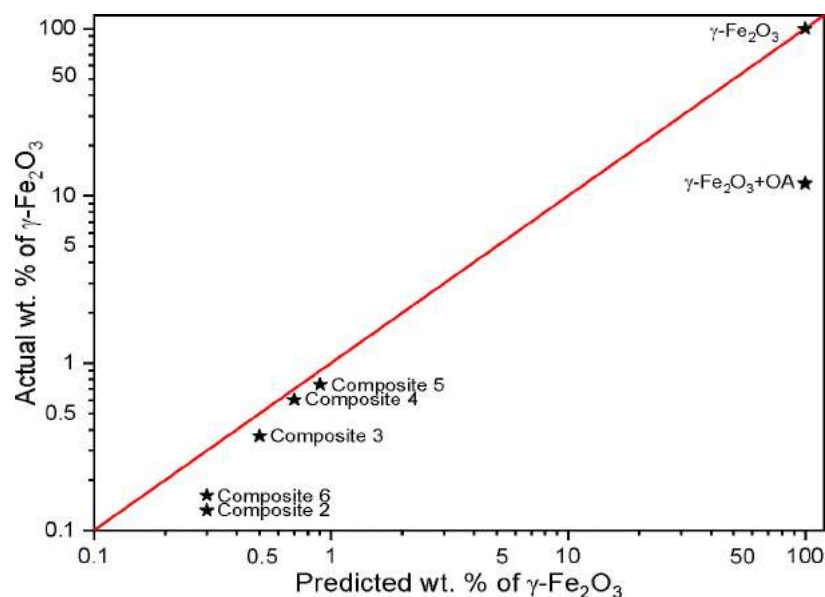


Figure 16. Predicted vs. estimated content of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in the Samples 1–2 and Composites 2–6.

It is well known that maghemite ($\gamma\text{-Fe}_2\text{O}_3$) in bulk exhibits long-range ferromagnetic order with a Curie temperature of about 890 K, a magnetic hysteresis with a coercive field below 200 Oe at room temperature, and saturation magnetization up to 75 emu/g (while lower for $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles) [81,83–88]. Balaraju et al., did not observe the saturation of magnetization of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles (ca. 39 nm, rhombohedral structure) up to ± 10 kOe [89]. Interestingly, Suber et al., reported on the antiferromagnetic behavior of Fe_2O_3 nanoparticles of various sizes and shapes [90]. For example, the Morin phase transition (transition from pure antiferromagnet to ferromagnet) for rhombohedral nanoparticles was observed around 190 K, and then the blocking process at around 60 K; while for spherical nanoparticles, the Morin transition disappeared, and superparamagnetic behavior was observed [90].

The synthesized nanocomposites were indeed hybrid systems, and $M(H)$ curves were measured at various temperatures to confirm the presence of magnetic hysteresis (Figure 17). All compounds revealed a similar shape of magnetic hysteresis in a blocked state ($T_B > 380$ K), with average H_c ranging from 129 Oe (Composite 2) to 166 Oe (Composite 6) at 300 K, and successively increasing as the temperature decreased, to reach values between 295 Oe (Composite 2) and 352 Oe (Sample 2) at 10 K. Moreover, the hysteresis loop for each sample narrowed with increasing temperature. Magnetic properties of Samples 1–2 and Composites 2–6 are gathered in Table 2. Both the magnetic remanence, M_R , and the coercive fields, H_c , were temperature-dependent. In our case, saturation of magnetization was not observed, even for the highest magnetic field (around 50 kOe). The increase in temperature from 10 K to 300 K caused the magnetization in the highest magnetic field (50 kOe) to decrease from about 75 emu/g to about 65 emu/g. This phenomenon could be explained by the increase in thermal energy that was supplied to the nanocomposite system. The higher thermal energy was responsible for the larger fluctuations at the individual nanoparticle level. This, in turn, means that for a given magnetic field, fewer spins will be oriented towards the external magnetic field, so the magnetization will be lower; e.g., nanoparticles with higher thermal energies have greater freedom of movement, which makes it difficult to organize their spins using the same magnetic field.

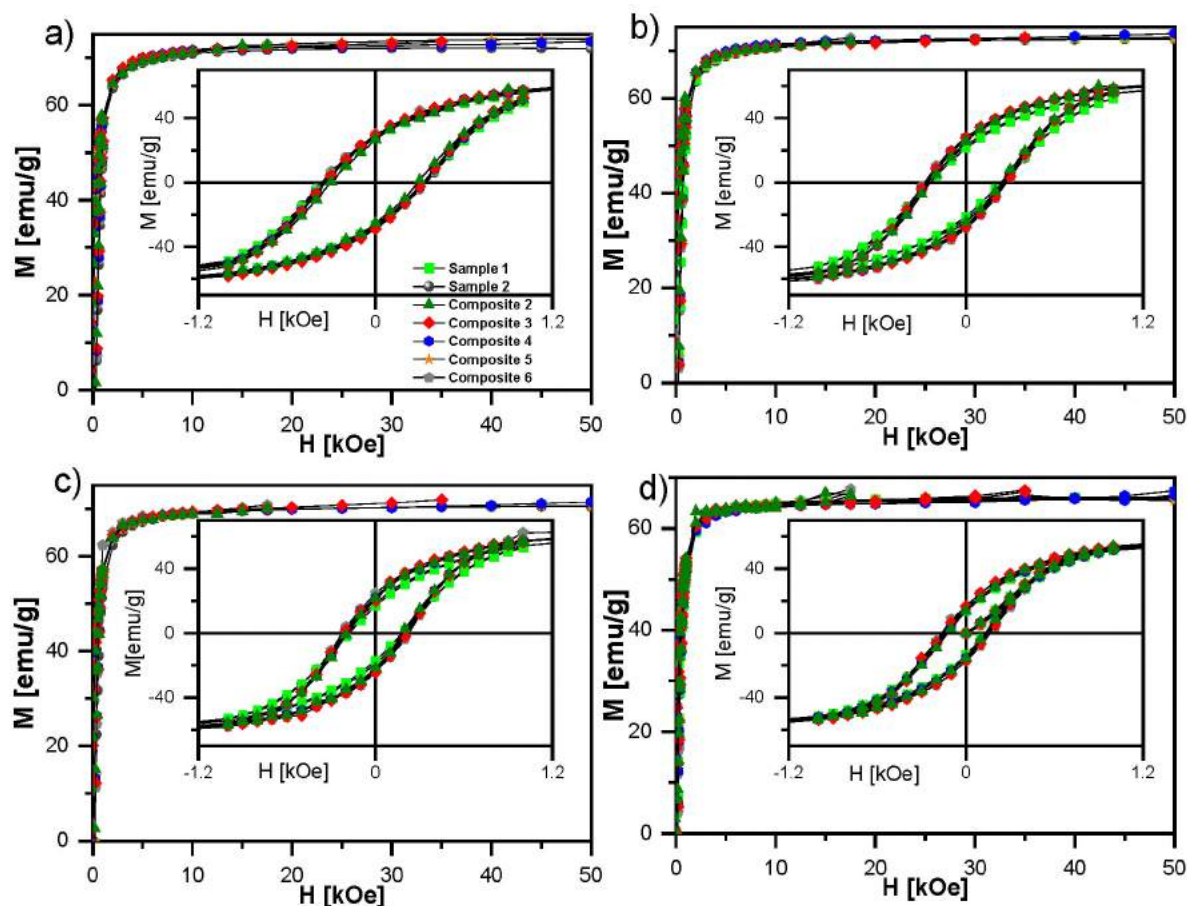


Figure 17. Magnetization vs. external magnetic field and magnetic hysteresis (insets) for Samples 1–2 and Composites 2–6 measured at 10 K (a), 100 K (b), 200 K (c), and 300 K (d). All values were scaled to values for the γ - Fe_2O_3 nanoparticles (Sample 1). The solid lines in all figures are a guide for the eye. The legend in graph (a) is the same for all graphs.

Table 2. Magnetic properties of Samples 1–2 and Composites 2–6. Average M_R and M_S were normalized by taking the concentration of $\gamma\text{-Fe}_2\text{O}_3$.

Sample/ Composite	T[K]	Aver. H_c (Oe)	Aver. M_S (emu/g)	Aver. M_R (emu/g)	Aver. M_R/M_S
Sample 1	300	133.5	66.20	13.56	0.205
	200	179.6	70.76	17.06	0.241
	100	240.9	72.83	21.18	0.291
	10	335.0	73.29	27.16	0.371
Sample 2	300	152.3	65.60	14.98	0.228
	200	200.9	70.48	18.90	0.268
	100	260.4	72.16	22.82	0.316
	10	352.1	71.97	28.36	0.394
Composite 2	300	128.7	66.65	14.74	0.221
	200	185.6	69.69	21.68	0.311
	100	242.0	71.75	25.01	0.349
	10	294.5	72.46	25.98	0.359
Composite 3	300	154.3	67.29	16.86	0.251
	200	213.9	71.78	22.14	0.308
	100	269.7	72.66	27.79	0.382
	10	330.3	73.16	28.98	0.396
Composite 4	300	147.2	66.87	15.20	0.227
	200	209.3	71.56	22.48	0.314
	100	267.8	73.63	27.45	0.373
	10	330.6	73.45	28.26	0.385
Composite 5	300	145.9	65.98	15.01	0.227
	200	201.3	70.53	22.64	0.321
	100	258.9	72.49	26.71	0.368
	10	330.4	73.90	27.38	0.371
Composite 6	300	165.6	67.38	16.75	0.249
	200	225.7	70.52	24.06	0.341
	100	277.8	72.41	28.39	0.392
	10	344.1	72.44	29.28	0.404

Moreover, the analysis of the dependence of the average H_c in relation to the estimated-actual content of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (Figure 18b) resulted in the following observations:

- An increase in H_c for the samples with content ranging between ca. 0.3 wt % and 0.9 wt % (ca. +15% increase in H_c for 0.37(5) wt % (Composite 3) in comparison to Sample 1);
- A significant decrease in H_c (down to -10%) for the nanocomposite with the lowest concentration of 0.13(6) wt % (Composite 2).

Novotná et al. observed quite different behavior for hysteresis loops, namely narrowing the hysteresis loops for nanocomposites in relation to pure nanoparticles [82]. Of course, in the first approximation, the differences could be explained by different nanoparticle sizes (ca. 4 nm by Novotná et al., and ca. 50 nm in our case).

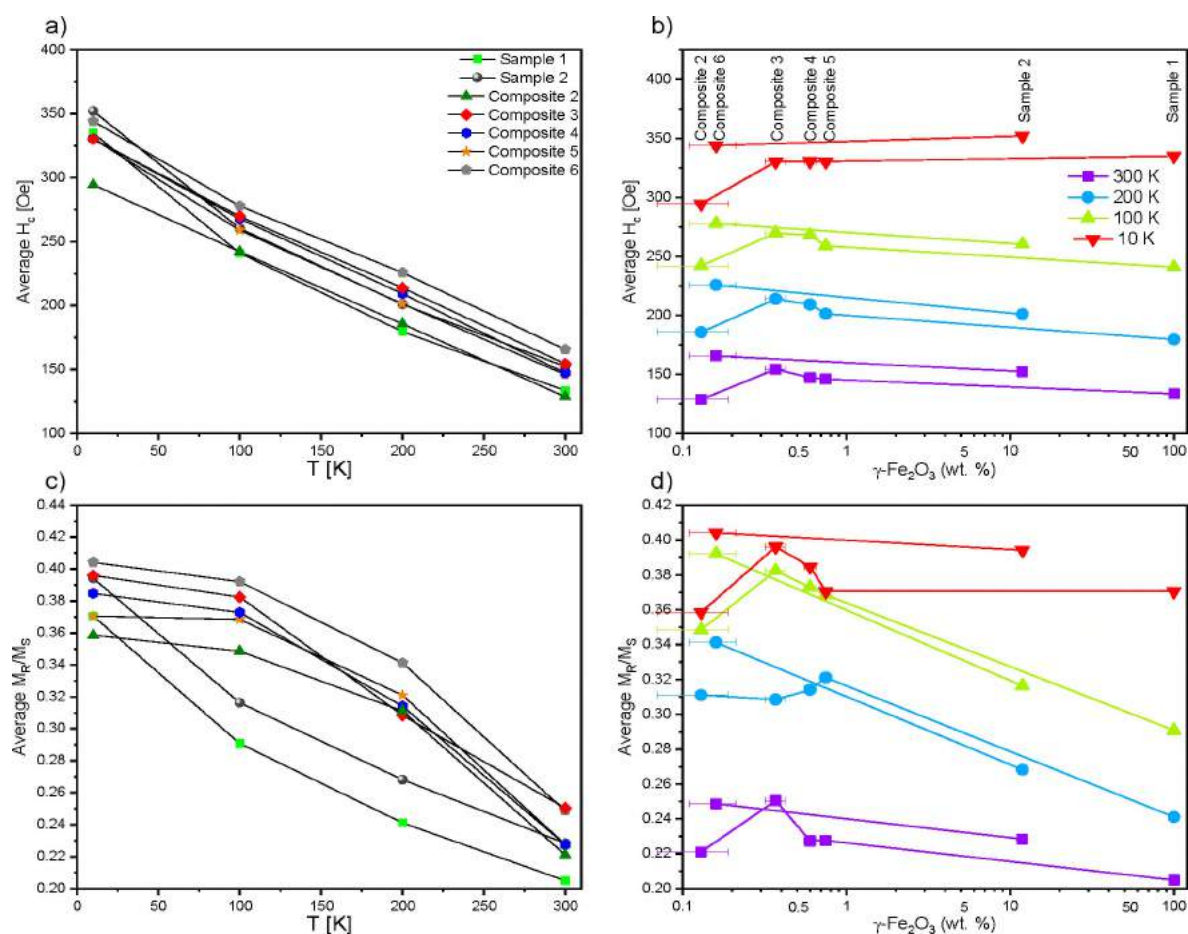


Figure 18. Temperature (a) and estimated weight percent (wt %) of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (b) dependencies of the average coercive field, and temperature (c) and estimated $\gamma\text{-Fe}_2\text{O}_3$ wt % (d) dependencies of the average remanence ratio (remanent magnetization M_R /saturation magnetization M_S) for Samples 1–2 and Composites 2–6. The solid lines in all figures are a guide for the eye. The legend in graph (a) is the same for graph (c), while the legend in graph (b) is the same for graph (d).

It is also worth mentioning that oleic acid significantly improved the performance of magnetic hysteresis for materials with decorated nanoparticles, leading to an approximately 12% increase for Sample 2, and approximately 36% for Composite 6. Similar trends with minor deviations were also observed for the average remanence ratio (remanent magnetization M_R /saturation magnetization M_S) versus temperature and estimated concentration of $\gamma\text{-Fe}_2\text{O}_3$ (Figure 18c,d). At each studied temperature, the H_c increased while M_R and M_S decreased for the $\gamma\text{-Fe}_2\text{O}_3$ sample treated with oleic acid versus the untreated one. In the case of nanocomposites, the H_c for the temperatures of 300 K, 200 K, and 100 K was the highest for Composite 3, while no significant differences were observed for the studied samples at a temperature of 10 K. At the lowest temperature saturation of magnetization, M_S was the highest for the composite with the highest concentration of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, and the M_S for each sample increased with decreasing temperature (which was to be expected). The magnetic properties of the oleic-acid-treated and original samples differed significantly, which is still not well understood by us, but is very exciting for future research using other matrices or other forms of iron (III) oxides (e.g., $\epsilon\text{-Fe}_2\text{O}_3$). Furthermore, Martínez-Miranda et al. used $\text{Fe}_{48}\text{Co}_{52}$ nanoparticles (ca. 11 nm) decorated with various surfactants as dopants to 8CB, and showed that PEG (3000) (polyethylene glycol) and NHS/PEG (3000) (N-Hydroxysuccinimide/polyethylene glycol) surfactant had different effects on the orientation of 8CB molecules in the magnetic field [78]. Summing

up, the magnetic behavior of nanocomposites (Composite 2–5) was similar to that of pure $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Therefore, the nanoparticles' incorporation into the organic liquid crystalline matrix (EHPDB) did not affect their properties in the blocked state, which was especially visible in the hysteresis loops (Figure 17).

2.5. Fourier Transform Mid-Infrared (FT-MIR) Spectroscopy Results

Low amounts of the nanoparticles used in the experiments did not result in sufficiently large structural changes in the liquid crystalline system to be observable by IR spectra at room temperature [39]. However, the nanoparticles, even at such low concentrations, notably affected the thermal response of the system, as revealed by DSC. The changes in the thermal response could be also checked by IR spectroscopy. It is known that IR spectra are extremely sensitive to variations in intermolecular interactions during phase transitions. Thus, IR investigation of phase transitions can bring additional valuable information on the overall supramolecular arrangement of the liquid crystalline system, and suggest possible structural implications of the nanoparticles in intermolecular interactions within the system. Therefore, we investigated IR spectra from 100 °C down to 10 °C upon cooling the system from the isotropic to ordered crystal phase. The purpose of the IR investigations was to draw conclusions about the molecular behavior of the investigated materials by analyzing spectral band parameters such as peak maximum position and full width at half maximum (FWHM) of some IR bands arising from the vibrational modes of various functional groups present in EHPDB in the function of temperature.

Figure 19 presents temperature evolutions of the peak maximum position of four bands arising from the vibrational modes within aromatic rings and epoxy and ester groups. The vertical arrows denote phase transitions temperatures observed for pure EHPDB at about 80 and 58 °C during cooling. The first transition observed with this spectroscopic technique was connected to the N*–TGBA*, whereas the second one was connected to the SmC*–Cr transition. The higher temperature transition was gently accented by a small rise in the peak position values, and was visible at about the same temperature region for all six studied composites. The lower temperature transition to the ordered crystal phase was clearly visible when shifting the band towards larger wavenumbers in the case of all results, except for the band related to the epoxy group (Figure 19b), where we observed the opposite effect—shifting towards smaller wavenumbers. Spectroscopic results confirmed that this transition occurred at a significantly higher temperature for pure EHPDB in comparison to the composites with the $\gamma\text{-Fe}_2\text{O}_3$ admixture. Comparing the results shown in Figure 19a,b, it can be noted that at 100 °C, the peak positions of both bands for all six investigated composites were more or less the same. However, this changed after cooling samples to 10 °C, where differences in positions were obvious. Considering the band associated with the stretching mode of epoxy group, the lowest value of the peak position was observed for pure EHPDB. Then, for composites with nanoparticles, it shifted to a larger wavenumber in the following order: Composite 6, Composite 2, Composite 5, Composite 4, Composite 3. This could be explained by the fact that generally, the higher the concentration of nanoparticles, the more distorted the molecular structure, with weaker interactions of epoxy groups. Molecules in pure EHPDB were better aligned, and thus the interactions of epoxy groups were stronger, which was visible in the IR spectrum by the lower wavenumber (higher wavelength, lower energy) at which the IR stretching band appeared. Exactly the opposite order in the position of the band associated with the bending mode within the aromatic ring can be observed in Figure 19a.

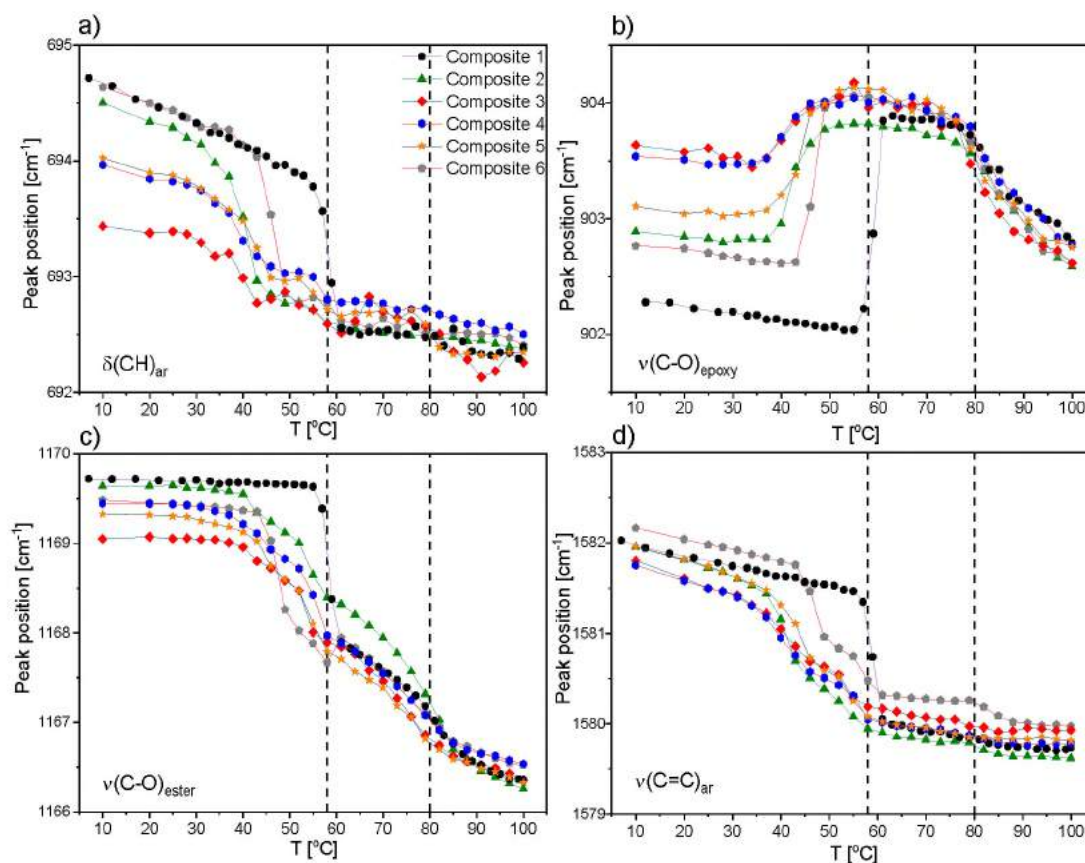


Figure 19. Temperature dependencies of peak maximum position for four selected IR bands connected to $\delta(\text{CH})_{\text{ar}}$ (a), $\nu(\text{C-O})_{\text{epoxy}}$ (b), $\nu(\text{C-O})_{\text{ester}}$ (c), and $\nu(\text{C=C})_{\text{ar}}$ (d) obtained for Composites 1–6 during cooling from the isotropic phase. The legend in graph (a) is the same for all graphs. The vertical dashed and dotted lines represent the $\text{SmA}^*-\text{SmC}^*$ and SmC^*-Cr_1 phase transition temperatures (during cooling) for pure EHPDB, respectively.

Taking into consideration the results obtained for the band related to the $\nu(\text{C=C})_{\text{ar}}$ mode, it was clear that for pure EHPDB, the transition to an ordered crystal phase was the sharpest, and occurred in one step (Figure 19d). In turn, the shape of the curves in the vicinity of the SmC^*-Cr transition region for all the other composites with admixture of $\gamma\text{-Fe}_2\text{O}_3$ was different. As can be seen, the conversion to this phase occurred in two steps (two distinguishable increases in the value of peak position were visible), which may have indicated a slightly different mechanism of this transition; for example, through an intermediate state. The same two-step increase in the peak position value at $P(T)$ for composites with $\gamma\text{-Fe}_2\text{O}_3$ also could be observed for the band connected to the ester group, but it was less pronounced (see Figure 19c).

Figure 20 presents the temperature dependencies of the full width at half maximum (FWHM) of two bands connected to the stretching modes of ester and epoxy group. This band parameter was very sensitive to molecular dynamics and ordering of the investigated group. Taking into consideration the results in Figure 20a obtained for the band associated with the ester group, it was clear that for pure EHPDB, the transition to ordered crystal phase was the sharpest, and occurred in one step, whereas for all the other composites with admixture of $\gamma\text{-Fe}_2\text{O}_3$, it occurred in two steps (two distinguishable declines in FWHM value were visible). These results were very consistent with the ones previously described (Figure 19c,d).

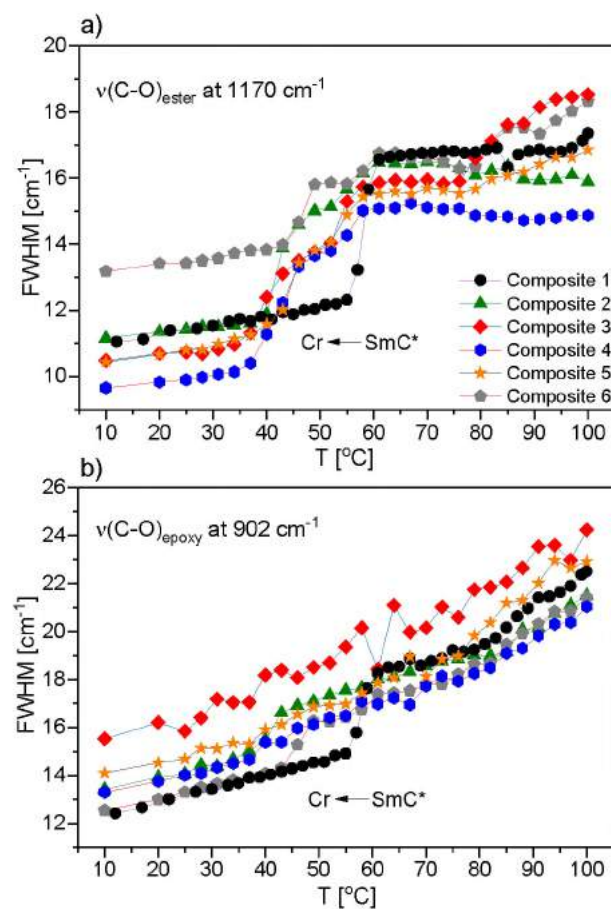


Figure 20. Temperature dependencies of the full width at half maximum (FWHM) of two selected IR bands connected to $\nu(\text{C-O})_{\text{ester}}$ (a) and $\nu(\text{C-O})_{\text{epoxy}}$ (b) modes obtained for pure EHPDB and nanocomposites during cooling from the isotropic phase. The positions of these two bands are given for pure EHPDB at room temperature. The legend in graph (a) is the same for all graphs.

Figure 20b shows the temperature dependencies of FWHM for the band associated with the stretching mode of the epoxy group. These results showed that for pure EHPDB and Composites 2 and 6, the transition to the ordered crystal phase was sharper. In the cases of composites with a larger amount of nanoparticles (0.5 wt %, 0.7 wt %, and 0.9 wt % $\gamma\text{-Fe}_2\text{O}_3$), no distinct decline in FWHM value was observed at $\text{FWHM}(T)$. The FWHM value decreased gradually in the entire investigated temperature range, which may suggest that the structure was less ordered in the low-temperature range for Composites 3–5 in comparison to Composites 1, 2, and 6. Moreover, at higher temperatures in liquid crystalline phases, the arrangement of molecules was more distorted, and hence the transition to the ordered crystal phase occurred in a less cooperative way, which also caused a decrease in the phase transition temperature.

Figure 21 presents the temperature dependencies of the peak maximum position of two IR bands associated with the $\nu(\text{C=O})$ and $\nu_{\text{as}}(\text{CH}_2)$ stretching modes, upon doping with various amounts of nanoparticles, in the investigated system. Infrared vibrations of carbonyl group and CH_2 methylene groups within hydrocarbon side chain were very sensitive to a change in molecular interactions. In the case of all six investigated composites, the transition from the SmC^* to Cr phase was clearly visible. Both parts of the EHPDB molecule, the carbonyl group and hydrocarbon chain, were involved in this transition.

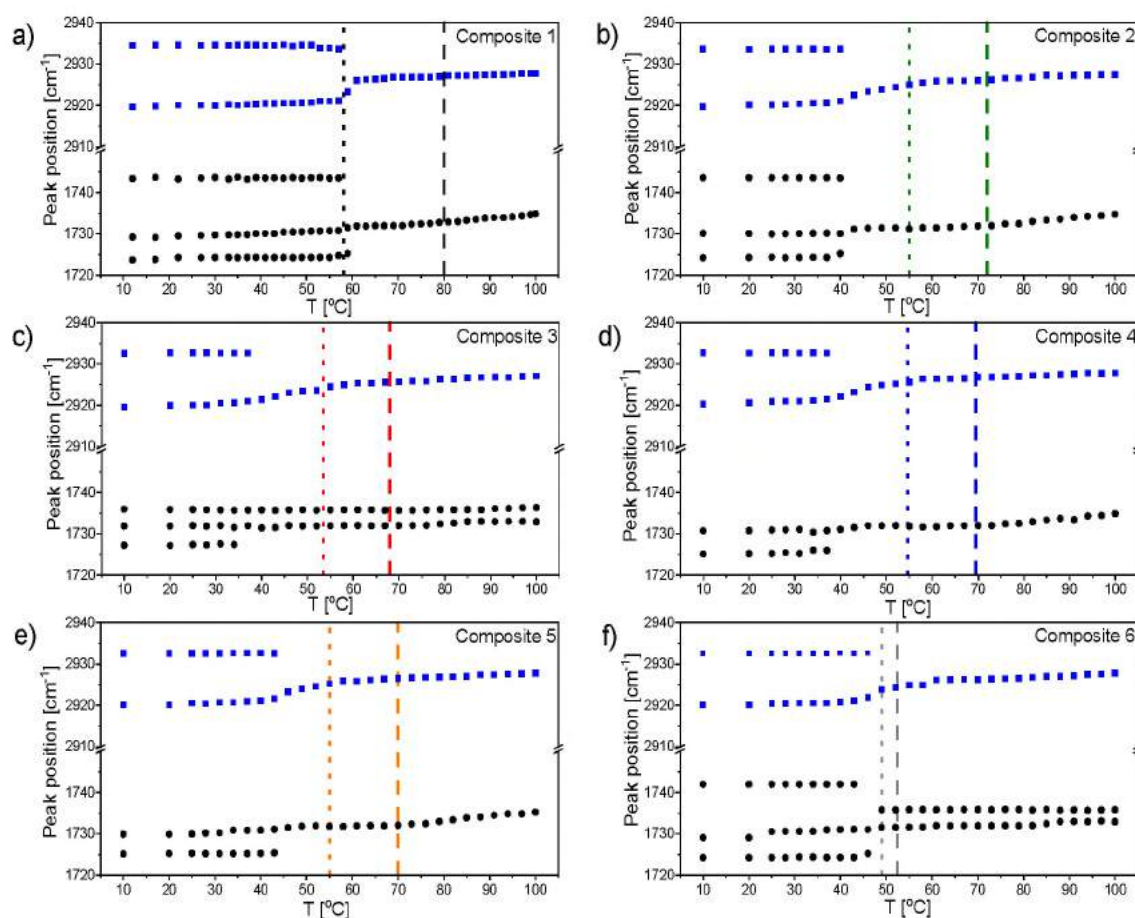


Figure 21. Temperature dependencies of the peak maximum position of two IR bands connected to $\nu(\text{C}=\text{O})$ (black circles) and $\nu_{\text{as}}(\text{CH}_2)$ (blue squares) modes obtained for pure EHPDB—Composite 1 (a), Composite 2 (b), Composite 3 (c), Composite 4 (d), Composite 5 (e), and Composite 6 (f) during cooling from the isotropic phase. The vertical dashed and dotted lines represent the $\text{SmA}^*-\text{SmC}^*$ and SmC^*-Cr_1 phase transition temperatures obtained during cooling by DSC, respectively.

The thermal behavior of the $\nu_{\text{as}}(\text{CH}_2)$ band was identical for all six systems. At 100 °C, it appeared at about 2928 cm^{-1} , which proved that a highly disordered ‘liquidlike’ material was formed. The position of this band almost did not change in a wide range of temperatures. This suggested that also in the N^* , TGBA^* , SmA^* , and SmC^* phases, the hydrocarbon chain was completely melted. At the SmC^*-Cr phase transition, it split into two components, which was a result of interactions of molecules in a unit cell. In turn, the thermal behavior of the $\nu(\text{C}=\text{O})$ band was more complex, and differed depending on the admixture concentration, which proved that $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles modified the EHPDB matrix. For Composite 1 (pure EHPDB), there was one maximum observed in the liquid crystalline phases that corresponded well to one type of carbonyl group interacting in the same way with the environment. At the transition to the ordered crystal phase, the band split into three components, which indicated that three different subpopulations were present in the molecular structure. One shoulder was visible at a larger wavenumber at about 1743 cm^{-1} , which could be attributed to the carbonyl group freely vibrating, and thus not being involved in the intermolecular interactions. This type of carbonyl group was also observed for Composites 2 and 6, and thus with the lowest amount of nanoparticles. The other two components, with maxima at about 1732 and 1725 cm^{-1} , most probably were connected with two types of carbonyl groups involved in the intermolecular interactions, which were of a different nature. In the case of the compositions with a larger admixture of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, Composites 4–5, temperature evolutions of positions of both investigated bands were identical—they both split into two components at $P(T)$.

Interestingly, at high temperatures for Composites 3 and 6, the $\nu(\text{C}=\text{O})$ band was not fully symmetrical, and two components of this band could be distinguished.

3. Materials and Methods

3.1. Materials

The pure EHPDB compound and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (diameter <50 nm) are commercially available, and were purchased in Sigma Aldrich (Sigma Aldrich Co., Saint Louis, MO, USA). According to the manufacturer, the purity of LC matrix—EHPDB was 98% (product number 328537), while the purity of the NPs was not given (product number 544884).

3.2. UV-Vis (Ultraviolet-Visible Spectroscopy)

Solid state UV-vis/NIR absorption spectra for Samples 1–2 and Composites 1–6 were recorded in reflectance mode using a JASCO MSV-370 microUV-vis/NIR spectrometer (JASCO Corporation, Tokyo, Japan) equipped with a LINKAM LTS420 hot stage with a programmable T96 system controller and an LNP96 cooling option under flow of dry nitrogen gas (Linkam Scientific Instruments Ltd., Epsom, England), for solid samples spread on the surface of a 0.5 mm thick quartz plate mounted with Kapton tape on a heating plate. The measurements were conducted in the temperature range of 0–120 °C at a rate of 2 °C/min. Each 4 min spectrum measurement was preceded by a 2 min waiting time for temperature stabilization.

3.3. FDDS (Frequency Domain Dielectric Spectroscopy)

In order to determine the dielectric properties of the new synthesized nanocomposites, a Turnkey Impedance Spectrometer Concept 81 (Novocontrol Technologies GmbH & Co. KG, Montabaur, Germany) was used. Measurements were carried out by using planar cells with gold-coated electrodes (ca. $C_0 = 50$ pF, active area 25 mm², AWAT Company, Warsaw, Poland) in the frequency range of 0.5–10⁶ Hz (measuring voltage 0.5 V). ITO cells were not used to eliminate a parasitic relaxation process around 1 MHz (coming from indium tin oxide, a very pronounced process often covers/overlaps the relaxation process of studied materials), while parasitic relaxation coming from the Au electrodes was outside of the measuring frequency range [91]. The composites were introduced into the measuring cells due to the capillary effect at a temperature slightly above the clearing point, and slowly cooled down. Due to the planar alignment of the liquid crystal molecules in the cells, the perpendicular component of the dielectric permittivity was measured [92]. The measurements were taken during cooling from 110.0 to 25.0 °C with a 1.0 °C temperature interval.

3.4. SQUID (Superconducting Quantum Interference Device Magnetometry)

Magnetic measurements were performed on Samples 1–2 of about 1 mg and Composites 1–6 of about 10 mg. The samples were placed at the bottom of gelatin capsules (approximately 30 mg), blocked with nitrocellulose varnish (approximately 20 mg after drying), and quartz wool (10–15 mg). Next, capsules were placed inside Kapton tubes and mounted on a magnetic test rod. Measurements were conducted by using a Quantum Design MPMS XL magnetometer (Quantum Design Inc., San Diego, CA, USA). All direct-current (DC) measurements were corrected for the diamagnetic contribution of the sample holder and the EHPDB liquid crystal matrix.

3.5. FT-MIR (Fourier Transform Mid-Infrared Spectroscopy)

Temperature-dependent Fourier transform mid-infrared (FT-MIR) absorption measurements were performed in transmission mode using a VERTEX 70v vacuum spectrometer (Bruker, Billerica, MA, USA) for bulk samples of Composites 1–6. More details on this experiment can be found in our recent paper [39]. The band parameters (peak maximum position and FWHM) of chosen bands at different temperatures were obtained by fitting

the Lorentz function using OriginPro, Version 2020 (OriginLab Corporation, Northampton, MA, USA).

4. Conclusions

We showed the influence of the γ -Fe₂O₃ nanoparticle admixture, as well as of oleic acid, on the physical properties of the ferroelectric liquid crystal EHPDB by using light absorption in the UV-vis and MIR ranges, dielectric spectroscopy, and magnetic superconducting quantum interference device magnetometry methods.

It was found that both pure (Sample 1) and oleic-acid-decorated (Sample 2) γ -Fe₂O₃ nanoparticles absorbed in the 200–700 nm range with distinct absorption bands around 225, 350, 500, and 650 nm; however, the intensities of the absorption bands were smaller for Sample 2; while above 750 nm, both materials were transparent. All Composites 1–6 were completely transparent in the range of 500–850 nm, regardless of temperature, and the temperature dependence of the absorbance for selected wavelengths showed distinct discontinuities at the phase transition temperatures, with a visible plateau in the liquid crystalline ferroelectric SmC* and isotropic phases. In the absorption spectra of the nanocomposites (Composites 2–5), a decrease in the absorption in the UV range and the appearance of additional absorption bands in the 350–600 nm region compared to the pure LC matrix (Composite 1) were observed. In our opinion, nanoparticles in the organic matrix played the role of scattering centers of incident light, and with the increase in nanoparticle concentration, the intensity of the scattered light increased, and thus the absorption decreased.

The dielectric spectroscopy method allowed us to register and interpret relaxation processes appearing in the liquid crystalline and crystal phases in Composites 1–5. Two relaxation processes in the liquid crystalline N* phase were revealed, namely MWS and the molecular s-process. The observed decrease in the relaxation frequency of the s-process in nanocomposites was related to the presence of nanoparticles in the LC matrix, which hindered molecular reorientation (molecules in Composites 2–5 needed a longer time for reorientation). In turn, in the liquid crystalline TGBA* and SmA* phases, in addition to the MWS process, a soft mode was registered (with the exception of Composite 2) in a narrow temperature range. In the liquid crystalline ferroelectric SmC* phase, the MWS process was still observed, and additionally, the Goldstone mode (however, for Composite 2, the GM was covered by the very strong MWS process). On the other hand, the origin of the additional relaxation process registered in this phase for Composites 4 and 5 was not fully explained. It may have been related to the movement of nanoparticles in the form of aggregates or the collective movement of nanoparticles (or aggregates) with the surrounding organic molecules, and the impurities (not ions) existing in the LC matrix. In addition, a strong modification of the Goldstone mode in the SmC* phase was observed (e.g., extension of the relaxation time by about 12 times) after introducing even the smallest amount of γ -Fe₂O₃ nanoparticle admixture, which, as already mentioned, may have been caused by difficulties in the reorientation of organic molecules in the presence of nanoparticles. In general, in the liquid crystalline phases, the doping caused an increase in the dielectric constant. In turn, in the crystal phase, the MWS process disappeared and a new one, most likely of a molecular nature, and weakly dependent on the concentration of γ -Fe₂O₃ nanoparticles, appeared. The specific conductivity increased over the entire frequency range with an increase in the γ -Fe₂O₃ nanoparticles' concentration.

Based on the results obtained by the SQUID method, it was found that the blocking temperature of the used γ -Fe₂O₃ nanoparticles was above 380 K, and the nanoparticles retained their properties in the LC matrix; therefore, for Composites 2–5, the liquid crystalline ferroelectric SmC* phase coexisted with the magnetically blocked state of the nanoparticles. Evidence of the presence of nanoparticles in the blocked state in Composites 2–5 was the similar shape of the hysteresis loop, which narrowed with increasing temperature. Saturation magnetization decreased with increasing temperature, which was related to the higher thermal energy of nanoparticles. However, it turned out that the coercive field

depended not only on temperature, but also on the concentration of nanoparticles. The coercive field was greater for Composites 2–5 than for pure nanoparticles (Sample 1); therefore, nanoparticles immersed in the LC matrix required a higher magnetic field to invert the magnetization (especially for Composite 3). The addition of oleic acid additionally increased the coercive field and saturation magnetization.

Infrared absorption spectroscopy results showed that addition of the γ -Fe₂O₃ nanoparticles had an influence on the SmC*–Cr phase transition temperature of liquid crystal EHPDB, and moderated its molecular arrangement. Parts of the EHPDB molecule containing oxygen, such as carbonyl, ester, and epoxy groups, as well as aromatic rings, were sensitive to changes in intermolecular interactions and/or dynamics due to the presence of nanoparticles.

To sum up, oleic acid used to decorate nanoparticles, on the one hand, prevented the agglomeration of nanoparticles, causing better homogeneity in the LC matrix, which in turn increased the coercive field and the M_R , while decreasing the M_s and strongly modifying the temperature of phase transitions (narrowing the mesophases). It also influenced the absorption of light in the UV-vis range in the nanocomposites. However, further studies of the effect of oleic acid (and other surfactants) on the characteristic parameters of organometallic nanocomposites, with particular emphasis on the amount of surfactant used (at a constant concentration of nanoparticles), seem necessary.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/ijms23010050/s1>.

Author Contributions: Conceptualization, S.L.; methodology, S.L.; validation, S.L. and M.M.; formal analysis, S.L., O.S. and N.G.; investigation, S.L., O.S., K.K. and N.G.; writing—original draft preparation, S.L.; writing—review and editing, M.M.; visualization, S.L., O.S. and N.G.; supervision, M.M. and S.-i.O.; project administration, M.M.; funding acquisition, S.L., O.S., S.-i.O. and M.M. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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Supplementary Material

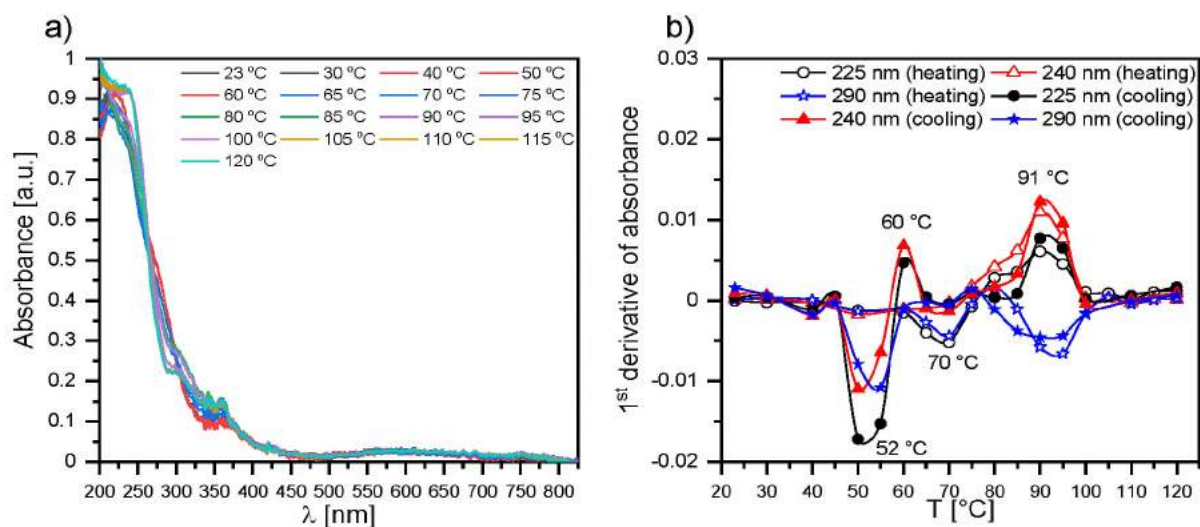


Figure S1. Solid state UV-Vis absorption spectra of Composite 1 (pure EHPDB) at several chosen temperatures in the 200–850 nm range during heating (a) and temperature dependence of the first derivative of the absorbance for selected wavelengths 225, 240 and 290 nm during heating and cooling (b).

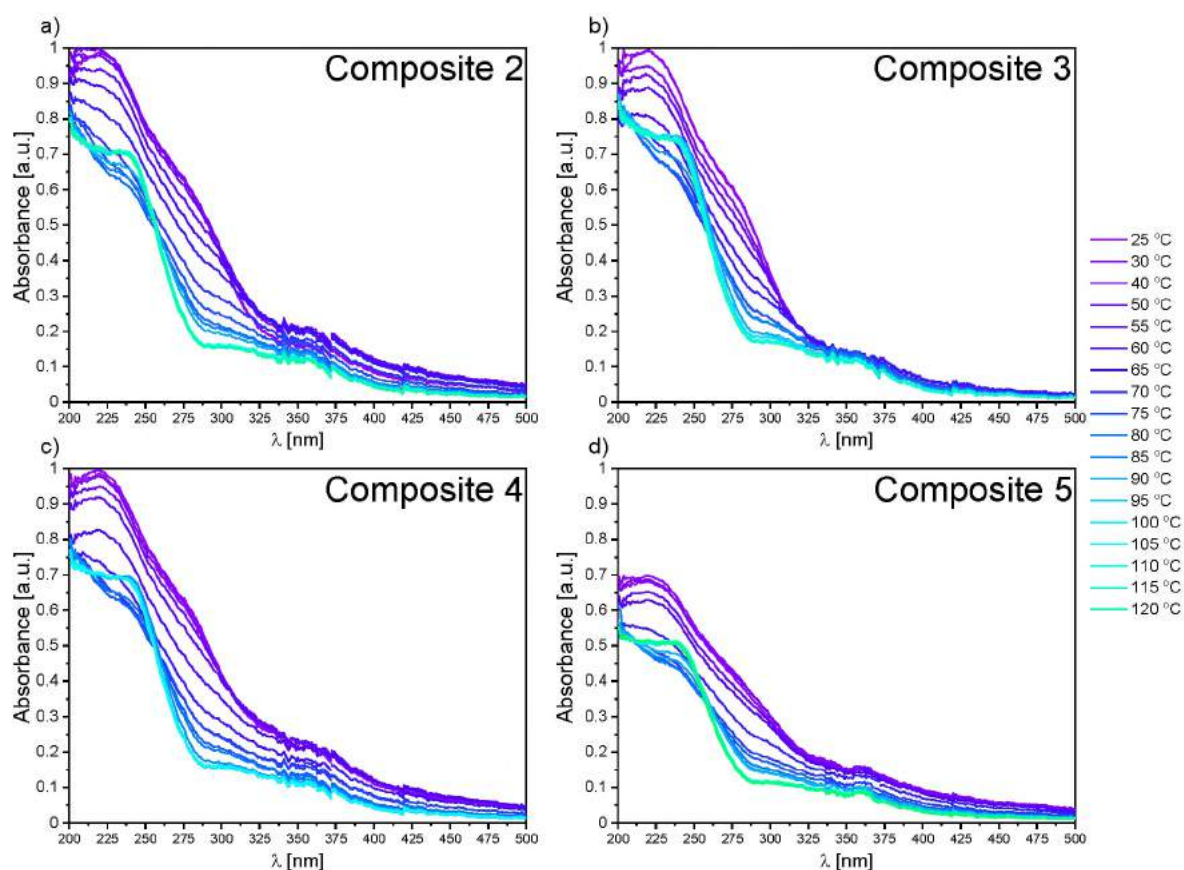


Figure S2. Solid state UV-Vis absorption spectra of Composites 2–5 at several chosen temperatures in the 200–500 nm range during heating. The legend from the right side is for all graphs.

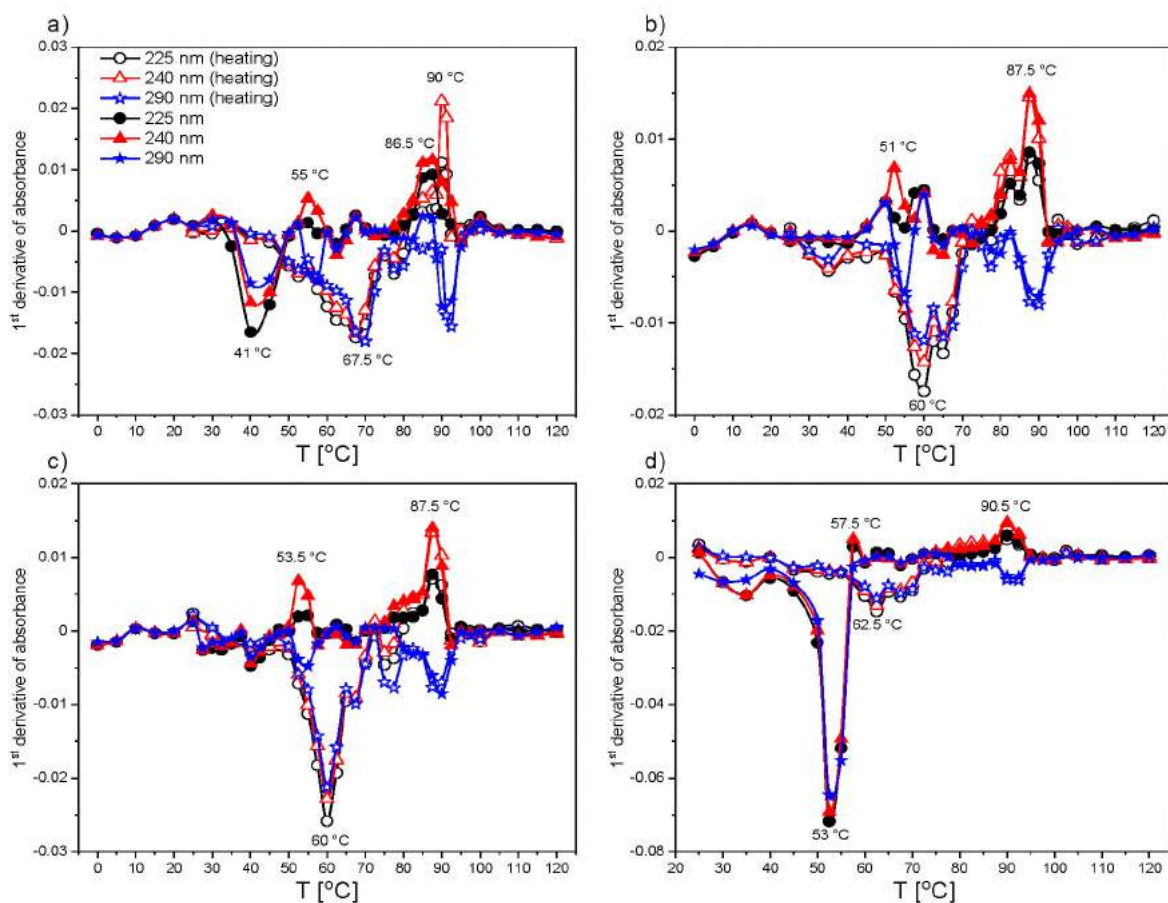


Figure S3. Temperature dependence of the first absorbance derivative for selected wavelengths (225, 240, 290 nm) for Composites 2–4 during heating and cooling. The given temperatures correspond to the phase transition temperatures.

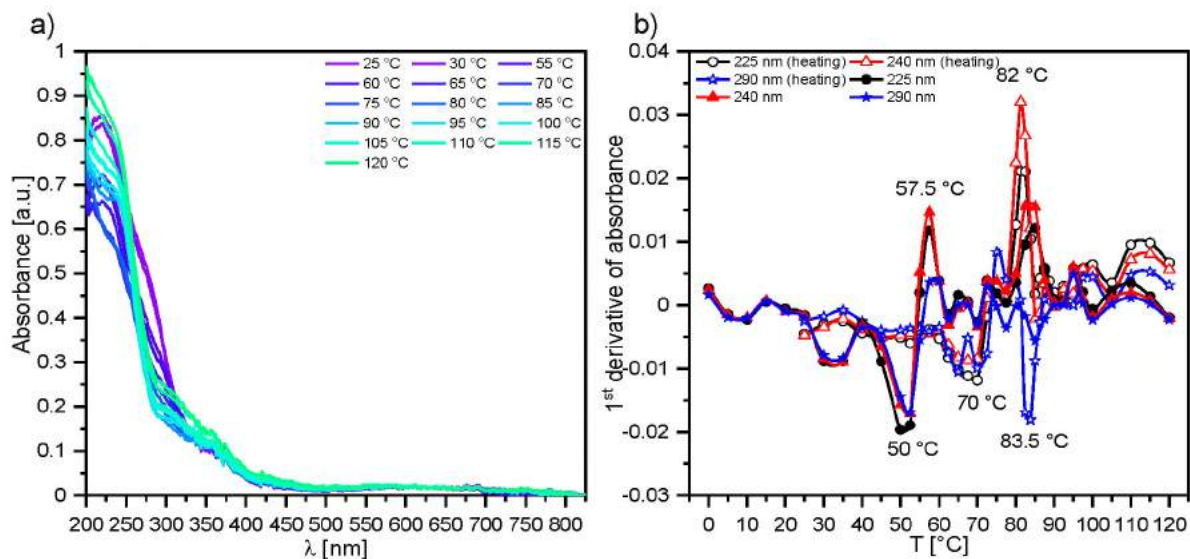


Figure S4. Solid state UV-Vis absorption spectra of Composite 6 at several chosen temperatures in the 200–850 nm range during heating (a) and temperature dependence of the first derivative of absorbance for selected wavelengths 225, 240 and 290 nm during heating and cooling (b).

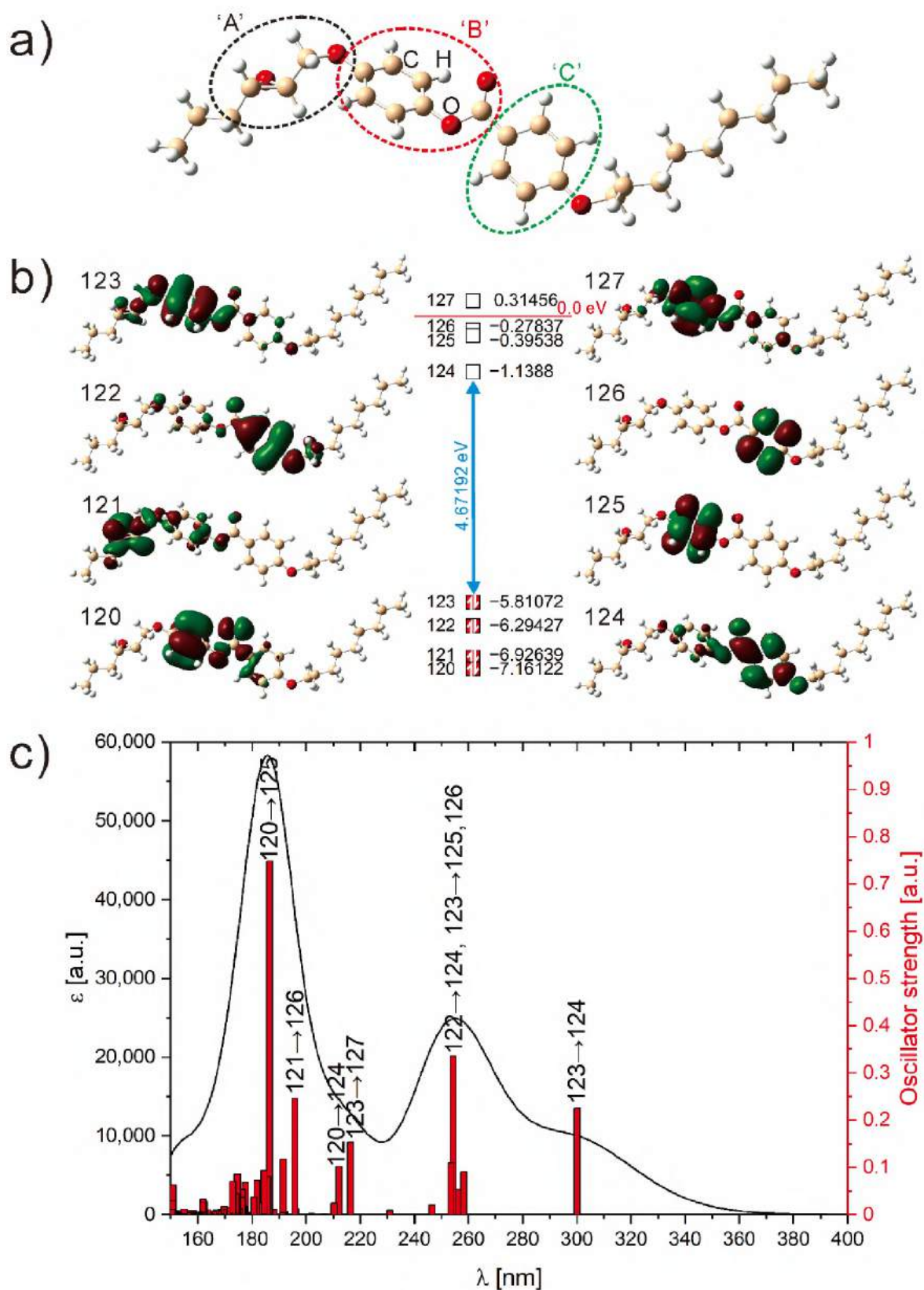


Figure S5. Model for optimized structure of EHPDB molecule used for calculation (a). Energy level diagram in eVs with calculated frontier molecular orbitals (b). Blue arrow and number correspond to the HOMO-LUMO gap. Calculated UV-Vis spectrum for optimized structure of EHPDB molecule (c). Red bars indicate electronic transitions with the largest contributions while legend above bars indicate electronic states involved in transition.

Table S1. List of atomic coordinates for optimized structure of EHPDB molecule.

Atom	X	Y	Z	Atom	X	Y	Z
C	2.1355	-1.7731	1.7295	H	18.7163	-6.4138	3.3196
C	16.9662	-6.67	1.4823	H	19.5618	-7.2845	0.4477
O	17.5989	-7.9895	1.7894	H	19.3947	-5.4226	0.8071
C	18.3242	-6.7769	2.2839	H	15.8922	-7.0283	3.4813
C	19.539	-6.4753	1.2862	H	15.6587	-5.2811	2.7627
C	15.7528	-6.413	2.5014	H	20.8657	-5.7703	2.9961
C	20.9204	-6.5073	2.0949	H	21.1219	-7.5865	2.4865
C	22.0976	-6.0631	1.1035	H	21.7464	-6.1956	0
O	14.479	-6.8472	1.8596	H	22.3645	-4.9446	1.2944
C	13.2898	-6.0524	1.8825	H	23.0369	-6.7264	1.2944
C	11.9971	-6.7122	1.9612	H	11.9392	-7.8749	2.019
C	13.3565	-4.5992	1.8143	H	14.3911	-4.0658	1.7538
C	10.7765	-5.9258	1.9678	H	9.7435	-6.4618	2.0306
C	12.1328	-3.8114	1.8217	H	12.1885	-2.6484	1.7677
C	10.8396	-4.4732	1.8963	H	5.7912	-5.2256	2.37
O	9.6371	-3.6925	1.8897	H	8.1924	-1.381	2.2373
C	8.4122	-4.1925	2.4323	H	3.578	-3.8497	2.1924
O	8.393	-5.3253	3.007	H	5.9759	0	2.0545
C	7.1139	-3.3776	2.3165	H	2.3423	-2.4405	3.8919
C	5.8328	-4.0628	2.3017	H	0.7655	-1.4437	3.5125
C	7.1637	-1.9288	2.2274	H	0	-3.822	3.8548
C	4.6036	-3.2961	2.2017	H	4E-4	-3.5521	1.9704
C	5.9322	-1.1625	2.1258	H	2.2389	-4.7767	1.7185
C	4.6462	-1.8431	2.1131	H	2.4766	-4.8496	3.6058
O	3.4319	-1.0871	2.0103	H	0.1743	-6.2538	3.722
C	1.4898	-2.2664	3.1164	H	0.2418	-6.361	1.8226
C	0.6709	-3.6365	2.92	H	2.5102	-7.5705	1.9061
C	1.6923	-4.868	2.7438	H	2.6407	-7.2993	3.7857
C	0.878	-6.251	2.7929	H	0.4021	-8.6975	4.0916
C	1.9063	-7.4789	2.8987	H	0.4111	-9.0525	2.2214
C	1.0777	-8.8291	3.151	H	2.7229	-10.226	2.4276
C	2.0861	-10.0534	3.3884	H	2.7911	-9.81	4.284
C	1.2389	-11.3758	3.7158	H	0.913	-11.8846	2.719
H	1.435	-1.0144	1.189	H	1.8962	-12.115	4.3324
H	2.3498	-2.6756	1.0239	H	0.2926	-11.0877	4.3324
H	16.6109	-6.1354	0.5095				

Table S2. List of calculated the first 25 excited states with oscillator strengths (f) for optimized structure of EHPDB molecule.

The Excited State	Transition		ΔE [eV], λ [nm], Oscillator Strength [a.u.]
1	123 -> 124	0.70335	Singlet-A, 4.1305 eV 300.17 nm f = 0.2260 $\langle S^{*2} \rangle \geq 0.000$
2	118 -> 124	-0.27413	Singlet-A, 4.8001 eV 258.30 nm f = 0.0911 $\langle S^{*2} \rangle \geq 0.000$
	121 -> 124	-0.36861	
	121 -> 127	0.15271	
	122 -> 124	0.23654	
	123 -> 126	0.44480	
3	120 -> 124	-0.34653	Singlet-A, 4.8415 eV 256.09 nm f = 0.0528 $\langle S^{*2} \rangle \geq 0.000$
	122 -> 124	-0.25683	
	122 -> 125	0.32247	
	123 -> 125	0.43452	
4	118 -> 124	-0.15895	Singlet-A, 4.8737 eV 254.39 nm f = 0.3359 $\langle S^{*2} \rangle \geq 0.000$
	120 -> 124	-0.15580	
	121 -> 127	-0.12444	
	122 -> 124	0.50773	
	122 -> 125	0.16938	
	123 -> 125	0.10294	
	123 -> 126	-0.34003	
5	118 -> 124	0.45562	Singlet-A, 4.8894 eV 253.58 nm f = 0.1100 $\langle S^{*2} \rangle \geq 0.000$
	121 -> 124	0.24850	
	121 -> 127	0.10203	
	122 -> 124	0.29195	
	123 -> 126	0.30331	
6	120 -> 124	0.25940	Singlet-A, 5.0289 eV 246.54 nm f = 0.0202 $\langle S^{*2} \rangle \geq 0.000$
	122 -> 125	-0.37178	
	123 -> 125	0.53377	
7	118 -> 124	-0.40403	Singlet-A, 5.3687 eV 230.94 nm f = 0.0098 $\langle S^{*2} \rangle \geq 0.000$
	121 -> 124	0.53980	
	123 -> 126	0.16477	
8	122 -> 126	0.70133	Singlet-A 5.5626 eV 222.89 nm f = 0.0002 $\langle S^{*2} \rangle \geq 0.000$
9	121 -> 126	-0.28317	Singlet-A, 5.7308 eV 216.35 nm f = 0.1536 $\langle S^{*2} \rangle \geq 0.000$
	123 -> 127	0.62473	
10	119 -> 124	0.24260	Singlet-A, 5.8430 eV 212.19 nm f = 0.1021 $\langle S^{*2} \rangle \geq 0.000$
	120 -> 124	0.48546	
	122 -> 125	0.40384	
11	119 -> 124	0.65286	Singlet-A, 5.8942 eV 210.35 nm f = 0.0240 $\langle S^{*2} \rangle \geq 0.000$
	120 -> 124	-0.15430	
	122 -> 125	-0.17068	
12	118 -> 125	0.27758	Singlet-A, 6.0051 eV 206.46 nm f = 0.0013 $\langle S^{*2} \rangle \geq 0.000$
	121 -> 125	0.64849	
13	120 -> 125	0.11877	Singlet-A 6.1379 eV 202.00 nm f = 0.0024 $\langle S^{*2} \rangle \geq 0.000$
	122 -> 127	0.68693	
14	118 -> 125	0.62777	Singlet-A, 6.3183 eV 196.23 nm f = 0.0122 $\langle S^{*2} \rangle \geq 0.000$
	121 -> 125	-0.27155	
15	118 -> 125	-0.12436	Singlet-A, 6.3308 eV 195.84 nm f = 0.2456 $\langle S^{*2} \rangle \geq 0.000$
	118 -> 126	0.55308	

	121 -> 126	0.31534	
	123 -> 127	0.13476	
16	119 -> 126	0.37406	Singlet-A, 6.4302 eV 192.81 nm f = 0.0009 <S**2>0.000
	120 -> 126	0.56814	
	121 -> 127	-0.11596	
17	119 -> 126	0.41361	Singlet-A, 6.4543 eV 192.09 nm f = 0.0068 <S**2>0.000
	120 -> 126	-0.38587	
	121 -> 127	-0.16811	
	123 -> 129	0.31762	
	123 -> 131	0.12462	
18	116 -> 124	0.23025	Singlet-A, 6.4716 eV 191.58 nm f = 0.1179 <S**2>0.000
	117 -> 124	0.59557	
	121 -> 126	0.14132	
	123 -> 129	-0.15735	
19	117 -> 124	0.13988	Singlet-A, 6.4811 eV 191.30 nm f = 0.0034 <S**2>0.000
	118 -> 126	-0.13327	
	119 -> 126	-0.34348	
	120 -> 126	0.12315	
	123 -> 129	0.49678	
	123 -> 131	0.19739	
	123 -> 133	0.10558	
20	122 -> 128	0.37823	Singlet-A, 6.5932 eV 188.05 nm f = 0.0112 <S**2>0.000
	123 -> 128	0.55861	
21	116 -> 124	0.20560	Singlet-A, 6.6481 eV 186.50 nm f = 0.7486 <S**2>0.000
	117 -> 124	-0.21538	
	118 -> 126	-0.23947	
	119 -> 125	0.21078	
	120 -> 125	0.43376	
	121 -> 126	0.22520	
22	116 -> 124	-0.11393	Singlet-A, 6.6743 eV 185.76 nm f = 0.0803 <S**2>0.000
	119 -> 125	0.65434	
	121 -> 126	-0.10887	
23	112 -> 124	0.19937	Singlet-A, 6.7207 eV 184.48 nm f = 0.0936 <S**2>0.000
	116 -> 124	0.46500	
	117 -> 124	-0.17961	
	118 -> 127	-0.15722	
	120 -> 125	-0.23204	
	121 -> 127	-0.16804	
	122 -> 128	0.13126	
	123 -> 133	-0.13578	
24	107 -> 124	0.15305	Singlet-A, 6.7372 eV 184.03 nm f = 0.0015 <S**2>0.000
	109 -> 124	0.26722	
	110 -> 124	-0.11988	
	111 -> 124	0.19258	
	112 -> 124	0.37539	
	115 -> 124	-0.33331	
	116 -> 124	-0.15318	
	117 -> 124	0.10588	
	120 -> 125	0.10294	
25	118 -> 127	0.19228	Singlet-A, 6.7947 eV 182.47 nm f = 0.0245 <S**2>0.000
	121 -> 127	0.21709	
	122 -> 128	0.48744	

Table S3. List of atomic coordinates for ‘planar’ EHPDB molecule.

Atom	X	Y	Z	Atom	X	Y	Z
C	5.47221	-2.5107	-0.60355	H	-10.23004	1.17922	1.29781
C	-8.36095	0.6968	0.22883	H	-9.8744	-1.50468	-0.21298
O	-9.40905	1.10694	-0.66462	H	-10.40326	-1.35721	1.47605
C	-9.77589	0.48124	0.57779	H	-8.21632	2.67209	1.02497
C	-10.44645	-0.8687	0.48434	H	-7.16712	1.48542	1.85367
C	-7.5601	1.80383	0.87121	H	-12.47003	-0.12974	0.71867
C	-11.9042	-0.76885	0.01581	H	-11.92316	-0.24832	-0.9574
C	-12.58935	-2.13099	-0.10555	H	-12.06563	-2.77879	-0.82896
O	-6.50586	2.28139	0.03726	H	-12.60462	-2.66137	0.86213
C	-5.30563	1.62408	0.01339	H	-13.63213	-2.02738	-0.44545
C	-4.32343	2.20238	-0.80822	H	-4.58109	3.10741	-1.36065
C	-4.99838	0.45943	0.73022	H	-5.73375	-0.02747	1.36993
C	-3.05488	1.64129	-0.91316	H	-2.30108	2.10473	-1.54657
C	-3.71964	-0.10115	0.62848	H	-3.46885	-1.00818	1.181
C	-2.75459	0.48314	-0.18589	H	2.19216	1.1939	-0.12605
O	-1.53805	-0.19479	-0.29163	H	-0.32046	-2.2673	-0.55797
C	-0.34738	0.48732	-0.21758	H	4.21594	-0.22473	-0.28934
O	-0.26804	1.68749	-0.07975	H	1.71232	-3.71281	-0.73686
C	0.80844	-0.43497	-0.33055	H	5.42346	-1.59827	1.36278
C	2.09576	0.11564	-0.26092	H	5.76511	-3.33185	1.34584
C	0.67427	-1.82605	-0.50097	H	7.8058	-2.19416	1.97041
C	3.2316	-0.68624	-0.35595	H	8.05161	-2.86737	0.36064
C	1.79831	-2.63362	-0.6002	H	7.65893	-0.59086	-0.65686
C	3.08899	-2.0743	-0.53074	H	7.32997	0.0699	0.94753
O	4.111	-2.96026	-0.65428	H	9.67135	-0.5212	1.66507
C	5.98795	-2.383	0.8297	H	9.99448	-1.19774	0.06735
C	7.4936	-2.09	0.91643	H	9.5793	1.06237	-0.97497
C	7.91473	-0.7027	0.41286	H	9.25435	1.73951	0.62222
C	9.41002	-0.42028	0.59476	H	11.59711	1.14814	1.34974
C	9.84067	0.96285	0.09565	H	11.92195	0.46959	-0.24711
C	11.33503	1.24648	0.27903	H	11.50415	2.72691	-1.29083
C	11.76613	2.6294	-0.22093	H	11.17939	3.40508	0.30521
C	13.26003	2.90345	-0.03344	H	13.87388	2.16538	-0.57767
H	6.03464	-3.29306	-1.13621	H	13.5376	3.90409	-0.40215
H	5.58344	-1.57559	-1.17684	H	13.54658	2.84885	1.0308
H	-7.78272	-0.16538	-0.12775				

Table S4. List of calculated the first 25 excited states with oscillator strengths (f) for ‘planar’ EHPDB molecule.

The Excited State	Transition		ΔE [eV], λ [nm], Oscillator Strength [a.u.]
1	123 -> 124	0.70328	Singlet-A, 3.7065 eV 334.50 nm f = 0.2535 $\langle S^2 \rangle \geq 0.000$
	117 -> 124	-0.15514	
	118 -> 124	0.15592	
2	119 -> 124	-0.35303	Singlet-A, 4.1199 eV 300.94 nm f = 0.0739 $\langle S^2 \rangle \geq 0.000$
	120 -> 124	0.12629	
	121 -> 124	-0.35605	
	122 -> 124	0.39191	
3	120 -> 124	-0.31977	Singlet-A, 4.4230 eV 280.31 nm f = 0.0097 $\langle S^2 \rangle \geq 0.000$
	122 -> 125	0.28814	

	123 -> 125	0.54506	
4	121 -> 124	-0.39317	Singlet-A, 4.4371 eV 279.42 nm f = 0.1201 <S**2>0.000
	121 -> 127	0.16869	
	122 -> 124	-0.28707	
	123 -> 126	0.46020	
5	120 -> 124	0.33583	Singlet-A, 4.5315 eV 273.60 nm f = 0.0463 <S**2>0.000
	122 -> 124	-0.24274	
	122 -> 125	-0.35422	
	123 -> 125	0.39292	
	123 -> 126	-0.14252	
6	118 -> 124	-0.11928	Singlet-A, 4.5857 eV 270.37 nm f = 0.2036 <S**2>0.000
	119 -> 124	0.30990	
	120 -> 124	0.11627	
	121 -> 124	0.12768	
	121 -> 127	0.10476	
	122 -> 124	0.40008	
	122 -> 125	-0.20588	
	123 -> 125	0.20816	
	123 -> 126	0.26267	
7	117 -> 124	-0.12542	Singlet-A, 4.7730 eV 259.76 nm f = 0.0305 <S**2>0.000
	118 -> 124	0.12843	
	119 -> 124	-0.32172	
	121 -> 124	0.43825	
	121 -> 127	0.16494	
	123 -> 126	0.33756	
8	121 -> 126	-0.23526	Singlet-A, 5.2327 eV 236.94 nm f = 0.1533 <S**2>0.000
	122 -> 126	0.11869	
	123 -> 127	0.62160	
9	119 -> 125	0.13200	Singlet-A, 5.2791 eV 234.86 nm f = 0.0591 <S**2>0.000
	120 -> 124	-0.35113	
	121 -> 125	0.40235	
	122 -> 125	-0.37373	
	123 -> 127	0.11784	
10	120 -> 124	0.30226	Singlet-A, 5.3602 eV 231.30 nm f = 0.0563 <S**2>0.000
	121 -> 125	0.54606	
	122 -> 125	0.25095	
11	119 -> 126	-0.11192	Singlet-A, 5.3940 eV 229.86 nm f = 0.0277 <S**2>0.000
	122 -> 126	0.66766	
	123 -> 127	-0.12259	
12	117 -> 124	-0.19378	Singlet-A, 5.4341 eV 228.16 nm f = 0.0031 <S**2>0.000
	118 -> 124	0.58031	
	119 -> 124	0.32559	
13	115 -> 124	0.12820	Singlet-A, 5.5323 eV 224.11 nm f = 0.0036 <S**2>0.000
	117 -> 124	0.60097	
	118 -> 124	0.30094	
	119 -> 124	-0.12426	
14	117 -> 125	0.15184	Singlet-A, 5.6847 eV 218.10 nm f = 0.0237 <S**2>0.000
	118 -> 125	-0.19546	
	119 -> 125	0.50366	
	120 -> 125	-0.27682	
	121 -> 125	-0.16855	
	122 -> 127	-0.25127	

15	118 -> 125	-0.10816	Singlet-A, 5.7222 eV 216.67 nm f = 0.0032 <S**2>0.000
	119 -> 125	0.29022	
	120 -> 125	0.11133	
	122 -> 127	0.59092	
16	116 -> 124	0.13723	Singlet-A, 5.8422 eV 212.22 nm f = 0.2235 <S**2>0.000
	118 -> 126	-0.10566	
	119 -> 126	0.42070	
	120 -> 126	-0.17106	
	121 -> 126	0.39124	
	122 -> 127	-0.11257	
	123 -> 127	0.10427	
17	123 -> 128	-0.17375	Singlet-A, 5.8828 eV 210.76 nm f = 0.0065 <S**2>0.000
	114 -> 124	0.10177	
18	116 -> 124	0.66601	Singlet-A, 5.9471 eV 208.48 nm f = 0.0369 <S**2>0.000
	119 -> 126	0.25900	
	120 -> 125	-0.11406	
	120 -> 126	-0.11429	
	121 -> 126	-0.10412	
	123 -> 128	0.57129	
	123 -> 130	0.11413	
19	119 -> 126	-0.15914	Singlet-A, 6.0095 eV 206.31 nm f = 0.0038 <S**2>0.000
	120 -> 126	0.10989	
	121 -> 127	0.11700	
	123 -> 130	0.59928	
	123 -> 131	-0.16079	
20	123 -> 138	-0.12987	Singlet-A, 6.0471 eV 205.03 nm f = 0.0229 <S**2>0.000
	115 -> 124	0.34686	
	117 -> 124	-0.11531	
	117 -> 126	-0.22305	
	118 -> 126	0.10840	
	119 -> 127	0.19956	
	120 -> 125	0.10035	
	121 -> 127	0.38777	
21	123 -> 126	-0.13044	Singlet-A, 6.1044 eV 203.11 nm f = 0.4016 <S**2>0.000
	123 -> 130	-0.15059	
	115 -> 124	0.39247	
	117 -> 126	0.22897	
	119 -> 125	0.10519	
	119 -> 126	-0.13490	
	120 -> 125	0.24255	
	121 -> 126	0.15604	
	121 -> 127	-0.23771	
22	122 -> 127	-0.13954	Singlet-A, 6.1447 eV 201.77 nm f = 0.0063 <S**2>0.000
	122 -> 128	-0.11262	
	123 -> 128	0.17716	
	112 -> 124	0.10525	
	113 -> 124	-0.10746	
	114 -> 124	0.31542	
	115 -> 124	0.26422	
	116 -> 124	-0.11814	
	119 -> 126	0.10383	
	120 -> 125	-0.29128	

	120 -> 126	0.34837	
	121 -> 126	0.12390	
23	114 -> 124	-0.18238	Singlet-A, 6.1484 eV 201.65 nm f = 0.0947 <S**2≥0.000
	115 -> 124	-0.14505	
	119 -> 126	0.17306	
	120 -> 125	0.22991	
	120 -> 126	0.55219	
24	117 -> 125	-0.13124	Singlet-A, 6.1771 eV 200.72 nm f = 0.0022 <S**2≥0.000
	118 -> 125	0.62448	
	119 -> 125	0.28416	
25	112 -> 124	0.17334	Singlet-A, 6.2169 eV 199.43 nm f = 0.1866 <S**2≥0.000
	113 -> 124	-0.11065	
	114 ->124	0.45043	
	115 -> 124	-0.19646	
	120 -> 125	0.26942	
	122 -> 127	-0.11567	
	122 -> 128	-0.14503	
	123 -> 128	0.14629	

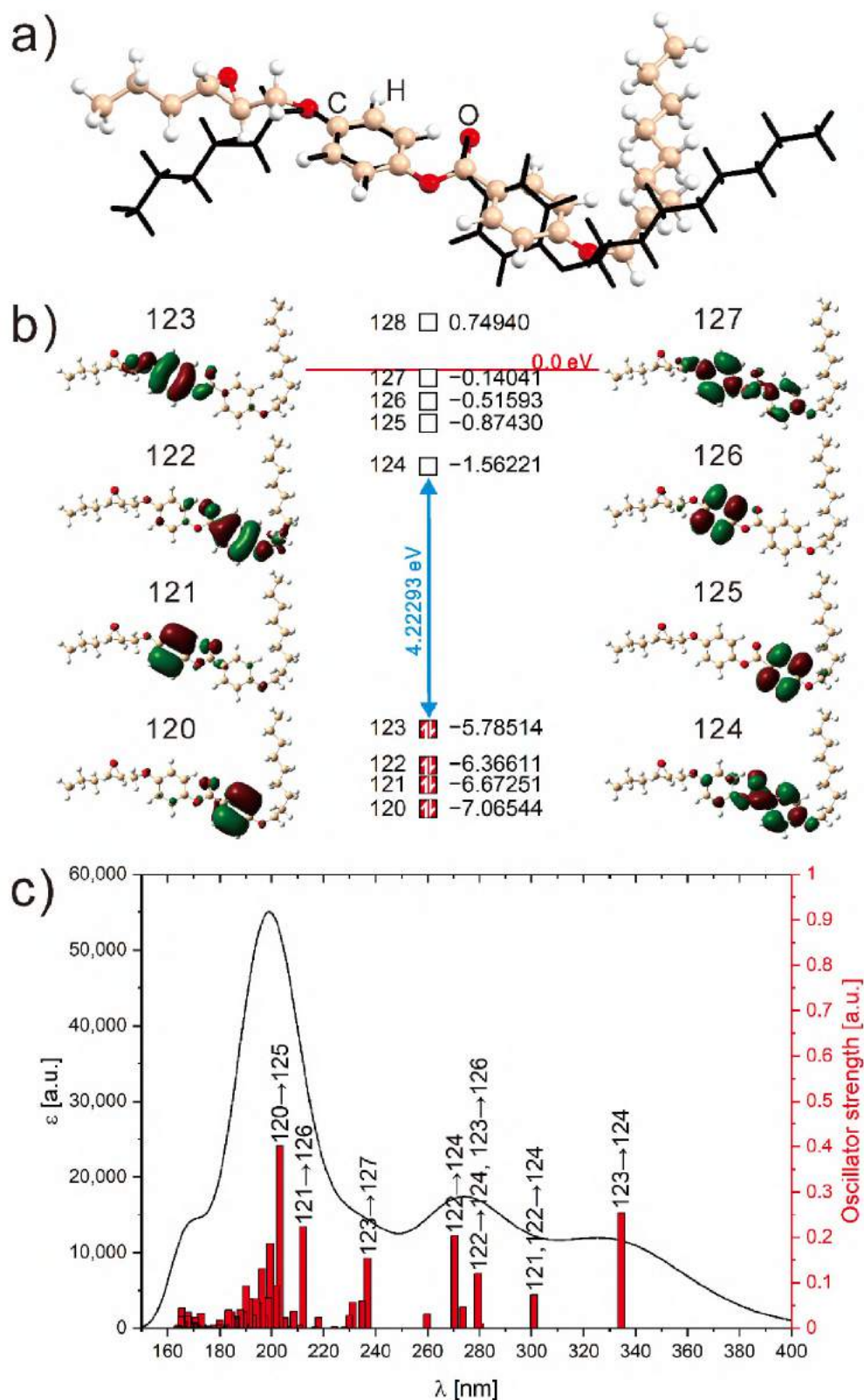


Figure S6. Model of 'planar' EHPDB molecule used for calculation (a). Black sticks indicate an overlapped optimized structure of EHPDB. Energy level diagram in eVs with calculated frontier molecular orbitals (b). Blue arrow and number correspond to the HOMO-LUMO gap. Calculated UV-Vis spectrum for 'planar' EHPDB molecule (c). Red bars indicate electronic transitions with the largest contributions while legend above bars indicate electronic states involved in transition.

Article

Nanocomposites Based on Antiferroelectric Liquid Crystal (S)-MHPOBC Doping with Au Nanoparticles

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Abstract: Modification of the physical properties of the (S)-MHPOBC antiferroelectric liquid crystal (AFLC) by doping with low concentrations of gold nanoparticles is presented for the first time. We used several complementary experimental methods to determine the effect of Au nanoparticles on AFLC in the metal–organic composites. It was found that the dopant inhibits the matrix crystallization process and modifies the phase transitions temperatures and switching time, as well as increases the helical pitch and spontaneous polarization, while the tilt angle slightly changes. We also showed that both the LC matrix and Au nanoparticles show strong fluorescence in the green light range, and the contact angle depends on the temperature and dopant concentration.

Keywords: antiferroelectric liquid crystal; Au nanoparticles; metal–organic composites; localized surface plasmon resonance



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1. Introduction

The process of doping soft matter with various types of nanomaterials, such as nanoparticles, nanorods, and quantum dots, is a fairly convenient alternative to designing new materials without a typical chemical approach. This way is technically simpler, economically cheaper, and what is the most important, it gives very promising effects: modification of the parameters of a soft matter matrix (liquid crystal, and polymer). It should also be noted here that a more sophisticated approach is the liquid crystal gold nanoparticles (NPs) synthesis, in which the mesogenic unit is chemically bonded to the NP's surface. This approach produces materials with a high Au content, as opposed to doping, where agglomeration occurs at higher concentrations [1–13]. Hybrid materials such as liquid crystal + nanomaterials have been the subject of research for the last few years [14–16]. Since nematic liquid crystals (NLCs) are the most widely used in the industry, great interest is focused on them as a matrix for the production of nanocomposites. However, it seems that more complex phases such as the ferroelectric SmC* or the antiferroelectric SmC*_A can also be modified in the same way. Our research and this paper are an attempt to fill in the gap, in which the antiferroelectric SmC*_A phase is an organic matrix doped with Au nanoparticles. We have chosen gold nanoparticles, because they are very often used as a dopant, and their synthesis and properties are well-described in the literature [17,18]. Below, we provide a brief overview of the research of nanocomposites based on liquid crystals and Au nanoparticles to demonstrate the need for our research and explain our motivation.

Considering calamitic non-chiral nematic liquid crystals, it was shown that, after doping with Au nanoparticles (decorated with different surfactants), depending on the liquid crystal (LC), the photoluminescence (PL) increases, the red shift appears for the absorption band as a result of localized surface plasmon resonance (LSPR), the nematic-isotropic phase transition temperature and threshold voltage decrease, and the Fréedericksz voltage for both $H = 0$ and $H > 0$ increase [19–22]. It was also found that the relaxation frequency decreases after doping, as explained by the generation of a local electric field in the nanocomposite [23]. In another case, the absorption increased after doping with Au NPs, and a blue shift was noted for LSPR [24,25]. On the other hand, by doping polymer dispersed LC (PDLC) with Au nanoparticles, the significant increase of the relative light transmission was noted and explained by the increase in a local electric field by excitation of the nanoparticles' surface plasmons [26]. Tiwari et al. gave direct evidence for the presence of surface plasmons in NLC doped with Au NPs [27]. A liquid crystal elastomer exhibiting the N phase was also doped with Au nanoparticles by Montazami et al., who showed the increase of the nematic–isotropic phase transition temperature and stiffness of the nanocomposite (Young modulus increases) [28]. Likewise, Au nanoparticles have been used as a dopant to NLCs from the cyanobiphenyls homologous series (nCB). Depending on the homolog of the defect-free layers, increases in the dielectric anisotropy $\Delta\epsilon$, the optical anisotropy Δn , elastic constant K , viscosity γ , and broadening of the N phase were found [29–33]. The modifications of the material parameters were explained as a results of creating clusters of two different types: (a) nanoparticle clusters with LC molecules (for smaller concentrations) and (b) nanoparticle clusters among themselves (for higher concentrations) [34]. In turn, the red shift of LSPR after doping was explained by the anchoring of LC molecules to the Au surface [35]. For the binary mixtures 5CB:6CB (various concentrations) doped with Au NPs, a large decrease in the viscosity γ , threshold voltage, and τ_{off} was found [36]. An admixture of Au NPs also caused an increase of the specific electric conductivity in the N and Is phases and broadening of the N and SmA phases [37–39]. Au nanoparticles have been also used to align NLC molecules. For example, Urbański et al. achieved homeotropic ordering in planar cells, which is presumably due to Au NP accumulation at the interface polymer/NLC and opposes the polymer effects [40], while Hegmann et al. found that Au NPs with hydrophobic ligands introduced into NLC can form birefringent stripe domains separated by homeotropically aligned LC molecules [41,42]. In turn, Yoshida et al. stabilized the blue phase by trapping nanoparticles in disclination lines, which lowered the empty volume and free energy [43].

The discotic liquid crystals (DLC) have also been used as a matrix for doping with Au nanoparticles, and depending on the liquid crystal used as the host matrix, it was found, for example, that after doping the decrease of the Col_h–Is phase transition temperature, an increase of the optical energy gap and an increase of the conductivity was observed [44,45].

A few papers presented the influence of gold nanoparticles on ferroelectric liquid crystals (FLC). For example, after doping a decrease of the Goldstone mode's relaxation frequency and the SmA*–SmC* phase transition temperature, an increase of the conductivity was found [46]. Additionally, after doping with Au NPs, an increase of the photoluminescence (PL) intensity without changing the qualitative PL spectrum, the memory effect and an increase of the tilt angle were observed [15,16,47]. Fluorescent LC materials are still a rare group, because the shapes and structures of many fluorescent moieties are not optimal for mesophase formation [48]. FLCs were also doped with Au nanorods, similar to how it was done by Podgornov et al. and Shukla et al. [49,50].

As shown above, mainly nematic liquid crystals have been used as a matrix for doping with Au nanoparticles, although discotic and polymeric and even ferroelectric liquid crystals have also been used. However, no antiferroelectric liquid crystals were doped. Therefore, we prepared two composites based on the well-known AFLC—(S)-MHPOBC doped with various concentrations of Au nanoparticles: Composite 2 (0.2 wt. % Au NPs) and Composite 3 (0.5 wt. % Au NPs) and compare their properties with the undoped sample—Composite 1 (0.0 wt. % Au NPs) by using the following complementary methods:

polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction, fluorescent confocal polarizing microscopy, ultraviolet–visible spectroscopy, optical/scanning electron microscopy, contact angle, and electro-optic measurements. It has been shown how many AFLC parameters can be changed by a small amount of Au nanoparticles in a surprising and intriguing manner. We interpret the results of the research on new hybrid materials on various planes, determining the influence of the admixture on both the phase sequence and the helix pitch, fluorescence, morphology, and wettability of the layers, as well as electro-optic parameters (switching time, tilt angle, and spontaneous polarization). We use the nomenclature recommended by the IUPAC—in particular, the phase composed of chiral molecules is denoted by adding an asterisk to the name of the phase [51].

2. Results and Discussion

2.1. Results of Polarizing Optical Microscopy (POM) Method

By using the polarizing microscopy method, textures for the SmA^* , SmC^*_α (which is often noted as ferrielectric one, and other designations $\text{SmC}^*_{1/3} = \text{SmC}^*_{\text{FI}}$), SmC^* , SmC^*_γ , SmC^*_A , SmI^* , and $\text{SmI}^* + \text{Cr}_1$ phases were registered with decreasing temperatures for Composites 1–3. As an example, the textures for Composite 3 are presented in Figure 1, while all the Composites are in Figure S1 (in the Supplementary Materials). It is seen that all the Composites studied exhibit a rich phase polymorphism, which is usually observed for optically pure (S)-MHPOBC or (R)-MHPOBC [52]. In the SmA^* phase, director n (also represents the optical axis in this uniaxial phase) is oriented along the smectic layer normal k [51].

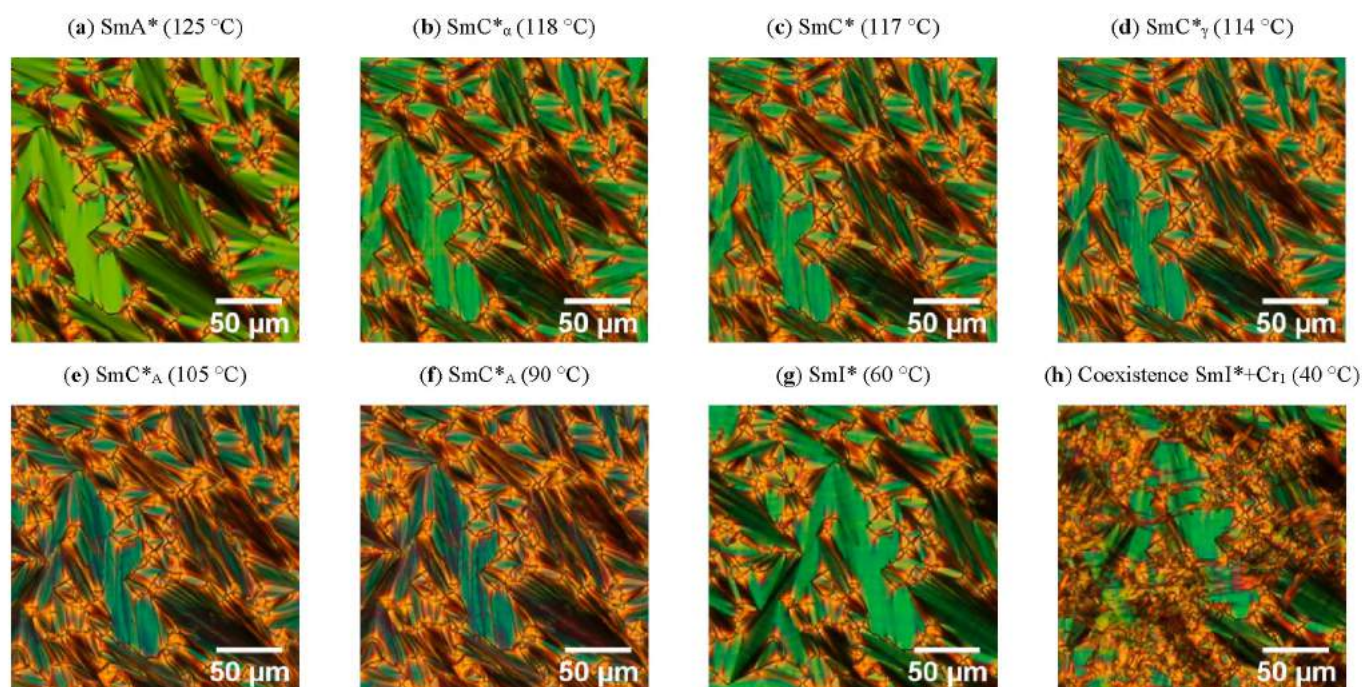


Figure 1. Textures under cross-polarizers registered during cooling with a rate of 2 °C/min for Composite 3: SmA^* (a), SmC^*_α (b), SmC^* (c), SmC^*_γ (d), SmC^*_A at 105 °C (e), SmC^*_A at 90 °C (f), SmI^* (g), and the coexistence of two phases, SmI^* and Cr_1 (h). All images present the same sample area.

On cooling from the isotropic liquid, the SmA^* phase starts to form as anisotropic, elongated ovules (commonly called batonnets) for all Composites. Finally, the observed textures for the SmA^* phase in all Composites contain topological focal conic defects leading to focal conic fan textures in the SmA^* phase for Composites 1–3. The smectic layers are arranged in Dupin’s cyclides, which include a pair of focal conics [53]. The considered focal conic defects are usually common when the molecules anchor strongly to the cell

surface or other nucleation points (e.g., an admixture or spacers) and the defects appear in random places on the texture (Supplementary Materials Figure S2) [54]. No effect of the Au nanoparticles was observed on both fans and focal conic defects in the texture of the SmA* phase.

The SmC*_α sub-phase appeared immediately below the SmA* phase and is usually very narrow (1 to 2 °C), although there are some reports about a wider SmC*_α sub-phase (ca. 3 °C) in the analogs of (S)-MHPOBC [55–57]. Both the SmA* and SmC*_α phases are uniaxial, with good approximation (optical axis is along the normal layer). However, the SmC*_α phase shows a helical structure with tilted molecules, but the tilt angle is much smaller than in the SmC* phase, and the helix pitch is usually of the order of several smectic layers [53]. As is seen in Figure 1 and Figure S1, though the texture of the SmC*_α phase is slightly different from the texture of the SmA* phase (the visible ripples formation), the difference between textures of the SmC*_α and SmC* phases was difficult to find; they were similar, and the distinction between these phases was based on a subtle color change and more visible striation along the fan regions. Usually, the focal conic defects degeneration in the form of their breaking and separation is observed at the transition to the SmC*_γ phase. However, it was not observed by us for Composites 1–3. In our case, the SmC*_γ phase was identified on the basis of the appearance of strong striations across the fans regions [51]. During further cooling down, the SmC*_A was recognized by a slight color change. Focal conic defects persist in the phase transition and are present throughout the SmC*_A phase. Moreover, the stripes appear in the low temperature range of this phase (Figures 1 and S1). The transition between the SmC*_A and SmI* antiferroelectric phases is well-visible as the color of the texture changes. Dierking also reported about striations in the SmC*_A, as well as in the SmI*, phases for pure MHPOBC [53]. At a low temperature range, the SmI* phase, the nucleation of the crystallization is visible (Figures 1 and S1), which results in the coexistence of these two phases over a wide temperature range, until full crystallization occurs. Interestingly, the crystallization process (nucleation and crystallization propagation) was much faster in a pure matrix (Composite 1) than in Composites 2 and 3. For the pure matrix, the Cr₁ phase can be observed practically already at 40 °C (Figure 1h). This proves that the admixture inhibits the crystallization process.

Summarizing, the addition of Au nanoparticles did not change the texture of all the phases identified in the Composites studied. Therefore, one can conclude that an admixture has no visible effect on the molecular ordering (e.g., the focal conic defects). Focal conic defects disappear only during the crystallization process. At the present stage, it is difficult to conclude whether the admixture modifies the nucleation or the crystallization propagation. However, due to the article's nature, we do not focus on the crystallization process.

2.2. Results of Differential Scanning Calorimetry (DSC) Method

The calorimetric curves with three strong anomalies were recorded during heating for Composites 1–3 (Figure 2). Additionally, the anomalies corresponding to the following phase transitions: SmC*_A–SmC*_γ, SmC*_γ–SmC*, and SmC*_α–SmA* are visible in the insets in Figure 2a. The SmC*–SmC*_α phase transition is not visible, although it was observed by Chandani et al. for (R)-MHPOBC at a very low heating rate [58]. It is related to the rate of temperature changes. In our case, the heating/cooling rate was equal to 10 °C/min, and therefore, only one anomaly corresponding to the SmC*–SmC*_α–SmA* phase transition is visible. Moreover, four crystal phases are visible, which has not been previously reported for pure (S)-MHPOBC. Interestingly, additional phases were registered within the crystal region for Composite 3 (with the highest Au nanoparticles amount) (Figure 2b,c). During cooling, the same phase transitions were registered, except the transitions in the crystal region (see Supplementary Materials Figure S3). Figure S3b presents the influence of Au nanoparticles on the transition temperatures of the Iso–SmA*, SmC*_A–SmI*, and SmI*–Cr₁ phase transitions. The Iso–SmA* phase transition for Composite 2 is decreased by 0.3 °C as compared to Composites 1 and 3, while the SmI*–Cr₁ phase transition for Composite 3 is

increased by 0.4 °C as compared to Composites 1 and 2. In turn, the SmC^*_A – SmI^* phase transition temperature is not disturbed by the admixture. To sum up, the admixture of the Au nanoparticles slightly and differently influences the particular phase transitions during cooling and heating as well. The individual phase transition temperatures were determined based on the so-called onset T_o or peak T_p temperatures. The latter is marked with an asterisk in the phase sequences (only applies to transitions around 120 °C due to the difficulty of determining T_o) (Table 1).

It was found that the enthalpy change ΔH decreases with the increasing concentration for the Iso– SmA^* phase transition during cooling, as was also observed by Tripathi et al. for other liquid crystalline compounds [59]. In turn, the total ΔH connected with the phase transitions between sub-phases during cooling does not change, within the uncertainty limit, after doping.

Table 1. Phase sequences during heating and cooling for Composites 1–3 obtained by texture observations and the DSC method. The asterisk next to temperature denotes the peak temperature T_p , $\Delta T = \pm 0.1$ °C.

	Composite 1	
	Cr ₁ (53.1 °C) Cr ₂ (68.8 °C) Cr ₃ (73.7 °C) Cr ₄ (81.8 °C) SmC^*_A (*119.1 °C) SmC^*_γ (*119.9 °C) $\text{SmC}^*/\text{SmC}^*_\alpha$ (*122.0 °C) SmA^* (148.5 °C) Iso	
Heating	(S)-MHPOBC—Fernandes et al. [60]	
	SmC^*_A (118.2 °C) SmC^*_γ (119.2 °C) SmC^* (120.7 °C) SmC^*_α (*122.0 °C) SmA^*	
	Composite 2	
	Cr ₁ (52.5 °C) Cr ₂ (68.9 °C) Cr ₃ (73.7 °C) Cr ₄ (81.9 °C) SmC^*_A (*119.1 °C) SmC^*_γ (*119.9 °C) $\text{SmC}^*/\text{SmC}^*_\alpha$ (*122.0 °C) SmA^* (148.4 °C) Iso	
Cooling	Composite 3	
	Cr ₁ (60.0 °C) Cr ₂ (65.3 °C) Cr ₂ ' (70.5 °C) Cr ₃ (73.8 °C) Cr ₄ (81.9 °C) SmC^*_A (*119.9 °C) SmC^*_γ (*120.7 °C) $\text{SmC}^*/\text{SmC}^*_\alpha$ (*122.4 °C) SmA^* (148.9 °C) Iso	
	Composite 1	
	Iso (149.4 °C) SmA^* (122.0 °C) $\text{SmC}^*_\alpha/\text{SmC}^*$ (*119.5 °C) SmC^*_γ (*118.1 °C) SmC^*_A (65.0 °C) SmI^* (27.3 °C) Cr ₁	
	Composite 2	
	Iso (149.1 °C) SmA^* (121.8 °C) $\text{SmC}^*_\alpha/\text{SmC}^*$ (*119.5 °C) SmC^*_γ (*117.6 °C) SmC^*_A (63.1 °C) SmI^* (27.2 °C) Cr ₁	
	Composite 3	
	Iso (149.4 °C) SmA^* (122.3 °C) $\text{SmC}^*_\alpha/\text{SmC}^*$ (*119.8 °C) SmC^*_γ (*118.2 °C) SmC^*_A (64.8 °C) SmI^* (27.6 °C) Cr ₁	

The enthalpy change ΔH connected with the chosen phase transitions during heating is presented in Figure 2d. The greatest impact of the Au NPs on the enthalpy changes was found for the Cr₄– SmC^*_A phase transition in Composite 3 (an increase of ca. 26 J/g). Hence, even a small concentration of Au NPs (0.2 and 0.5 wt. %) strongly influences the transition between the crystal and liquid crystalline phases. Such an increase in the enthalpy change is inextricably linked with an increase of the entropy change ΔS in Composites 2 and 3. It cannot rule out that the surfactant-decorated Au nanoparticles (with a chemical structure similar to the end fragments of (S)-MHPOBC molecules) interact in a specific way with the LC molecules and are responsible for the energetic hindering of this phase transition. It is seen that ΔH after doping decreases in Composite 2 but increases in Composite 3 in the SmA^* –Iso phase transition. The slight increase in ΔH for the Cr₂–Cr₃ phase transition was registered for Composite 2. Concluding, the Au NPs admixture affects more the transition parameters within the crystal than the liquid crystalline phases during heating.

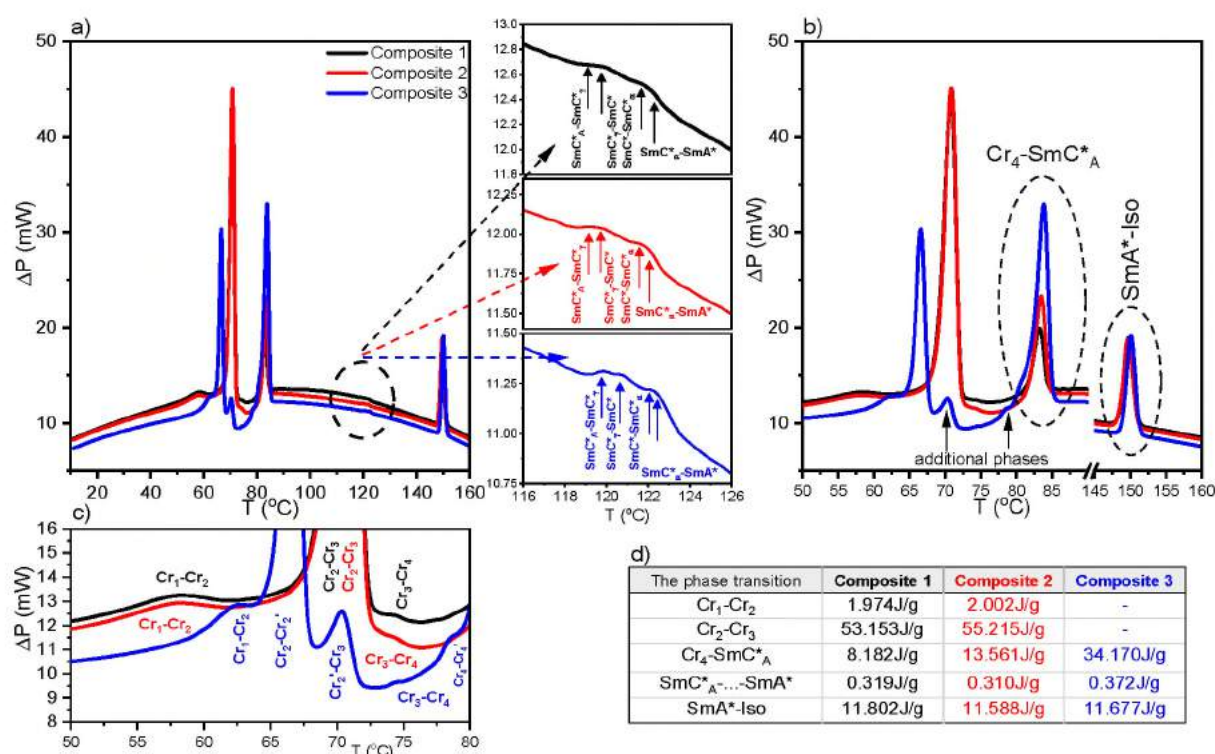


Figure 2. Calorimetric curves registered during heating for Composites 1–3 (a). Insets in (a) represent an enlarged temperature range of 116–126 °C for individual Composites. Enlarged temperature range of the DSC curves registered for Composites 1–3 with additional phase transition for Composite 3 marked by a vertical arrow (b), DSC curves at low temperature range (c), and table with the enthalpy changes for the chosen phase transitions (d).

Fernandes et al. determined the phase transition temperatures for (S)-MHPOBC by using differential scanning calorimetry with a 0.2 °C/min heating rate [60], and they are also presented in Table 1 for comparison. It seems that transition temperatures obtained by us for Composite 1 are in good agreement with those obtained by Fernandes et al., except that based on the onset temperature T_o ($SmC^*_A-SmC^*_\gamma$ and $SmC^*_\gamma-SmC^*$). Additionally, Fernandes et al. showed that, for the high optical purity of MHPOBC, the ferroelectric SmC^*_β sub-phase exists instead of the ferroelectric SmC^* phase (which appears for a lower purity of MHPOBC), while all sub-phases can exist in the intermediate optical purity compound [60]. According to the manufacturer, the chemical purity of our (S)-MHPOBC is 99%, but the optical purity is not specified. Taking the above into account, we assumed that we observed the ferroelectric SmC^* phase in the LC matrix. It should also be mentioned here that the temperature range of the SmI^* phase in (R)-MHPOBC strongly decreased with the decreasing cooling rate (from ca. 35 °C at 2.0 °C/min to disappearance at 0.5 °C/min), while the $SmC^*_A-SmI^*$ phase transition temperature was not dependent on the cooling rate [61]. We recorded the calorimetric curves with a fairly high heating/cooling rate equal to 10 °C/min; therefore, two distinct phase transitions were registered on the temperature scale: $SmC^*_A-SmI^*$ and SmI^*-Cr_1 . In turn, as we show below, in the case of TLI measurements, the time domain measurement is longer and the crystallization occurs at much higher temperatures, which essentially resulted in the coexistence of the SmI^* and Cr_1 phases. Such coexistence was registered by the polarizing microscope method at a 2 °C/min rate, as presented in Figure 1 and Figure S1.

2.3. Results of Transmitted Light Intensity (TLI) Method

Due to the difficulty in determining by DSC and texture observation methods the $SmC^*-SmC^*_\alpha$ and $SmC^*_\alpha-SmC^*$ phase transition temperatures, the complementary method,

i.e., TLI, was used. The transmitted light intensities versus temperature registered during cooling for Composites 1–3 are presented in Figure 3a, while Figure 3b,c present the enlarged temperature ranges 116–124 °C and 40–70 °C, respectively. As is seen, both the $\text{SmA}^*-\text{SmC}^*_\alpha$ and $\text{SmC}^*_\alpha-\text{SmC}^*$ phase transitions are visible as subtle changes in the intensities (small structural changes between these phases and sub-phase) for all Composites 1–3 studied. During further decreasing of the temperature at a rate of 2 °C/min, the transmitted light intensity increases down to the middle of the SmC^*_A phase by about 30%. Within the SmC^*_A phase, a parabolic shape for the TLI signal is observed for each sample. This phenomenon is probably connected with layer thickness changes, as it was revealed by the X-ray diffraction method, and will be presented below. A relatively small but distinct change in TLI dependence is visible at ca. 52 and 54 °C for Composite 1 and Composites 2 and 3, respectively (Figure 3c), which could be attributed to the initiation of the SmI^*-Cr_1 phase transition. Indeed, the SmI^* phase begins to coexist with the emerging Cr_1 phase, as confirmed by the inclusion of the Cr_1 phase in the SmI^* phase visible in the textures (Figure 1). The formation moment of the first nucleation points is related to the discontinuities in Figure 3c marked by dashed arrows. Below the discontinuity is the range of the two-phase coexistence. On the other hand, an anomaly around 26 °C associated with SmI^*-Cr_1 phase transition is visible in the DSC curves. It is most likely related to the different cooling rates in the various methods (10 °C/min in DSC and 2 °C/min in TLI). The $\text{SmC}^*_\alpha-\text{SmC}^*$ phase transition temperatures with the initiation temperature for the coexistence of the SmI^*-Cr_1 phases in Composites 1–3 are presented in Figure 3d. The phase coexistence of SmI^*-Cr_1 was not detected by the DSC method (the anomaly connected with the SmI^*-Cr_1 transition is narrow), which is probably connected to a higher cooling rate in the DSC method.

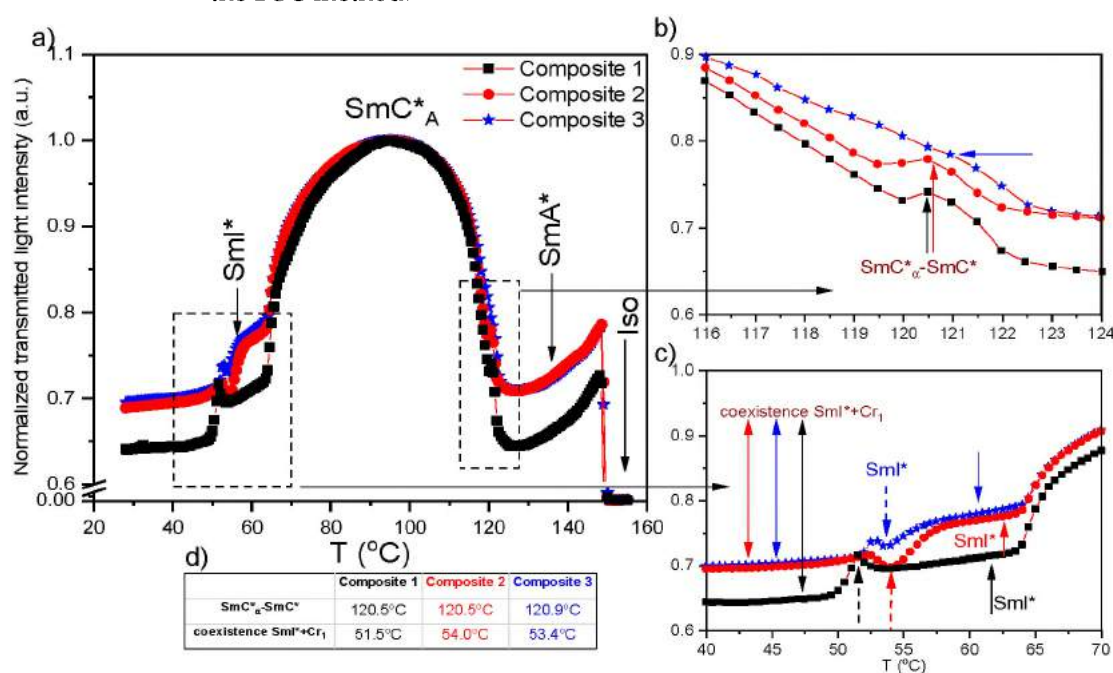


Figure 3. Temperature dependence of normalized transmitted light intensity during cooling (a), the selected temperature range in the vicinity of the $\text{SmC}^*_\alpha-\text{SmC}^*$ (b), and the $\text{SmC}^*_\text{A}-\text{SmI}^*-\text{Cr}_1$ phase transition (c), determined phase transition temperature for $\text{SmC}^*_\alpha-\text{SmC}^*$, and temperatures at which are observed the coexistence regime (d); the accuracy of the temperature determination is equal to ± 0.1 °C.

On the other hand, the Cr_1-Cr_2 , $\text{Cr}_4-\text{SmC}^*_\text{A}$, and SmA^*-Iso phase transitions are very well visible for all studied composites during heating (Figure S4). Interestingly, within the SmC^*_A phase, a monotonic decrease in the light intensity with increasing temperature is

visible (in contrast to a parabolic shape for cooling). In turn, the subtle $\text{SmC}^*-\text{SmC}^*_\alpha$ phase transition is visible in the enlargement presented in Figure S4c.

2.4. Results of X-ray Diffraction (XRD) Method

Representative diffraction patterns for the Composite 3 collected on cooling are shown in Figure 4a. The patterns of the SmA^* and SmC^*_A phases are similar, therefore the sub-phases SmC^*_α , SmC^*_γ , and the SmC^* phase existing in a narrow temperature range cannot be distinguished [61]. The hexatic SmI^* phase of (S)-MHPOBC is not observed in diffraction results due to slow cooling [61]—crystallization starts before the $\text{SmC}^*_\text{A}-\text{SmI}^*$ phase transition is reached. The position of the low-angle peak at $2\theta \approx 2.6^\circ$ is related to the smectic layer spacing (smectic layer thickness) D by the Bragg equation [62]. The temperature dependence of D is presented in Figure 4b. The layer thickness D is practically the same for all Composites 1–3 and equal to 34.5–34.8 Å in the SmA^* phase (increases slowly on cooling) while in the SmC^*_A phase, it decreases on cooling down to 33.4–33.6 Å at 95–100 °C, therefore the relative change of D in all smectic phases is ca. 4%. However, the increase of D on cooling below 95 °C (and decreasing of TLI signal at the same time) is an indicator of a subsequent hexatic phase, similarly to what was observed for other compounds [63,64]. Similar smectic layer spacing D was reported by Inui et al. for AFLC (TFMHPDOPB) while smaller ($D_{\text{max}} \sim 31 \text{ Å}$) for fluorinated orthoconic compound was reported by Milewska et al. [65,66]. Summarizing, both the transmitted light intensity and XRD methods confirm the existence of a hexatic phase below the anticlinic SmC^*_A one as was observed by the polarizing microscopy method.

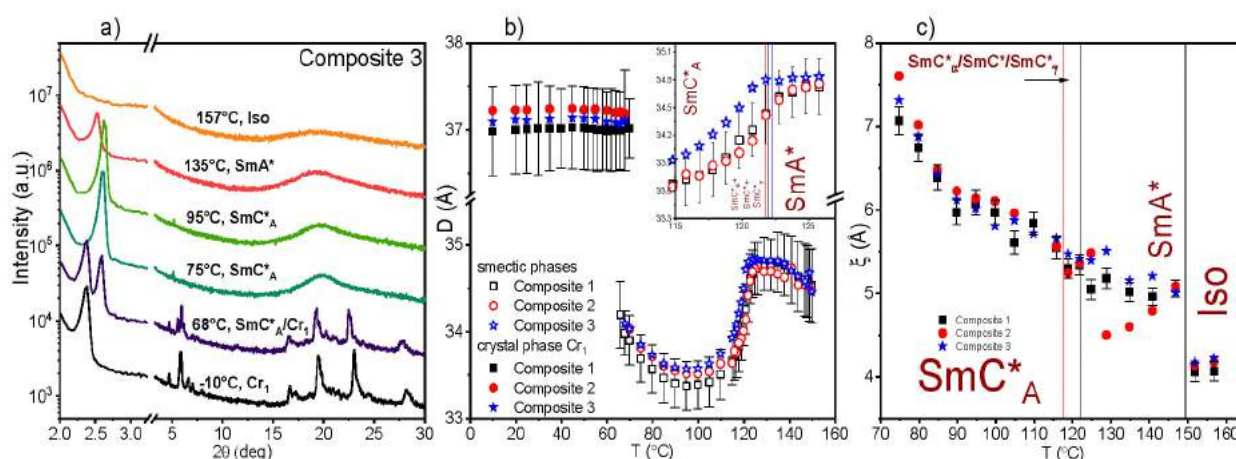


Figure 4. Diffraction patterns at several chosen temperatures as an example for Composite 3 (a), the temperature dependence of the smectic layer spacing/interplanar distance in a crystal phase (b), and the correlation length (c) on cooling for all Composites. The inset in (b) shows the high temperature range with colored lines representing the $\text{SmA}^*-\text{SmC}^*_\alpha$ phase transition temperature obtained by DSC method for all Composites.

The crystallization is indicated by arising of numerous sharp diffraction peaks, which are observed for all samples at 68–70 °C. The low-angle peak characteristic for a crystal phase is observed at $2\theta \approx 2.4^\circ$, which corresponds to the distance between the crystal planes (37.0–37.2 Å), constant with the decreasing temperature down to −10 °C.

The wide diffuse maximum at $2\theta \approx 20^\circ$ in the diffraction patterns of the isotropic liquid and smectic phases arises from the short-range positional order. In the scattering vector space ($q = 4\pi\sin\theta/\lambda$) the maximum has a form of a Lorentz distribution, $I(q) = (1 + \xi^2(q-q_0)^2)^{-1}$. The correlation length of the short-range order ξ , as well as its temperature dependence, is almost the same for studied Composites 1–3 except for the Composite 2 in the SmA^* phase where little decrease with temperature is visible (Figure 4c). The fast increase of ξ below 80 °C is caused by approaching the hexatic SmI^* phase [63]. The diffraction results show that the admixture of Au nanoparticles does not affect signif-

icantly the structural parameters of the smectic and the crystal phases for (S)-MHPOBC. Additionally, the crystallization process is not disturbed by Au admixture.

2.5. Results of Fluorescence Confocal Polarizing Microscopy (FCPM) Method

The fluorescence images in subsequent slices of the samples registered in the spectral range 490–590 nm in SmC^*_A phase (at 68 °C) are presented in Figure 5 while for selected temperature in this spectral range as well as in 430–455 nm are presented in Figure S5. Fluorescence was observed in both wavelength ranges for all Composites 1–3, however with different intensities. Interestingly, for Composites 2 and 3 the decrease in fluorescence intensity is visible in the 490–590 nm range with decreasing temperature in the SmC^*_A phase (68, 88 °C) as well as at higher temperatures for Composite 3. The places with more intense color at a particular slice of the Composites 1–3 can mean: a greater accumulation of Au nanoparticles (see Supplementary Materials Figure S5c) or structure defects (which is especially good visible for green fluorescence for all Composites 1–3 at 118 °C and 122 °C, Supplementary Materials Figure S5a,b). Au nanoparticles may accumulate in structural defects to minimize the free energy of the system, which causes an increase in fluorescence in these places. In turn, pure Au nanoparticles fluorescence is visible in the green (490–590 nm) range while it is not observed in blue (430–455 nm) as is seen in Figures 5 and S5c. We can state that this fluorescence is coming from Au nanoparticles because the surfactant decorated Au NPs (1-octanethiol) does not have fluorescence due to the lack of appropriate chromophores fragment.

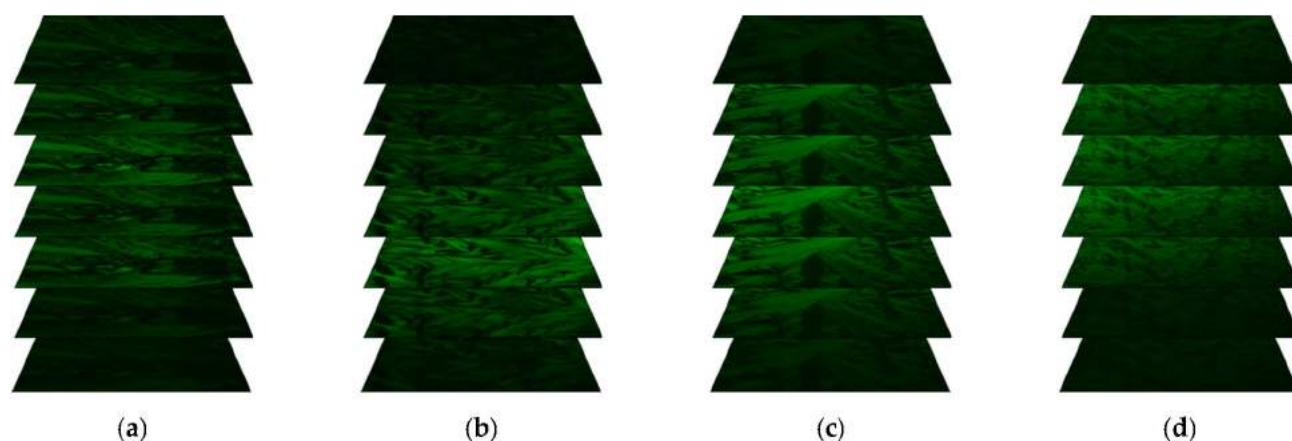


Figure 5. Fluorescence images in subsequent slices for the Au nanoparticles (at room temperature) (a), Composite 1 (b), Composite 2 (c), and Composite 3 (d) registered in the spectral ranges 490–590 nm. For Composites 1–3, the images were registered at 68 °C (SmC^*_A).

To sum up, from the qualitative point of view, the doping (S)-MHPOBC with Au nanoparticles affects the fluorescence intensity depending on the temperature (the phase). This can be a valuable application determinant for a given hybrid material. We have also analyzed the fluorescence images numerically (see Supplementary Materials Figures S6 and S7). It turned out that both in the green and blue ranges, there was an increase in the fluorescence intensity after doping with Au NPs and the increase is greater in the green light range.

2.6. Results of Ultraviolet–Visible (UV–Vis) Spectroscopy—Free Droplet Method

The temperature dependence of the helix pitch determined for Composites 1–3 is presented in Figure 6. The maximum absorbance along with the uncertainty was appointed based on fitting the Gaussian curve to the experimental data and the helix pitch values $p = \lambda_s / 2n_{\text{av}}$ in the SmC^* and $p = \lambda_s / n_{\text{av}}$ in the SmC^*_A phases were calculated (the average refractive index $n_{\text{av}} = 1.5$ for the SmC^* and SmC^*_A phases) [67,68]. The helix pitch in the SmC^*_γ phase was calculated as for the antiferroelectric SmC^*_A phase. A similar situation was for the SmI^* phase which is typically antiferroelectric. The helix pitch at the

SmC^*_γ – SmC^*_A phase transition is equal to 599.4, 603.5, and 661.2 nm for Composites 1, 2, and 3, respectively, and down to ca. 90 °C is almost constant. Below 90 °C for Composites 2 and 3, the helix pitch decreases with the decreasing temperature down to ca. 70 °C, where it slightly increases. It is most likely related to the SmC^*_A – SmI^* phase transition. In turn, for Composite 1 ((S)-MHPOBC) a very subtle increase in the helix pitch from about 90 °C is visible. In the SmI^* phase, the helix pitch is almost the same within the uncertainty for Composites 1 and 2 while it is larger about 48 nm for Composite 3.

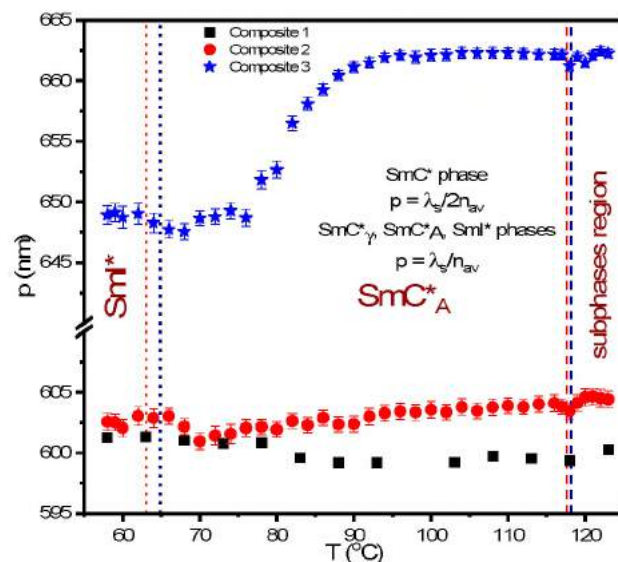


Figure 6. Temperature dependence of the helix pitch for Composites 1–3 obtained during cooling together with the relations between the helix pitch and the wavelength in the maximum transmission for the antiferroelectric and ferroelectric phases. The dashed and dotted vertical lines indicate the SmC^*_γ – SmC^*_A and SmC^*_A – SmI^* phase transition temperatures obtained by DSC.

However, the situation is different in the sub-phases and the SmC^*_A phase. Already in the SmC^*_γ phase, an increase in helix pitch is visible after the addition of Au nanoparticles (by approx. 5 nm for Composite 2 and approx. 62 nm for Composite 3). The value of the helix pitch for Composite 1 ((S)-MHPOBC) is similar as that observed for (R)-MHPOBC by Chandani et al. [58]. A decrease of the helix pitch with decreasing temperature is visible for Composites 2 and 3 in the SmC^*_A phase, in particular for Composite 3 from about 95 °C, which may be due to an increase in viscosity and a decrease in the mobility of Au NPs with decreasing temperature. In turn, in the low temperature range of the SmC^*_A phase, the helix pitch is practically the same for Composites 1 and 2, while, for Composite 3, it is about 45 nm longer. The matrix at low temperatures may act as a self-assembling medium for the nanoparticles. The agglomeration process (the overlapping of thiol chains of one nanoparticle with the another) at such a concentration (0.5 wt. %) should also be taken into account and may be responsible for the increase of helical pitch in Composite 3. It should be remembered the Au nanoparticles of 2–4 nm diameter are the same size as the smectic layer thickness (the length of the LC molecule). Thus, such an object disturbs the order of a large number of molecules producing structural defects as well as may be responsible for shifting the entire layer in the space, which will affect the helical pitch. Therefore, the increase in helical pitch after doping in Composites 2 and 3 is due to the presence of Au NPs and is greater for Composite 3 due to the presence of more Au NPs in Composite 3 than Composite 2. The greater number of Au nanoparticles in Composite 3 means that more of them will be located between smectic layers, so the helix pitch will be increased more. Taking into account the results of XRD, i.e., no influence of Au nanoparticles on the thickness of the smectic layers, it seems that decorated Au nanoparticles in the (S)-MHPOBC matrix accumulates mainly between the smectic layers, increasing the helix pitch. It is also possible that some of the Au nanoparticles will be

located in the smectic layers, which should be visible in the change of the tilt angle of the molecules and will be discussed later in the paper.

2.7. Results of Optical Microscopy (OM)/Scanning Electron Microscopy (SEM) Methods

High-resolution digital optical images were registered for two different types of illumination (ring and coaxial) for Au nanoparticles and pristine Composites as well as Au nanoparticles and Composites cooled to room temperature after being heated to 155 °C and kept at this temperature for 5 min (Figures 7, 8 and S8). The color of pristine Composite 1 was white while pristine Composites 2 and 3 were light pink, because the Au nanoparticles are pink (see Figures 7 and 8). It is seen that the color intensity correlates with the increase in the concentration of Au nanoparticles—it is pinker for Composite 3 with a higher concentration of Au nanoparticles. For pristine Au nanoparticles at 50× and 100× magnification, the network of white lines on the pink area is visible (Figure 7, upper row). In our opinion, these lines are microscale cracks that resulted from the evaporation of the solvent during sample preparation. At 400× and 2000× magnification, chaotically arranged pillars with a length of less than 30 µm are visible in the sub-micro scale. What is interesting, after heating to 155 °C, annealing at this temperature for 5 min, and cooling down to room temperature the color changes to purple and microscale lines are also visible while the pillar's structure is not (Figure 7, bottom row). In our opinion, the pillars visible at room temperature are Au nanoparticles which self-assemble through the chains of surfactant during isothermal evaporation of the solvent (toluene). In turn, heating to 155 °C causes the destruction of these structures due to thermal reorientation of the 1-octanethiol chains. The break of strong Au-S chemical bonds is also possible under the influence of temperature while the transition of surfactant is ruled out because the melting and boiling point of 1-octanethiol are −49 °C and 199 °C, respectively.

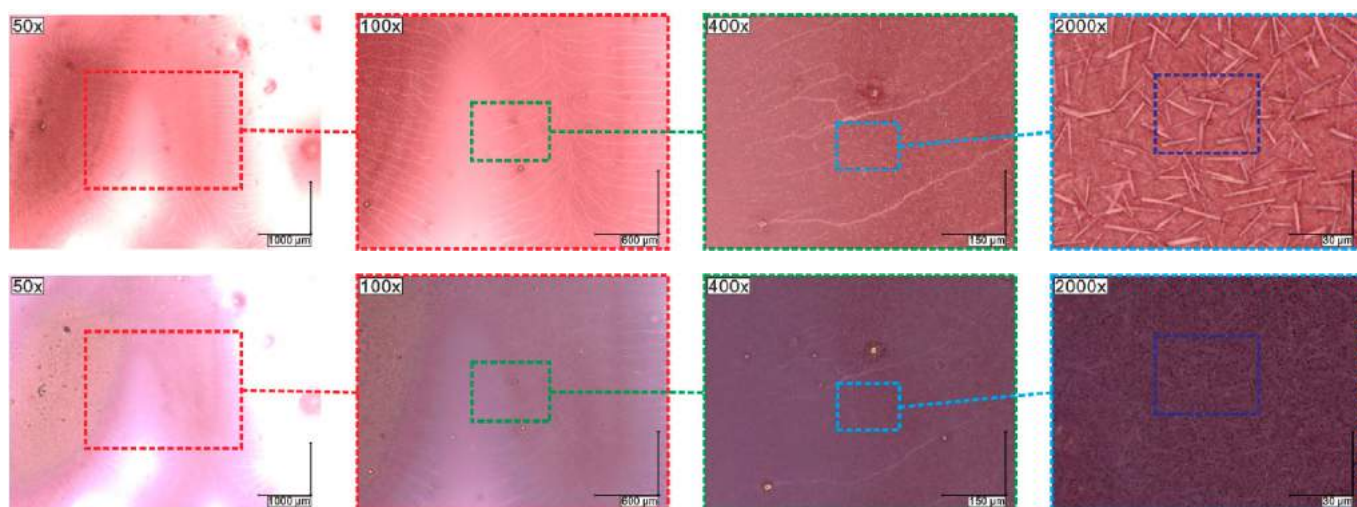


Figure 7. Room temperature digital optical images with ring illumination for pristine Au nanoparticles (**upper row**) and cooled to room temperature after being heated to 155 °C and kept at this temperature for 5 min (**bottom row**). The colored dotted squares represent the enlarged areas.

High-resolution digital optical images registered with coaxial illumination for Composites 1–3 at room temperature are presented in Figure S8 while for cooled to room temperature after being heated to 155 °C and kept at this temperature for 5 min in Supplementary Materials Figure S9. As is seen in Supplementary Materials Figure S8 there is no influence of Au nanoparticles (pillars are not visible) on the images of Composites 2 and 3, they are the same as for Composite 1. Probably, the use of sonication during the preparation of Composites 2 and 3 did not allow the formation of a lamellar structure, visible for pristine Au nanoparticles (prepared without sonication). On the other hand, for Composites 2 and 3, after heating and then cooling to room temperature, dark objects are visible, and invisible

before heating at 155 °C (Figures 8, S8 and S9). For example, for Composite 3, for a magnification of 2000 $\times$, dark objects appear in random places, not observed for pristine Composite 3, and for a magnification of 6000 $\times$, a lot of white dots additionally appear (Figure 8). The same is true for Composite 2, while these objects do not appear for Composite 1 (Supplementary Materials Figure S8). The number of these objects increases with the content of Au nanoparticles—it is higher for Composite 3 (Supplementary Materials Figure S8). In our opinion, annealing of Composites 2 and 3 at 155 °C (above the clearing temperature of (S)-MHPOBC) causes the movement of Au nanoparticles in the liquid crystal matrix (in the isotropic phase) which leads to their agglomeration, visible as dark objects (big aggregates) for a magnification of 2000 $\times$ and white spots (small aggregates) for 6000 $\times$. It should be noted here that before heating Au nanoparticles were well dispersed in the LC matrix and these objects were not visible. In summary, the annealing of pure Au nanoparticles changes their color from pink to purple while the annealing of Composites leads to the melting of the (S)-MHPOBC matrix and the formation of Au nanoparticle agglomerates of various sizes (e.g., white dots approx. 500 nm in diameter).

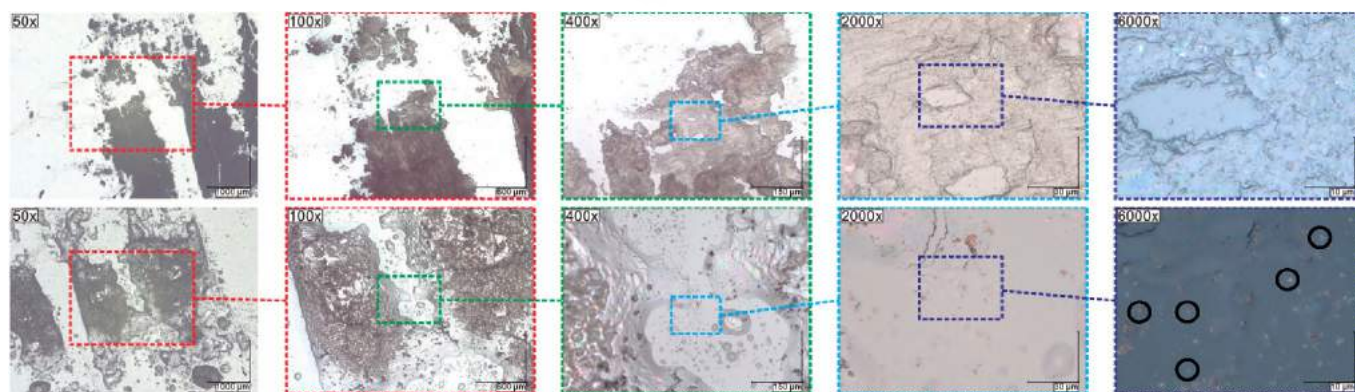


Figure 8. Room temperature digital optical images with coaxial illumination for those pristine (**the first row**) and cooled to room temperature after being heated to 155 °C and kept at this temperature for 5 min in Composite 3 (**second row**). The colored dotted squares represent the enlarged areas.

In SEM images at 50 $\times$ magnification, pristine (S)-MHPOBC forms many crystals while Composites 2 and 3 form larger flakes (Figure S10). For the remaining magnifications, the images are similar for all Composites, there is no visible influence of Au nanoparticles. For the 100 $\times$ and 400 $\times$ magnifications, flat terraces with a large area without any special features while for a magnification of 2000 $\times$ clear needle structures (representing clusters of matrix chains) are visible. On the other hand, SEM images of pristine Au nanoparticles, even at 50 $\times$ and 100 $\times$ magnification, show some irregular morphological structures, and at 400 $\times$ magnification, a very rough surface with numerous small anisotropic structures is visible. However, for 2000 $\times$ and 6000 $\times$, fairly flat terraces appear between these structures. These anisotropic structures appear to be large clusters decorated with Au nanoparticles that stick out above the terrace surface, thereby contributing to the roughness of the surface.

The real colors of the studied materials, obtained by superimposing the SEM images on the optical images, are shown in Figure 9. After evaporation of the solvent (toluene), Au nanoparticles have a strongly pink color, while the (S)-MHPOBC crystals become more and more intensely pink as the concentration of Au nanoparticles grows. As the intensity of the pink color at each image location for Composites 2 and 3 (Figure 9b,c) seems more or less the same, it means that the structures visible on the micrometer scale (terraces) contain well dispersed Au nanoparticles.

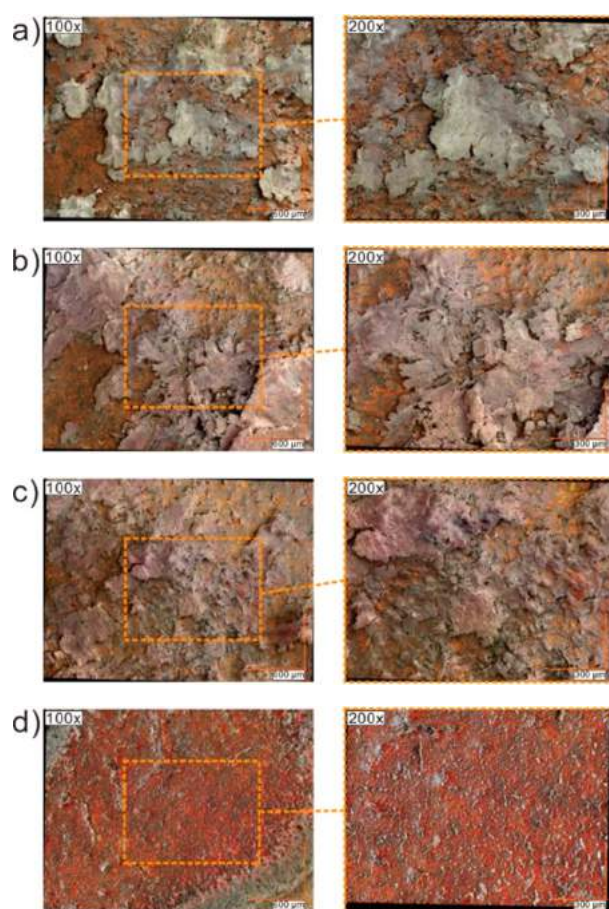


Figure 9. Real colored SEM images for Composite 1 (a), Composite 2 (b), Composite 3 (c), and Au nanoparticles (d) obtained by superimposing the SEM images on the optical images.

2.8. Results of Contact Angle (CA) Measurements

The study of the wettability of the Composites was carried out as a function of temperature. Exemplary water droplets deposited on the studied thin layers of Composites 1–3 and silicon wafer (reference) are shown in Figure S11. The contact angle Θ_{CA} of a pure silicon wafer (as a reference) is temperature independent and equal to ca. 55° in the studied temperature range (Figure 10a). On the other hand, the contact angle for Composites 1–3 in the range from 0°C to ca. 50°C is constant and equal to ca. 90° for Composites 1 and 3 and ca. 100° for Composite 2. Such high contact angles indicate poor wettability of the surface of Composites 1–3 by water in this temperature range. From a temperature of about 50°C , a continuous decrease in the contact angle with increasing temperature is visible, and near the phase transition to the SmC^*_A , in a narrow temperature range, a step is visible (dashed ellipses in Figure 10a), most likely related to the temporary coexistence of crystal and the SmC^*_A phases. A bigger contact angle (weaker wetting) for the Composite 2 at low temperatures (Figure 10b) may be connected with a relatively larger number of alkyl chains (fragments of the 1-octanethiol) terminated with a methyl group which is exposed on interface composite-air (a methyl group is a hydrophobic group decreasing the wettability). In turn, higher wetting of the surface of Composites 2 and 3 compared to Composite 1 is observed in the temperature range of about $40\text{--}80^\circ\text{C}$ (crystal phases region) because the conformational chains change with increasing temperature which improves the wettability. Moreover, the Θ_{CA} for the Composite 3 in the SmC^*_A phase is about 15° higher than for the Composites 1 and 2 (Figure 10c) but to explain this further research is needed.

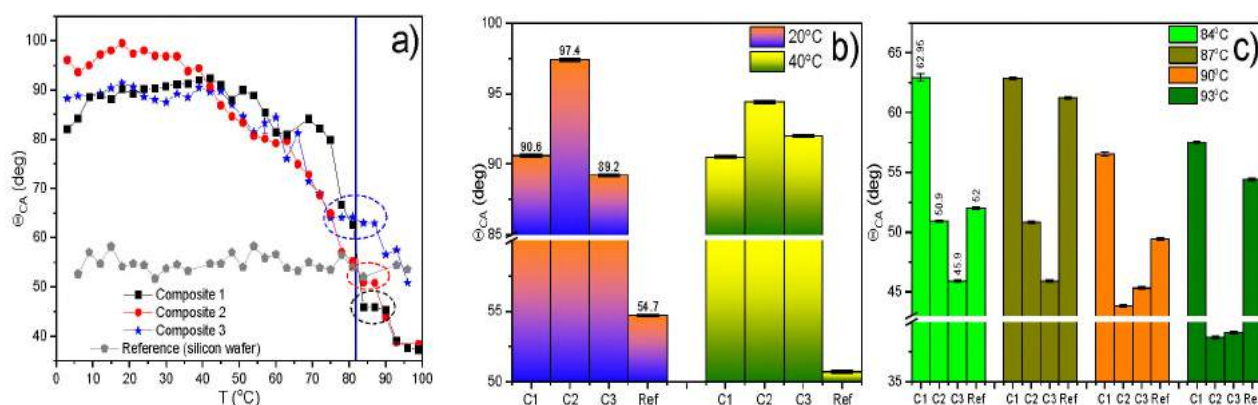


Figure 10. Temperature dependence of the contact angle for Composites 1–3 (C1, C2, and C3), and silicon wafer (Ref) during heating from 0 °C up to 100 °C (a). The dashed ellipses outline the step related to the $Cr-SmC^*_A$ phase transition. Bar chart of contact angle in the crystal phase for two chosen temperatures (b) and in the SmC^*_A phase for the four chosen temperatures (c). Error bar is a sum of systematic uncertainty and standard deviation for left and right drop contact angles.

2.9. Results of Electro-Optic (EO) Measurements

The effect of Au nanoparticles on the switching time was investigated in the broad temperature range (Figures 11 and S12). In the SmC^*_A phase (down to ca. 65 °C) the switching time is shorter than 100 μs while below 65 °C its significant increase is visible for all Composites (which is caused by an increase in viscosity). Such behavior is typical for antiferroelectric liquid crystals [57,69]. In the SmC^*_A phase (up to 95 °C) the switching time is shorter for Composite 3 than for Composite 1 while the longest is for Composite 2 while above 95 °C it is the same for Composites 1 and 3 and ca. 10 μs shorter than for Composite 2. The shorter switching time for Composite 3 relative to Composite 1 may be due to the local field modification (increase) after doping [70]. In our opinion, a shorter switching time for Composite 3 relative to Composite 1 may be due to several reasons. A decrease in the material viscosity after doping, modification of the local field that acts on the molecules, the agglomeration process as well as interactions between LC molecules and Au nanoparticles should be considered [70]. In our case, a shorter switching time for Composite 3 relative to Composite 1 may be due to the local field modification (increase) after doping, as a dominant factor.

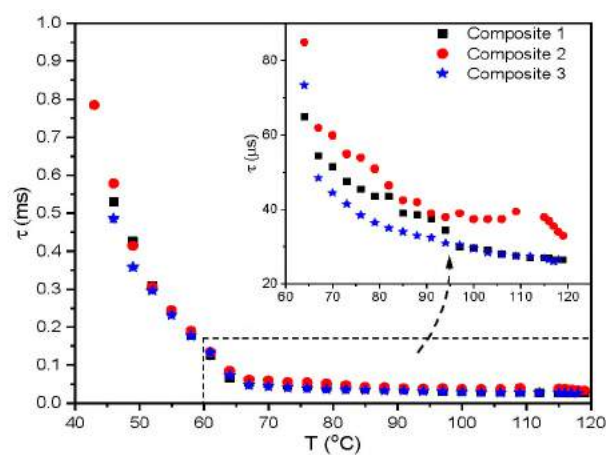


Figure 11. Temperature dependence of the switching time, $f = 50$ Hz, $U = 120$ V. The rectangular dashed area presents the SmC^*_A range at the inset.

The temperature dependence of the tilt angle in the SmC^*_A for all studied Composites is presented in Figure 12. The characteristic plateau is visible below ca. 85 °C for all the samples. At the lowest temperatures, a decrease in the tilt angle indicates the $SmC^*_A-SmI^*$

phase transition. There is no influence of concentration 0.2 wt. % Au nanoparticles on the Θ values (Composite 2) while Θ for Composite 3 is greater than for Composite 1, and this difference decreases as the temperature decreases (e.g., it is ca. 3° at 114°C). This behavior can be explained by the fact that with an increase in Au NPs concentration: (a) statistically, in more places a single smectic layer is disturbed and more smectic layers are disturbed, (b) 3D structures may form in the bulk by Au nanoparticles self-organization or (c) agglomeration process (although decorated NPs were used) can take place [71]. All of this is directly responsible for modifying the arrangement of LC molecules, and hence for changing the tilt angle—the primary order parameter. 1-octanethiol chains on adjacent Au NPs may interact, which may increase the tilt angle of LC molecules. An increase in Au nanoparticles concentration may cause self-assembly processes in many places of LC matrix ((S)-MHPOBC), which increases the tilt angle Θ . However, taking into account that the layer thickness $D(T)$, helix pitch $p(T)$ and tilt angle $\Theta(T)$ for Composites 1 and 2 are practically the same (the helix pitch is only increased by ca. 1 nm), one can assume that the low concentration of Au NPs does not disturb the original liquid crystal order. In turn, for Composite 3 the tilt angle as well as the helix pitch increases while the layer thickness does not change. Therefore, it seems that Au nanoparticles are located both in the layers (modification Θ) and between them (modification p) in Composite 3. The inset in Figure 12 shows a bar diagram with the Θ values for selected temperatures to better visualize the differences between Composite 1 and 3. The tilt angle determined by us is in good agreement with the tilt angle reported for MHPOBC analogous in several papers [72–77].

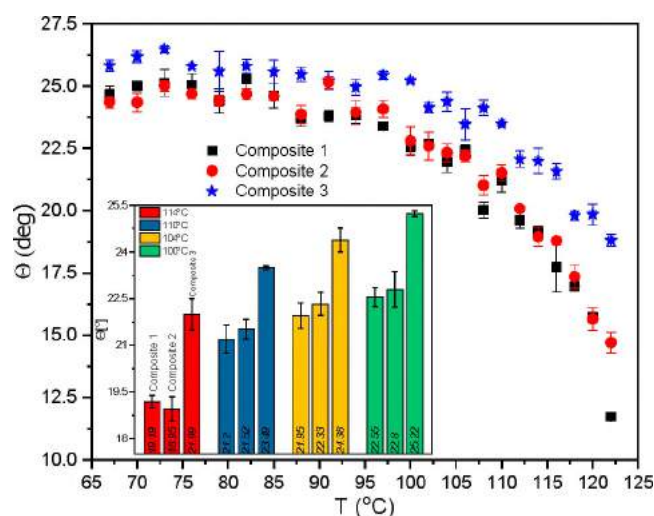


Figure 12. Temperature dependence of the tilt angle for Composites 1–3, $f = 50$ Hz, $U = 120$ V within the SmC^*_A phase. Inset shows the tilt angle for the chosen temperatures.

The spontaneous polarization P_s was determined in the SmC^*_γ , SmC^*_A , and SmI^* phases for all Composites. The results obtained for Composite 1 are in good agreement with the results presented in various papers [73,74,78–80] while for Composites 2 and 3 with the results presented in [81]. Figure 13a presents the spontaneous polarization versus applied voltage U_{AC} in the SmC^*_A (at 117°C) and as is seen the non-zero P_s is observed at 20 V for all Composites. Thus, the Au nanoparticles have no influence on the threshold voltage in this phase. The spontaneous polarization increases with further increasing the applied voltage, but no saturation is visible up to 160 V. The highest P_s is for Composite 3 while the lowest for Composite 1.

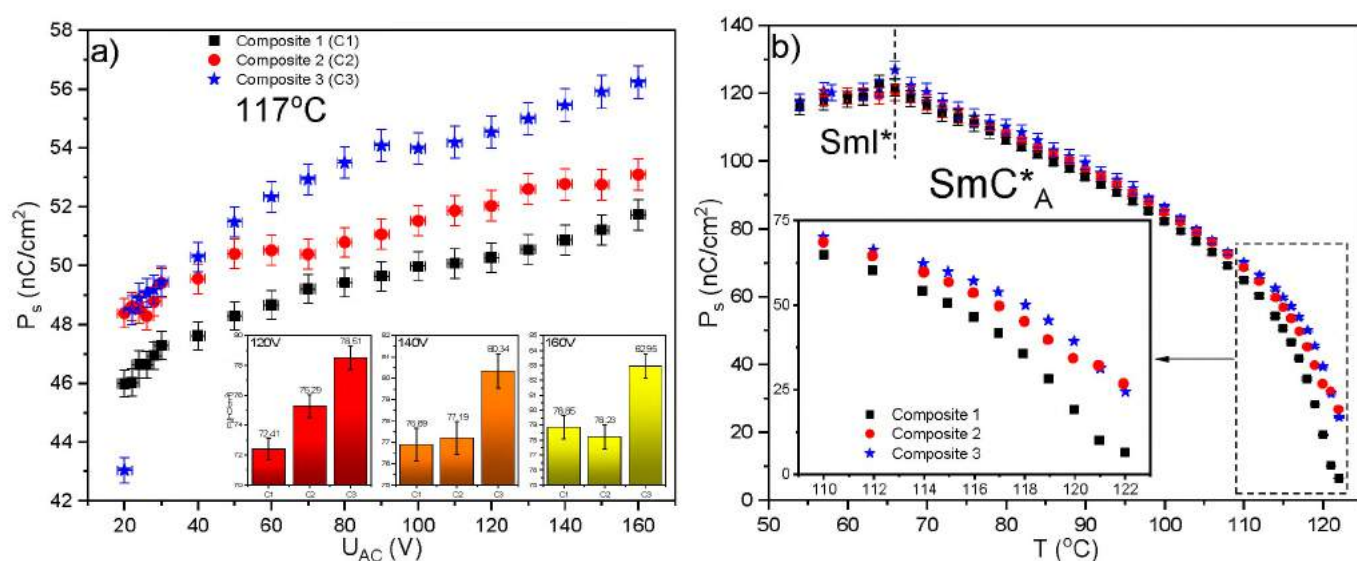


Figure 13. Spontaneous polarization versus applied voltage, $T = 117^\circ\text{C}$, $f = 50\text{ Hz}$ (a). The inset shows the P_s bar graphs for the selected amplitudes at $T = 105^\circ\text{C}$, $f = 50\text{ Hz}$. Temperature dependence of the spontaneous polarization in the SmC*_A and SmI* phases for all Composites (b). An enlarged high temperature range is presented in the inset, $\Delta U_{AC} = \pm 2\text{ V}$, $\Delta P_s = 1\%$.

It is known that the spontaneous polarization depends directly on the dipole moment of the LC molecule therefore its increase may be connected with the better ordering of LC molecules in the Composites 2 and 3 than in Composite 1 or with an effect of localized surface plasmon resonances. The localized plasmon resonance for Au nanoparticles appears in the visible wavelength range [71] and depends on many factors, such as size, shape, dielectric constant, environment, and even the distance between adjacent nanoparticles [82]. The samples of Composites were exposed to white light during the electro-optic measurements which may be responsible for the generation of localized surface plasmon resonance. Localized surface plasmon resonance is known to be associated with the oscillation of electrons on a metallic nanoparticle, excited by light at a frequency corresponding to that of electrons (see Figure 14) [71]. During these oscillations, the electron cloud shifts, and the dipole moment is induced, and consequently, the electric field near the surface of the nanoparticles is strongly amplified. Thus, LC molecules in the vicinity of such nanoparticles will locally sense a greater electric field than the applied external electric field. This enhancement quickly disappears as the distance from the nanoparticle surface increases and the absorption band for Au NPs in the LC matrix can be relatively wide. Due to the relatively large size of nanoparticles (comparable to the length of LC molecules), the plasmonic resonance of a given nanoparticle (enhancement of the electric field) will be felt by the greater number of LC molecules, the higher the concentration of Au in the nanocomposite, as it was observed by us (see Figure 13a). In summarizing, it appears that the LSPR is responsible for the increase in the spontaneous polarization P_s for Composites 2 and 3 relative to Composite 1 down to 90°C (see Figure 13), while below this temperature the spontaneous polarization, within the measurement uncertainty limit, is the same for Composites 1–3. Such a situation at lower temperatures may result, among others, from the increase in matrix viscosity.

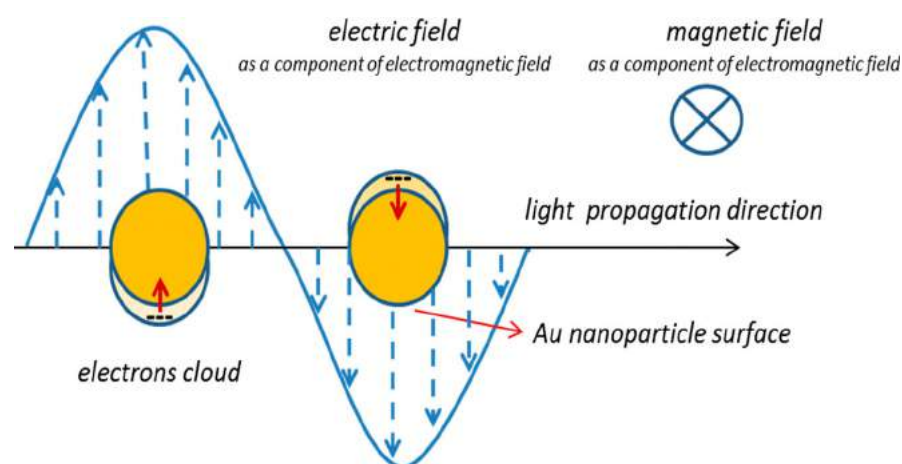


Figure 14. Schematic illustration of the localized surface plasmon resonance for spherical Au nanoparticles. Red arrows mean an induced dipole moment, which is the result of displacement electrons cloud (marked by “—”). The dashed arrows mean electric field lines, and the orange circle represents an Au nanoparticle.

It should be also noted here that, during the measurement of spontaneous polarization, around 97 °C the sample response splits into two peaks (the formation of the two helices) and slight wrinkles on the monodomain appear, which are evidence of the SmC*_A phase [73].

The increase of spontaneous polarization after doping the ferroelectric liquid crystal with Au NPs was reported by several authors. For example, Malik et al. explained this phenomenon by trapping parasitic ions by dopant while Shukla et al. attributed this to the chirality of decorating surfactant and the kind of material used to functionalize Au NPs [83,84]. In turn, two localized surface plasmon resonances were observed in the FLC mixture (CHS1) doped with Au nanorods: longitudinal ($\lambda \approx 851$ nm) and transverse ($\lambda = 541$ nm) [85]. The larger scattering is due to the bigger cross-section. According to Ahmad et al. Au nanoparticles can take colors in the range of orange, red, brown, etc., depending on the core size, and usually show an absorption band in the range of 500–550 nm [86]. The smaller nanoparticles have an absorption maximum of around 520 nm, the larger ones scatter more and the shape of the absorption band is widened with the maximum shifted towards the red light. After aggregation, the conduction electrons near the surface of each nanoparticle are delocalized and divided (shared) by the nearest nanoparticles which change the optical properties by shifting the surface plasmon resonance to lower energies (red shift). Therefore, non-aggregated Au nanoparticles absorb blue light while Au aggregated nanoparticles leads to significant shifts in the frequency of plasmon resonance towards red, broadening the absorption band and changing the solution color [86]. The simulated absorption spectra for Au nanoparticles (20–100 nm) in water turned out that for larger the diameter of nanoparticles, the absorption maximum shifts towards red light and the absorption efficiency initially increases with the size up to diameters equal to 70 nm, and then begins to decrease (radiation scattering begins to dominate over absorption) [87]. The determination of the exact wavelength at which the localized surface plasmon resonance occurs for the Au nanoparticles used requires further research. However, due to the spherically symmetric Au nanoparticles shape, only one absorption band associated with LSPR is expected. The influence of Au nanoparticles concentration on the (S)-MHPOBC absorption spectra will be also studied and presented in the next paper.

3. Materials and Methods

3.1. Materials

Commercially available liquid crystal (LC) abbreviated as (S)-MHPOBC (Sigma Aldrich Co., Saint Louis, MO, USA) was used as a liquid crystal matrix. Its chemical structure is shown in Figure 15a. The LC was in the form of white flakes and was used without chemical pre-purification. The commercially available 1-octanethiol-functionalized Au nanoparticles (spherical, diameter 2–4 nm) as a 2% *w/v* solution in toluene (Sigma Aldrich, Co., Saint Louis, MO, USA, Figure 15b) were used as an admixture. The size of Au nanoparticles was chosen as comparable to the average lengths of LC molecules. Due to the lack of commercial Au nanoparticles without surfactant, it is important to highlight the advantages and disadvantages of the decoration process. It is important because the surfactant chains can be largely responsible for modifying the matrix parameters. The nanoparticle functionalization is aimed at: (a) ensuring and controlling the miscibility of nanoparticles with the matrix (elimination of phase segregation processes) and (b) elimination or strong reduction of the agglomeration process. However, the functionalization procedure also has some disadvantages: (a) inhibition of direct interactions between the nanoparticle and the matrix molecules and (b) additional difficulties in the interpretation of the results for composites due to the presence of an additional chemical reagent—the decorating factor [82].

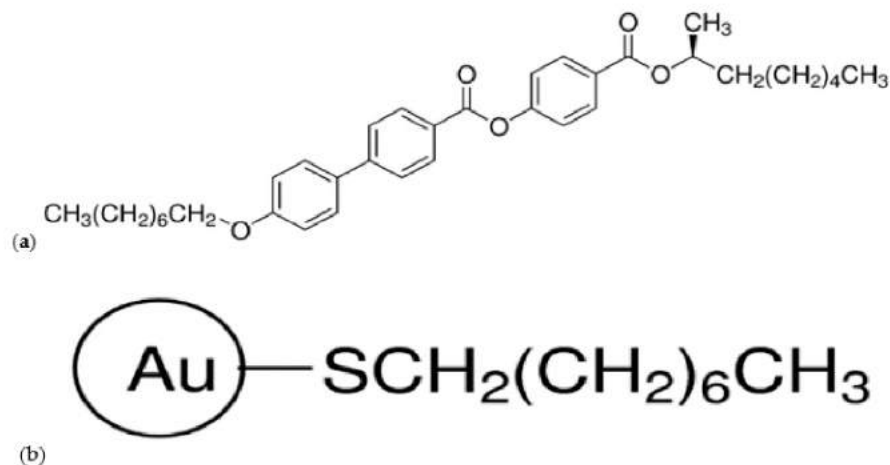


Figure 15. Chemical structure of liquid crystal (S)-MHPOBC (a) and the 1-octanethiol functionalized gold nanoparticle (b).

Three composites were prepared with three different concentrations of Au nanoparticles: Composite 1 (0.0 wt. % Au NPs—pure LC matrix), Composite 2 (0.2 wt. % Au NPs), and Composite 3 (0.5 wt. % Au NPs). We used low weight concentrations to not disturb the liquid crystal order in individual smectic layers. Composites 2 and 3 were prepared according to the following scheme:

1. Appropriate amounts of pure (S)-MHPOBC were weighed and flooded with the appropriate volume of Au nanoparticles solution (see Table 2) and 2 mL of toluene was added.
2. The solutions were left for a few hours (~19 h).
3. The solutions were sonicated for 30 min in the 30(on)/30(off) mode with amplitude $A = 40\%$ (in the presence of ice as an external cooling agent).
4. The solutions were placed on the magnetic stirrer (~100 °C, 1400 rpm) for about ~18–19 h to slowly evaporate half of the solvent volume.
5. The sonication process was performed for 15 min in the 45(on)/15(off) mode with $A = 40\%$.
6. The solutions were poured (~50 μL) on cleaned microscope slides and left for solvent evaporation under ambient conditions for over 70 h.

7. The prepared composites were gently scratched from a glass by metal blade and used for measurements.

Table 2. Mass and volume compositions of pure (S)-MHPOBC and nanoparticle solutions in toluene of Composites 1–3.

Composite	(S)-MHPOBC	Au NPs
Composite 1 (0.0 wt. %)	100.03 mg	–
Composite 2 (0.2 wt. %)	100.02 mg	10.02 μL
Composite 3 (0.5 wt. %)	60.00 mg	15.08 μL

The above procedure (but without the Au nanoparticles) was used to prepare Composite 1 (pure matrix). The prepared Composites 1–3 differed significantly in color, namely Composite 1 was completely white, Composites 2 and 3 adopted violet-brown colors, and their intensity depended on the concentration of Au NPs (see Figure 16b).

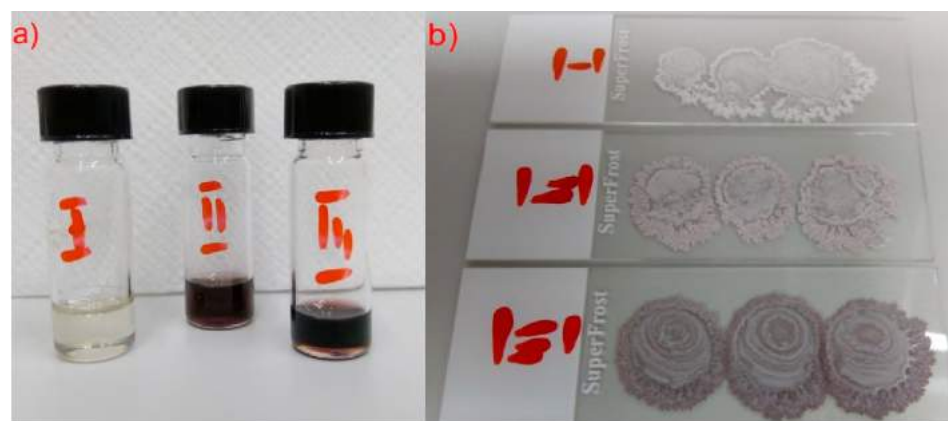


Figure 16. Composites as solutions (in 2ml toluene) (a) and after evaporation on the microscopic slides (b): I—Composite 1, II—Composite 2, and III—Composite 3.

After pouring the solutions on microscope slides and the toluene evaporating, we noticed the matrix is relatively fragile, it detached easily from the slide and took the powder form. However, after adding Au nanoparticles the situation was slightly different, the fragility degree decreased. In our opinion, the cause is the presence of a surfactant (1-octanethiol) rather than the presence of Au nanoparticles.

3.2. Polarizing Optical Microscopy and Electro-Optic Measurements

Nikon Eclipse LV100POL polarizing microscope (Nikon, Tokyo, Japan) equipped with Fine Instruments WTMS-14C heating stage (Elektronika Jadrowa, Cracow, Poland) coupled to a Canon EOS600D digital camera (Canon, Tokyo, Japan) and PC was used to determine the phase sequence of studied composites. The complete set for electric measurements included: Agilent 33120A AC voltage generator, F20-FLC Electronics amplifier, Agilent DSO6102A digital oscilloscope, INSTEC PD02 photodetector, tunable resistor system (a 100 k Ω resistor was used for all measurements), Canon EOS600D digital camera (Canon, Tokyo, Japan). Composites 1–3 were placed in ITO electro-optic cells with planar alignment (thickness 4.9 μm , active electrode area 25 mm², AWAT Company, Warsaw, Poland) by capillary effect at a temperature just above the clearing point and then slowly cooled down to room temperature.

The texture observations were carried out at cooling (155–0 $^{\circ}\text{C}$, cycle I) and heating (20–155 $^{\circ}\text{C}$, cycle II) at a rate of 2 $^{\circ}\text{C}/\text{min}$. The textures processing was performed using ImageJ (LOCI, University of Wisconsin, Madison, WI, USA).

The light transmitted intensity by the sample was measured with a photodetector. The time-domain signal was averaged to give an intensity value at a specific temperature.

Then all results for a given composite were normalized to the range [0, 1]. Measurements were taken both during heating and cooling in 0.5 °C steps with a rate 2 °C/min, there was 1 min before each measurement for temperature stabilization.

Before electro-optic measurements, the sample was heated up to an isotropic liquid and then slowly cooled down to the first phase below SmA* and aligned under an AC electric field (rectangular, 100 Hz, 120 V) for about 6–8 h. Among others, such a long time is due to the low helix pitch value for (S)-MHPOBC [88]. Measurements of the spontaneous polarization, switching time, and tilt angle (120 V_{pp}, 24.5 MV/m) were done every 1 °C. The reversal current method was used to measure P_s and τ while Θ was measured between Clark-Lagerwall states [89–91] by using a photodetector. A triangular signal was used for P_s measurements, while a rectangular signal was used for τ and Θ measurements. The numerical calculation was done using the Origin 2018 program (OriginLab, Northampton, UK). The uncertainty related to the P_s was equal to 1%. The systematic uncertainties of τ are related to the time oscilloscope base for a specific measurement cycle, while the uncertainty for Θ is a complex uncertainty: systematic uncertainty of 0.1° and statistical uncertainty resulting from the obtained values Θ_1 and Θ_2 .

3.3. Differential Scanning Calorimetry

The phase transition temperatures and their enthalpy changes during heating and cooling were determined by using a PerkinElmer DSC8000 differential scanning calorimeter (PerkinElmer, Waltham, MA, USA). The calorimeter was calibrated to the melting points of water and indium. Samples weighing 7.80 mg of Composites 1–3 were placed in aluminum cups and closed with a press. The measurement was done at a rate of 10 °C/min during heating (0–170 °C, cycle I) and cooling (170–0 °C, cycle II). Results were analyzed using Pyris software (Perkin Elmer, Waltham, MA, USA) and Origin 2020 (OriginLab, Northampton, UK).

3.4. X-ray Diffraction

XRD measurements were performed using the CuK α radiation with Empyrean 2 (Malvern Panalytical, Worcestershire, UK) diffractometer with Cryostream 700 Plus (Oxford Cryosystems) temperature attachment. The samples were introduced to capillaries (borosilicate glass, 0.3 mm diameter) by the capillary effect in the isotropic liquid phase. The XRD patterns were collected on cooling in geometry of a horizontal rotating capillary with a parabolic mirror on an incident beam. The measurement for a powder Si (SRM 640b) was performed to determine the zero of the diffractometer and reduce the systematic error in 2 θ values. The patterns were analyzed in WinPLOTR [92].

3.5. Fluorescence Confocal Polarizing Microscopy

The FCPM method was originally used to study liquid crystals due to the defects present in them. In our case, however, it is the method used to detect fluorescence in Composites 1–3 [93,94].

Olympus Fluoview 1200 fluorescence microscope (Olympus, Tokyo, Japan) with a diode laser (λ D 405 nm and λ D 473 nm) and the beam power equal to 1.24 mW was used. The low beam power value is intentional, to avoid light-induced reorientation of LC molecules. The collected images show the autofluorescence obtained simultaneously for two excitation wavelengths and detection ranges. The autofluorescence signal was detected in the spectral range 430–455 nm (blue) and 490–590 nm (green) in the reflection mode. To obtain the 3D image of the whole sample, the focused beam scans the sample in the horizontal plane (xy-directions) and then mechanical refocuses at different depths (z-direction) in the sample. Afterward there is repeating the horizontal scanning which produces another thin 'optical slice'.

3.6. Ultra-Violet-Visible Spectroscopy—Free Droplets

Measurement of the helix pitch was performed on a free droplet on a microscope slide using a spectroscopic method for wavelengths in the UV-VIS range (Liga microspectrometer, microParts GmbH, Dortmund, Germany). The sample's image was registered during very slow cooling from the isotropic phase, using the Linkam hot stage and temperature stabilizer. The cooling rate was very slow, with a step of 0.1 °C, and required a one-minute isothermal time before each measurement.

Due to the fact the measurements were made on a free droplet, without any alignment, the raw data in the form of transmission spectra are only used for qualitative interpretation—determination of the minimum transmission λ_s [95]. Since we do not know the geometric dimensions of the droplets, the absorbance (transmission) at a given wavelength and temperature can't be compared. However, different droplet thicknesses for Composites 1–3 do not affect the position of the maximum absorbance (minimum transmission).

3.7. Optical Microscopy/Scanning Electron Microscopy

Keyence VHX-7000 digital optical microscope using a built-in high-intensity LED light source was used to obtain the images of Composites 1–3 and pure Au nanoparticles. Each sample was mechanically dispersed with a metal roller on the surface of a chemically cleaned microscopic slide, obtaining a sample in the form of a square a few millimeters in size and a thickness up to ca. 100 μm . Each sample was imaged in two ways: as a pristine sample at room temperature and after annealing at 155 °C for 5 min and cooled down to room temperature. Digital optical images with high resolution were obtained by two different types of illumination: ring and coaxial. The first one gives the knowledge about the surface sample's color simultaneously with no appropriate depth of contrast. This illumination system was just to confirm (at high magnification) a real sample color. In turn, the coaxial system is associated with perfect image depth, and it permits the recognition of details.

Scanning electron microscopy imaging was performed with a Keyence VHX-D510 scanning electron microscope (SEM)—(tungsten TE gun, acceleration voltage 0.9 kV, backscattered electron imaging) for Composites 1–3 and pure Au nanoparticles mounted to the SEM specimen stubs with the double-sided adhesive copper tape without an additional sputter-coating with metal to preserve original color and morphology of materials for the comparative analysis. The scanning electron microscope was the tandem system that allows obtaining both SEM and optical images. The maximum magnification in optical system imaging is 200 $\times$. Additionally, there is an option of overlaying SEM and optical images to form the superimposed image, which is very helpful to obtain additional information.

3.8. Contact Angle Measurements

All contact angle measurements were performed on a DSA20E EasyDrop wettability system (KRÜSS, Hamburg, Germany). The studied composites were dissolved in toluene (the same concentrations for all samples) and then spin-casted (single shot 100 μL , 820 rpm, 40 s) on the silicon wafers. The silicon wafers (ca. 1.00 $\times$ 2.00 cm) were previously cleaned in isopropanol (with the ultrasonic bath addition) and purged with high purity compressed nitrogen. The layers were subjected to aging for about 24 h to evaporate any residual solvent and the contact angle measurements were carried out during heating in the range of 0–100 °C. The wetting agent was distilled water, dosed dropwise per layer by a syringe. Measurement points were collected every 3 °C and the contact angle for each droplet was determined from its left and right side using DropAnalyzer software (KRÜSS, Hamburg, Germany). Both angles were then averaged at a given temperature. After the measurement, the droplet was gently collected with a paper towel, in a non-contact manner on the studied surface. The accuracy of temperature was ± 0.1 °C, while the contact angle was subject to a systematic uncertainty of 0.1°. Measurements were made only up to 100 °C because the wetting agent used evaporates around 100 °C, so the measurements include crystalline phases and part of the antiferroelectric SmC^*_A phase. Our goal was to determine whether

the Au nanoparticles affect the surface wettability of prepared composites. A pure silicon wafer was used as a reference sample, the wettability of which was also studied under the same conditions as the composites. Due to the water solubility of the Au nanoparticles decorated layer, it was not possible to make CA measurements for Au NPs.

4. Conclusions

Properties of two composites based on antiferroelectric liquid crystal (S)-MHPOBC doped with two concentrations of Au nanoparticles: Composite 2 (0.2 wt. % Au NPs) and Composite 3 (0.5 wt. % Au NPs) were studied and compared with undoped (S)-MHPOBC (Composite 1). Based on the complementary methods, it was shown that many parameters are changed by a small amount of Au NPs.

Textures of the SmA^* , SmC^*_{α} , SmC^* , SmC^*_{γ} , and SmC^*_A phases were not changed after doping, which may indicate the good dispersion of Au NPs in the LC matrix. However, due to a large number of focal conic defects, Au NPs may accumulate in these defects, reducing the free energy of the layer. In turn, a wide temperature range of the SmI^* and Cr_1 phases coexists (as a result of crystallization inhibition) and a new Cr_2' crystal phase was revealed after doping.

Doping has a very slight influence on the phase sequence and transition temperatures; only additional crystal phases Cr_4' and Cr_2' were revealed for Composite 3 during heating. During heating, there was an increase of ΔH for the Cr_4 – SmC^*_A phase transition, as well as for transitions between sub-phases, while there was a decrease of ΔH for the SmA^* –Is transition both during heating and cooling that was observed after doping.

The smectic layer thickness does not change after doping in the uncertainty limit; only a slight modification of the correlation length in the SmA^* phase for Composite 2 was observed, which is evidence of the influence of Au nanoparticles on the ordering of LC molecules within the smectic layer. In turn, the increase of the helix pitch after doping with Au NPs was observed in the SmC^*_A phase, especially for Composite 3.

The surface morphology does not change after doping; however, after heating up to the isotropic phase (150 °C) and cooling down black objects, white spots appeared on the surfaces of Composites 2 and 3, which means that, in the isotropic liquid, the nanoparticles aggregate. In turn, pillar-like structures for pure Au nanoparticles were observed, which disappear when heated up to 150 °C. This is most likely related to the destruction of the lamellar structure formed by decorated nanoparticles at higher temperatures. The contact angle changed after doping, and it was the highest for Composite 2 in the crystal phase and Composite 3 in the SmC^*_A phase. The differences in Θ_{CA} reach even 15–17° compared to undoped (S)-MHPOBC (Composite 1), which means that the surface wettability is reduced. This may be the result of conformational changes in the surfactant chains decorated with Au NPs. Both in the range of green and blue light, we observed an increase in the fluorescence intensity after doping with Au nanoparticles, while, for the green light range, the gain is almost 100%.

The switching time decreased for Composite 3 and increased for Composite 2 in the antiferroelectric SmC^*_A phase. In turn, the tilt angle increased after doping in Composite 3, while it did not change in Composite 2 in the entire SmC^*_A phase. Spontaneous polarization increased after doping at the high temperature range of the SmC^*_A phase, while, below ca. 90 °C, no dopant influence was observed. The increase in P_s resulted from the induction of the dipole moment of Au NPs under the influence of the incident light.

In summary, we found that the admixture of gold nanoparticles with low concentrations affects the fluorescence and hydrophobicity of the composite layers, as well as the parameters of the SmC^*_A phase, such as the helix pitch, switching time, tilt angle, and spontaneous polarization, but an increase in the dopant concentration led to NP agglomeration. In turn, the admixture of Au NPs did not affect the phase sequence, thickness of the smectic layers, and correlation length in the SmC^*_A phase, as well as the helix pitch, switching time, tilt angle, and spontaneous polarization in the SmI^* phase.

However, there is still a lot of research to be done. First of all, based on the (S)-MHPOBC, new composites can be prepared and investigated whether the spontaneous polarization, contact angle, tilt angle, and enthalpy change for the $\text{Cr}_4\text{-SmC}^*_\text{A}$ phase transition will increase with the increasing concentration of Au NPs. It is also possible to check the influence of the Au nanoparticle sizes and the type of surfactants decorating them on these parameters and whether other antiferroelectric liquid crystals as the host matrix provide the same modifications as these parameters. It is also possible to investigate the effect of Au NP: (1) on the relaxation processes in the LC matrix by dielectric spectroscopy, (2) on the absorption bands by infrared spectroscopy, (3) on the maximum luminescence (hypsochrome or bathochrome shift) by means of photoluminescence measurements, and (4) on electronic transitions in the LC matrix by UV-Vis spectroscopy of thin layers.

The composites studied in this work are interesting from the point of view of applications as, for example, electric switches or for the production of thin hydrophobic films protecting against moisture. In turn, due to the fact that both the LC matrix and the composites show fluorescence in the visible range and are nontoxic, such materials can be used as dyes/markers for medical applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules27123663/s1>: Figure S1: Textures registered during cooling with a rate $2\text{ }^\circ\text{C}/\text{min}$ for Composites 1–3; (a–a'') SmA^* , (b–b'') SmC^*_α , (c–c'') SmC^* , (d–d'') SmC^*_γ , (e–e'') SmC^*_A at $105\text{ }^\circ\text{C}$, (f–f'') SmC^*_A at $90\text{ }^\circ\text{C}$, (g–g'') SmI^* and (h–h'') coexistence two phases SmI^* and Cr_1 . The orange perpendicular arrows in (a) represent crossed polarizer and analyzer. Scale bars in the right lower corner are the same for each image ($50\text{ }\mu\text{m}$). All images were obtained from the same sample area in each Composite. Figure S2: An example of the focal conic defect in focal conic fan texture for SmA^* phase (Composite 3) together with conic curves (hyperbola and ellipse). In the measuring cell plane lies the hyperbola, the ellipse in the planar anchoring is perpendicular to the substrate planes (is a projection on the hyperbola plane). These areas are degenerated smectic layers. Figure S3: The calorimetric curves registered during cooling for Composites 1–3 with the enthalpy changes for chosen phase transitions (a). Insets in (a) present an enlarged temperature range of $116\text{--}126\text{ }^\circ\text{C}$. DSC curves in the temperature range of the Iso-SmA^* and $\text{SmI}^*\text{-Cr}_1$ phase transitions (b). Figure S4: Temperature dependence of the normalized transmitted light intensity during heating (a), the selected temperature range in the vicinity of the $\text{Cr}_4\text{-SmC}^*_\text{A}$ (b), the $\text{SmC}^*\text{-SmC}^*_\alpha$ (c), and the $\text{Cr}_1\text{-Cr}_2$ phase transitions (d), and the $\text{SmC}^*\text{-SmC}^*_\alpha$ phase transition temperature for Composites studied (e). Figure S5: Fluorescence intensity in subsequent slices of the samples detected in the spectral ranges $490\text{--}590\text{ nm}$ (a) and $430\text{--}455\text{ nm}$ (b) at chosen temperatures for Composites 1–3 as well as for Au nanoparticles in the $490\text{--}590\text{ nm}$ (a') and $430\text{--}455\text{ nm}$ (b') (c). Figure S6: Fluorescence intensity of the Composite 1 (a) and Composite 3 (b) detected in the green light range at $118\text{ }^\circ\text{C}$. Figure S7: Fluorescence intensity of the Composite 1 (a) and Composite 3 (b) detected in the blue light range at $118\text{ }^\circ\text{C}$. Figure S8: Room temperature digital optical images with coaxial illumination for pristine Composite 1 (the first row), Composite 2 (the second row) and for Composite 3 (the third row). The colored dotted squares represent the enlarged areas. Figure S9: Room temperature digital optical images with coaxial illumination for Composite 1 (the first row), Composite 2 (the second row), Composite 3 (the third row) cooled to room temperature after being heated to $155\text{ }^\circ\text{C}$ and kept at this temperature for 5 min. The colored dotted squares represent the enlarged. Black circles indicate white spots—small aggregates of Au nanoparticles. Figure S10: SEM images for Composite 1 (a), Composite 2 (b), Composite 3 (c) and Au nanoparticles (d). The colored dashed rectangles represent the enlarged areas. Figure S11: Images for the water droplet deposited on the thin layer of Composites 1–3 and pure silicon wafer (reference) at selected temperatures. Figure S12: Amplitude dependence of reorientation times τ for $f = 50\text{ Hz}$ at $105\text{ }^\circ\text{C}$. The upper inset presents results for $f = 100\text{ Hz}$ at $117\text{ }^\circ\text{C}$. The bottom inset presents results for $f = 50\text{ Hz}$ at $117\text{ }^\circ\text{C}$. The dashed rectangular at insets have been shown the amplitude range where the changes are the highest.

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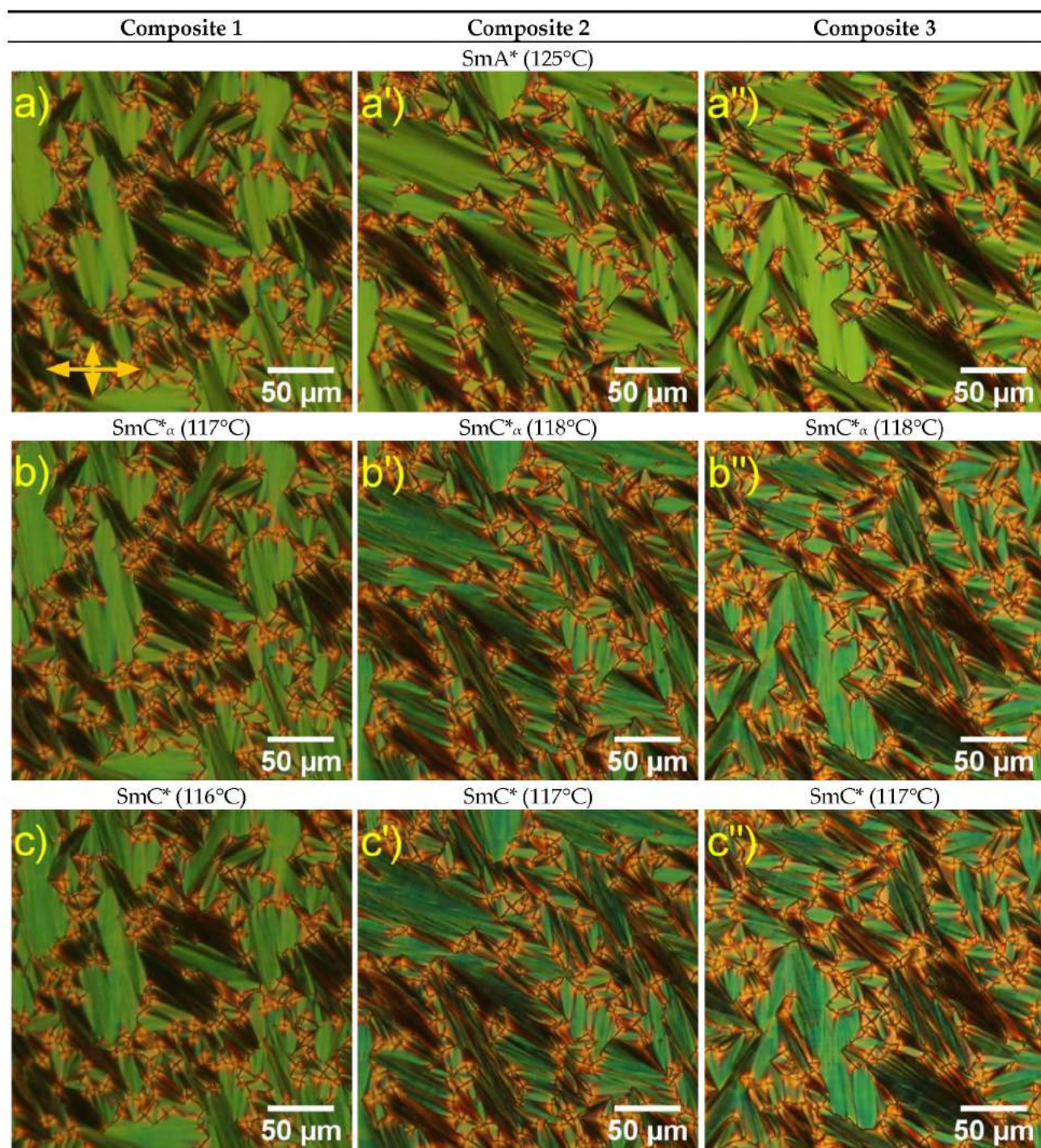
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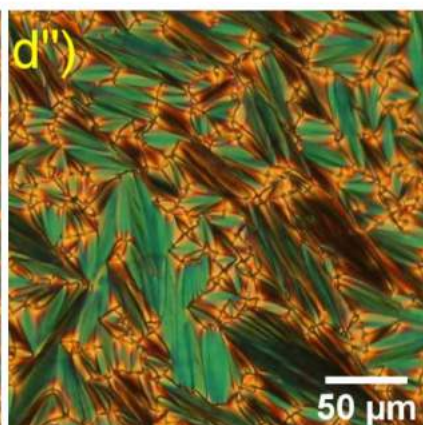
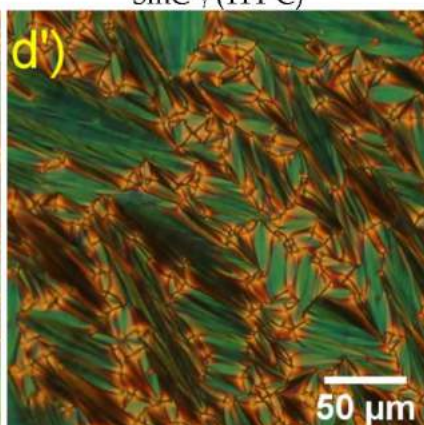
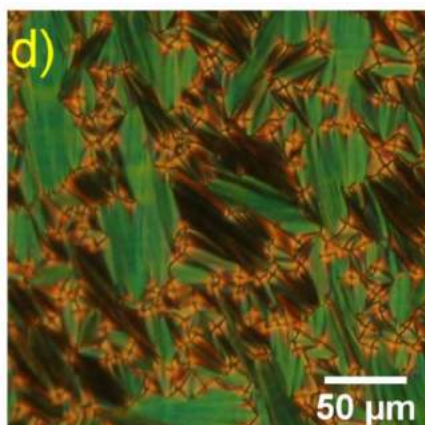
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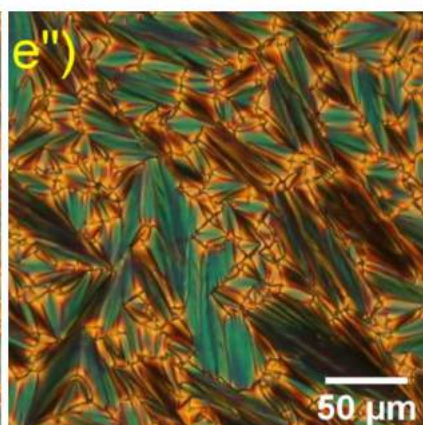
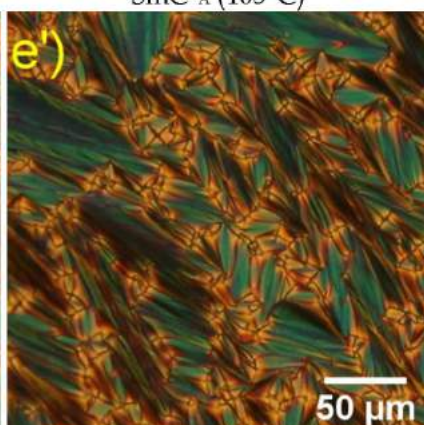
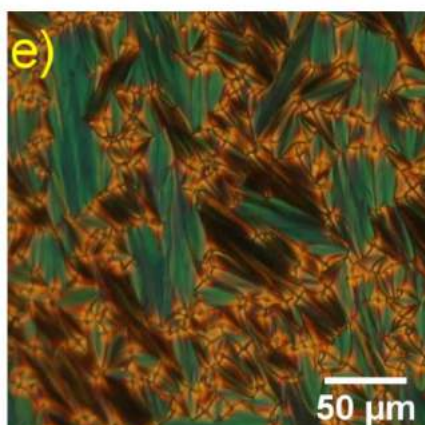
Supplementary Material



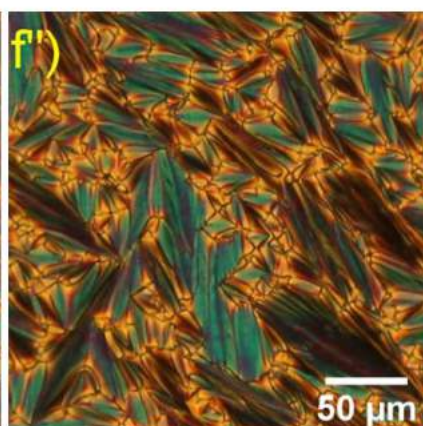
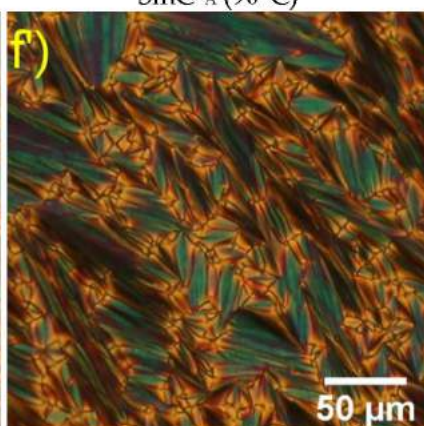
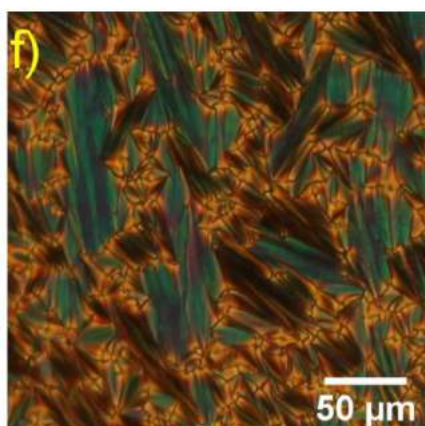
SmC^*_γ (114°C)



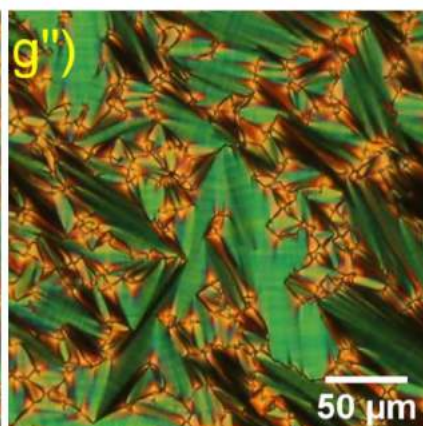
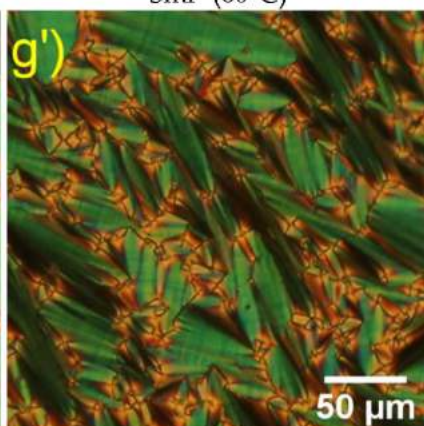
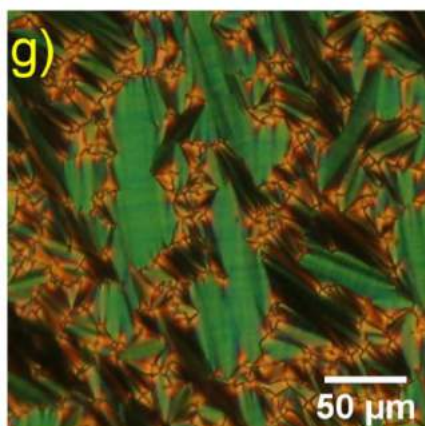
SmC^*_A (105°C)



SmC^*_A (90°C)



SmI^* (60°C)



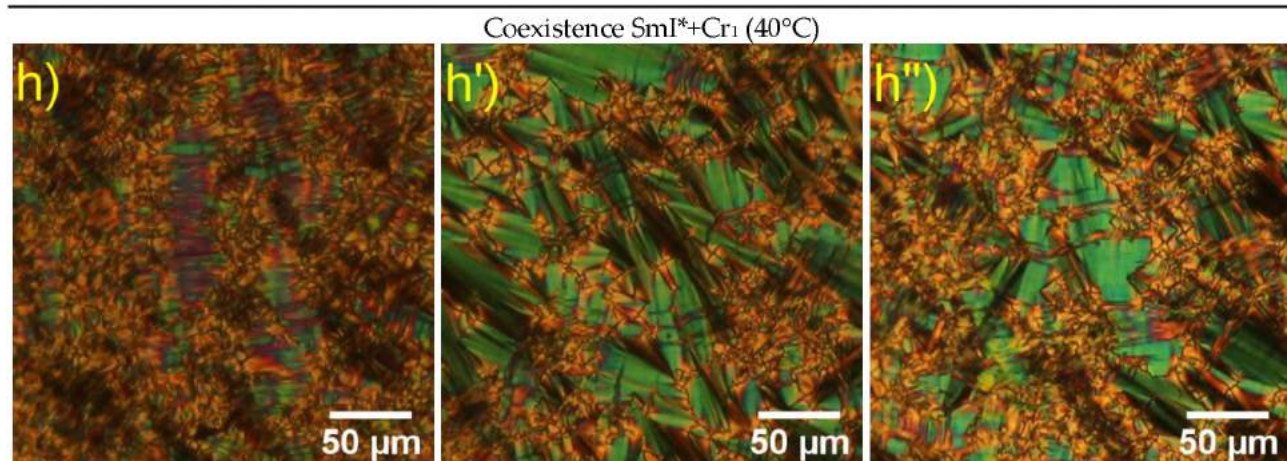


Figure S1. Textures registered during cooling with a rate $2^\circ\text{C}/\text{min}$ for Composites 1-3; (a-a'') SmA^* , (b-b'') SmC^*_{α} , (c-c'') SmC^* , (d-d'') SmC^*_{γ} , (e-e'') SmC^*_{A} at 105°C , (f-f'') SmC^*_{A} at 90°C , (g-g'') SmI^* and (h-h'') coexistence two phases SmI^* and Cr_1 . The orange perpendicular arrows in (a) represent crossed polarizer and analyzer. Scale bars in the right lower corner are the same for each image ($50\mu\text{m}$). All images were obtained from the same sample area in each Composite.

The considered focal conic defects are usually common when the molecules form a strong anchoring to the cell surface or other nucleation points (such nucleation points in the area between the glass plates can be e.g. an admixtures or spacers, eliminating the thickness gradient in the cell used). Hence the defects appear in random places on the recorded texture. Around the nucleation points, the molecules assume a radial orientation (the smectic layers thicknesses are preserved) and therefore the smectic layers must curve locally (see Fig. S2) around the nucleation centers [54]. Due to the liquid-like nature of SmA^* phase, adjacent nucleation centers grow and combine each other to form Dupin's cyclides. When the two nucleation centers grow and meet, the outer molecules' layers form a junction [54]. A line of hyperbolic optical discontinuity is formed at the junction site. The molecules at a junction are disorganized and between crossed polarizers considered area appears dark (dark cross). As Goodby reports, this defect type is easily formed when the cell thickness is more than $3\text{-}4\mu\text{m}$ (in our case about $5\mu\text{m}$) [54]. Fig. S2 shows an example of the topological focal conic defect formation with a clear marking of conic curves (ellipse and hyperbola) on the texture fragment for Composite 3, SmA^* phase, 140°C showing the crossing of the above-mentioned curves, formulating the defect. The plane in which the hyperbola lies for planar boundary conditions is parallel to the substrate cell planes [53].

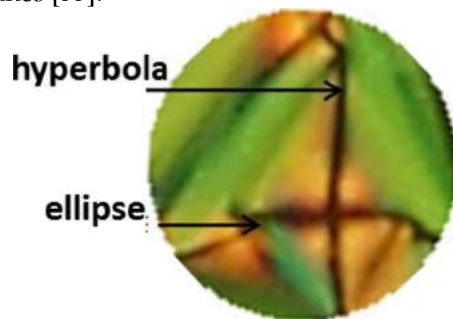


Figure S2. An example of the focal conic defect in focal conic fan texture for SmA^* phase (Composite 3) together with conic curves (hyperbola and ellipse). In the measuring cell plane lies the hyperbola, the ellipse in the planar anchoring is perpendicular to the substrate planes (is a projection on the hyperbola plane). These areas are degenerated smectic layers.

In the inset (Fig. S3a) is the table with ΔH values accompanied by the individual phase transitions. In addition to the increase in T_0 for the SmI^*-Cr_1 phase transition in Composite 3 versus Composite 1, also the ΔH value increased significantly relative to pure (S)-MHPOBC. As can be seen from the table, ΔH for this transition increases with the increase in the amount of Au nanoparticles. Similar behavior is observed for the $\text{SmC}^*_A-\text{SmI}^*$ phase transition. On the other hand, for the $\text{Iso}-\text{SmA}^*$ phase transition, the situation for all Composites 1-3 is completely different, the value of ΔH decreases with increasing concentration.

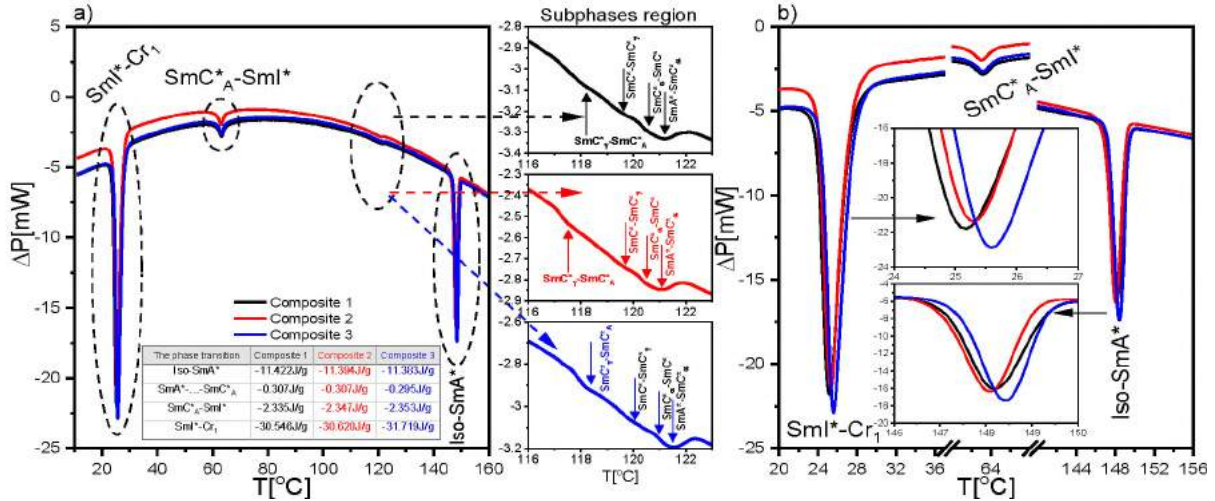


Figure S3. The calorimetric curves registered during cooling for Composites 1-3 with the enthalpy changes for chosen phase transitions (a). Insets in (a) present an enlarged temperature range of 116-126°C. DSC curves in the temperature range of the $\text{Iso}-\text{SmA}^*$ and SmI^*-Cr_1 phase transitions (b).

Fig. S4a shows the transmitted light intensity during the heating of Composites 1-3. Transitions Cr_1-Cr_2 , $\text{Cr}_4-\text{SmC}^*_A$, SmA^*-Iso are very clearly visible for all studied samples. Based on these measurements, it can be concluded Cr_1 is structurally very different from Cr_2-Cr_4 , as evidenced by a clear decrease in the transmitted light intensity in the transition to Cr_2 . The Cr_2-Cr_3 , Cr_3-Cr_4 transitions for Composite 2-3 are practically invisible optically, while for Composite 1 only in the form of small humps (regime between 60-80°C). This may indicate the influence of Au nanoparticles on the mentioned crystalline phases, e.g. by modifying the lattice parameters of these phases, which makes their structure very similar and we do not see the difference between them in optical measurements. Moreover, the Cr_1-Cr_2 transition temperatures are in agreement with those determined calorimetrically, but only for Composites 1-2. We noted a significant discrepancy of this temperature for Composite 3 around 7°C, which we do not fully understand. It is not excluded, the heating rate is responsible for it. At high temperature change rates, nanoparticles can acquire a large amount of thermal energy in a very short time, becoming not only mobile but also capable to show various movements at the molecular level, e.g. rotational (we should keep in mind that apart from their size 2-4nm, they are additionally covered with an organic surfactant, the surfactant kinetics under the influence of various temperature changes is unknown by us). Interestingly, within the SmC^*_A phase, we do not observe a parabolic light intensities variation, but only a monotonic decrease in light intensity with temperature, regardless of an admixture. Fig. S4b shows the enlarged $\text{Cr}_4-\text{SmC}^*_A$ phase transition range, while the vertical arrows do not correspond to the temperatures of this transition but the moment when only the SmC^*_A phase exists in the sample. For example, the temperature of the beginning $\text{Cr}_4-\text{SmC}^*_A$ phase transition for Composite 3 from the optical method is about 83.0°C ($\pm 0.5^\circ\text{C}$), while from the calorimetric method is about 81.9°C (0.1°C). Temperature mismatch of 0.5°C may

result from different measurement conditions (aluminum and glass heat exchangers). In Fig. S4c, the enlarged range of sub-phases; the arrows represent very subtle SmC^* - SmC^*_α phase transitions. In turn, in Fig. S4d the enlarged range between the crystalline phases with the largest structural differences. In the table (Fig. S4e) we noted the SmC^* - SmC^*_α transition temperatures, which are the values at the maximum of the subtle jumps in Fig S4c.

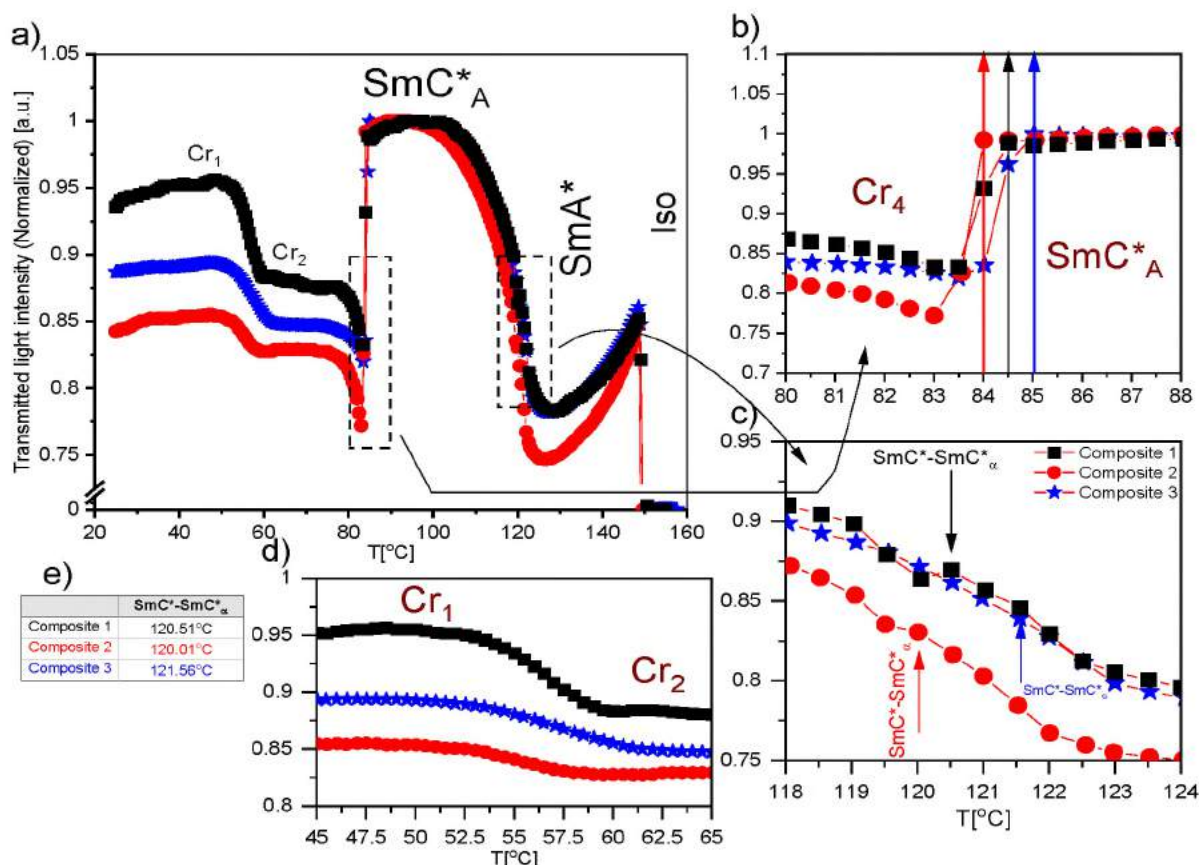
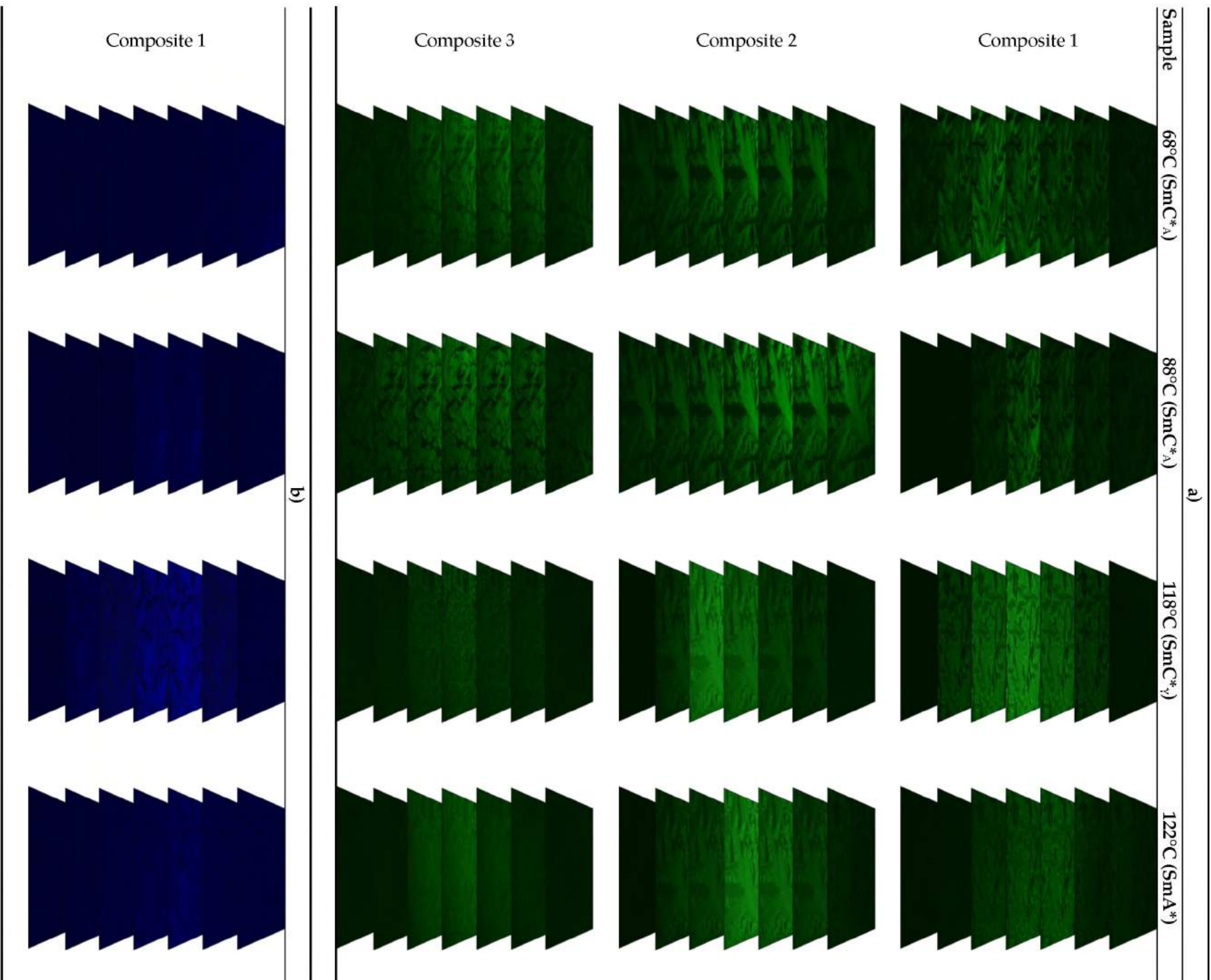


Figure S4. Temperature dependence of the normalized transmitted light intensity during heating (a), the selected temperature range in the vicinity of the Cr_4 - SmC^*_A (b), the SmC^* - SmC^*_α (c), and the Cr_1 - Cr_2 phase transitions (d), and the SmC^* - SmC^*_α phase transition temperature for samples studied (e).

A characteristic feature of this hexagonal phase is the molecules grouping on the smectic layer in such a way that their gravity centers form hexagons with an additional molecule inside. The molecules in this phase are tilted to the hexagon apex at a certain angle, and if chiral they form a helical superstructure. This superstructure is similar to the helical structure in the SmC^*_A phase, however, for the latter, there is no higher degree of center alignment in the smectic plane.

At the spectral range 430-455nm, the situation is a bit different. At 122°C the fluorescence intensity is the lowest for Composite 1, while it increases with the increase an admixture concentration. In turn, at 118°C very intensive fluorescence is present in Composite 1. Interestingly, for Composites 1-2 the fluorescence is very poor at 88°C and it is decreasing with the decrease in temperature (at 68°C there is no fluorescence). Meanwhile, for Composite 3 at 68 and 88°C, the fluorescence is quite clear visible. This phenomenon is not well understood by us. The mere Au nanoparticles present in samples should give similar results for Composite 2-3, however, the microscopic observations are different for them. This situation didn't note for 490-590nm spectral range. It is not likely, that the Composites 2-3 at 68°C were in different liquid crystal phases.



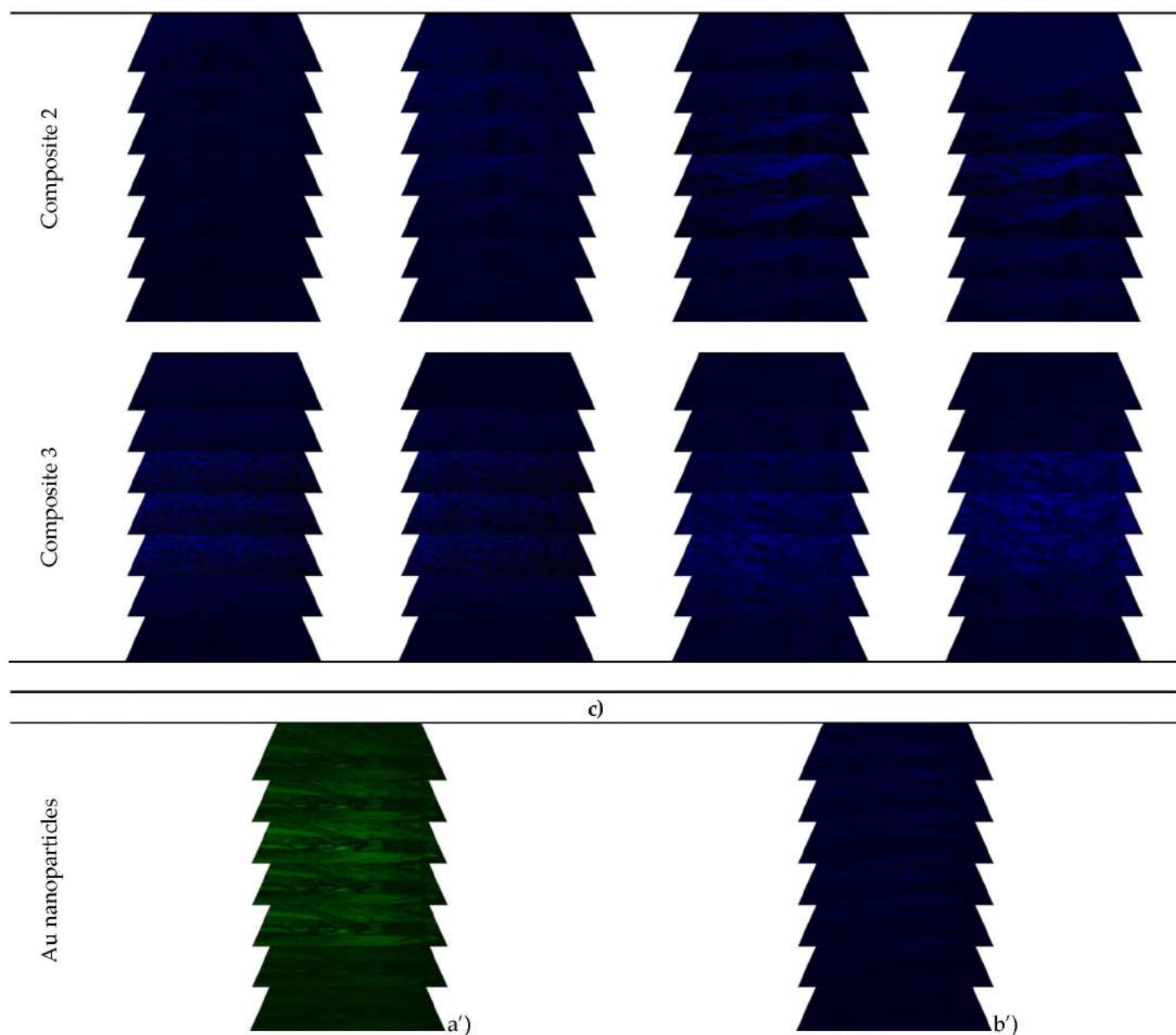


Figure S5. Fluorescence intensity in subsequent slices of the samples detected in the spectral ranges 490-590nm (a) and 430-455nm (b) at chosen temperatures for Composites 1-3 as well as for Au nanoparticles in the 490-590nm (a') and 430-455nm (b') (c).

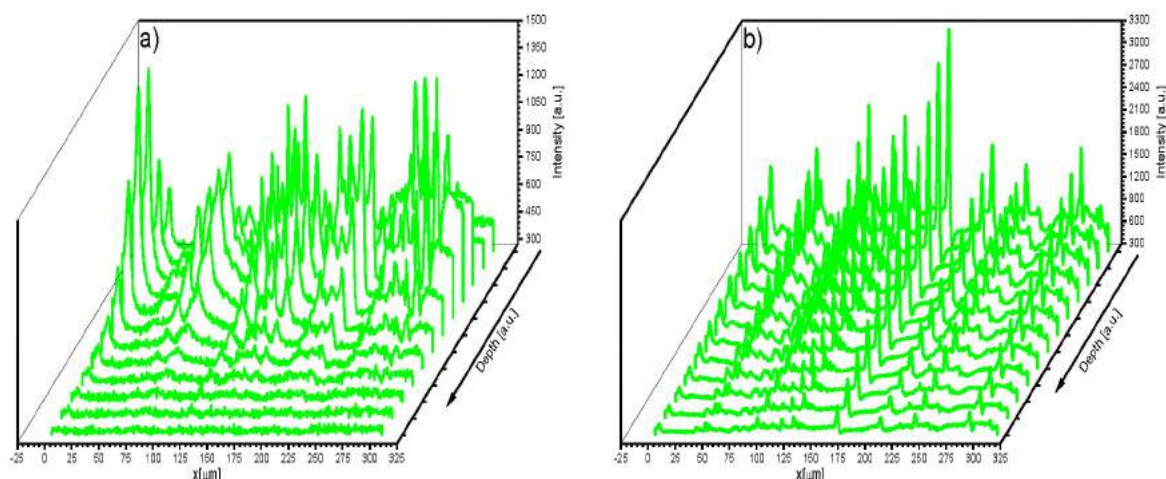


Figure S6. Fluorescence intensity of the Composite 1 (a) and Composite 3 (b) detected in the green light range at 118°C.

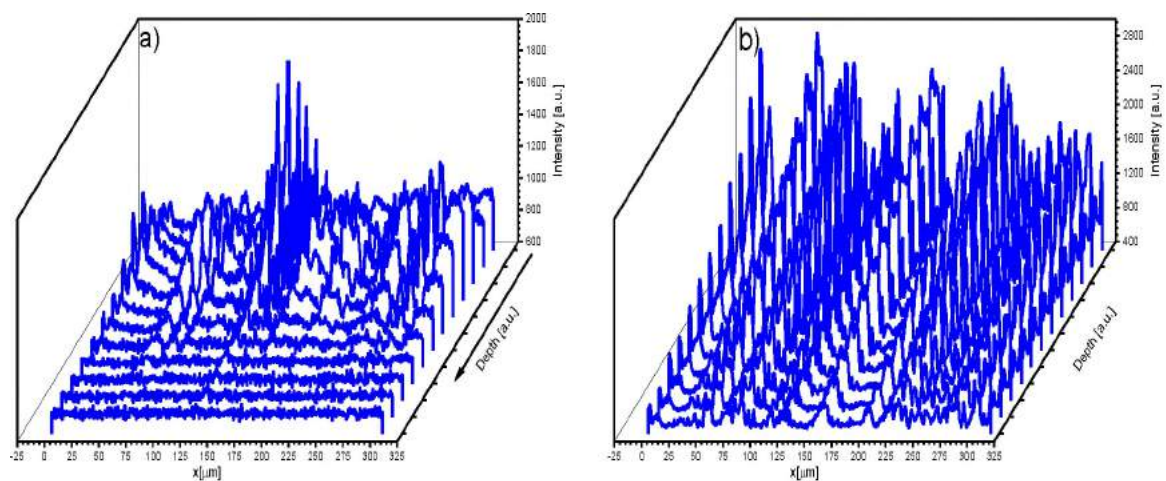


Figure S7. Fluorescence intensity of the Composite 1 (a) and Composite 3 (b) detected in the blue light range at 118°C.

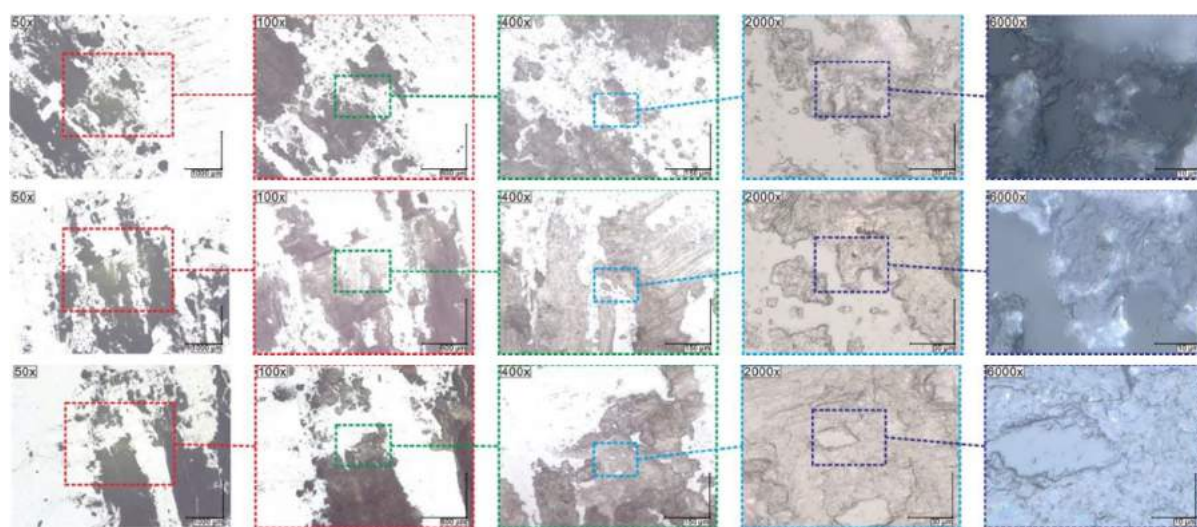


Figure S8. Room temperature digital optical images with coaxial illumination for pristine Composite 1 (the first row), Composite 2 (the second row) and for Composite 3 (the third row). The colored dotted squares represent the enlarged areas.

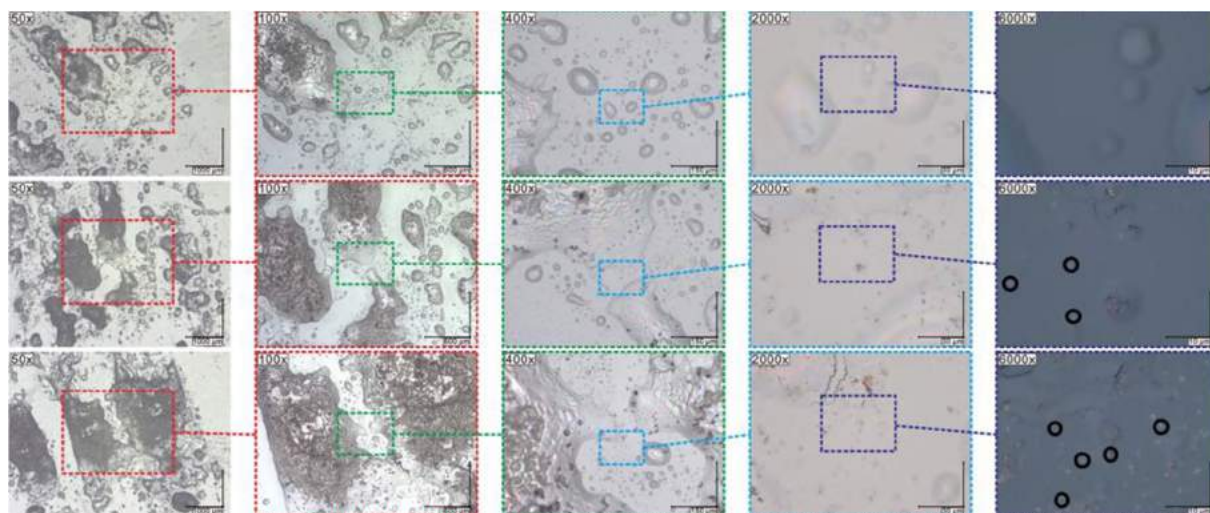


Figure S9. Room temperature digital optical images with coaxial illumination for Composite 1 (the first row), Composite 2 (the second row), Composite 3 (the third row) cooled to room temperature after being heated to 155°C and kept at this temperature for 5 minutes. The colored dotted squares represent the enlarged. Black circles indicate white spots – small aggregates of Au nanoparticles.

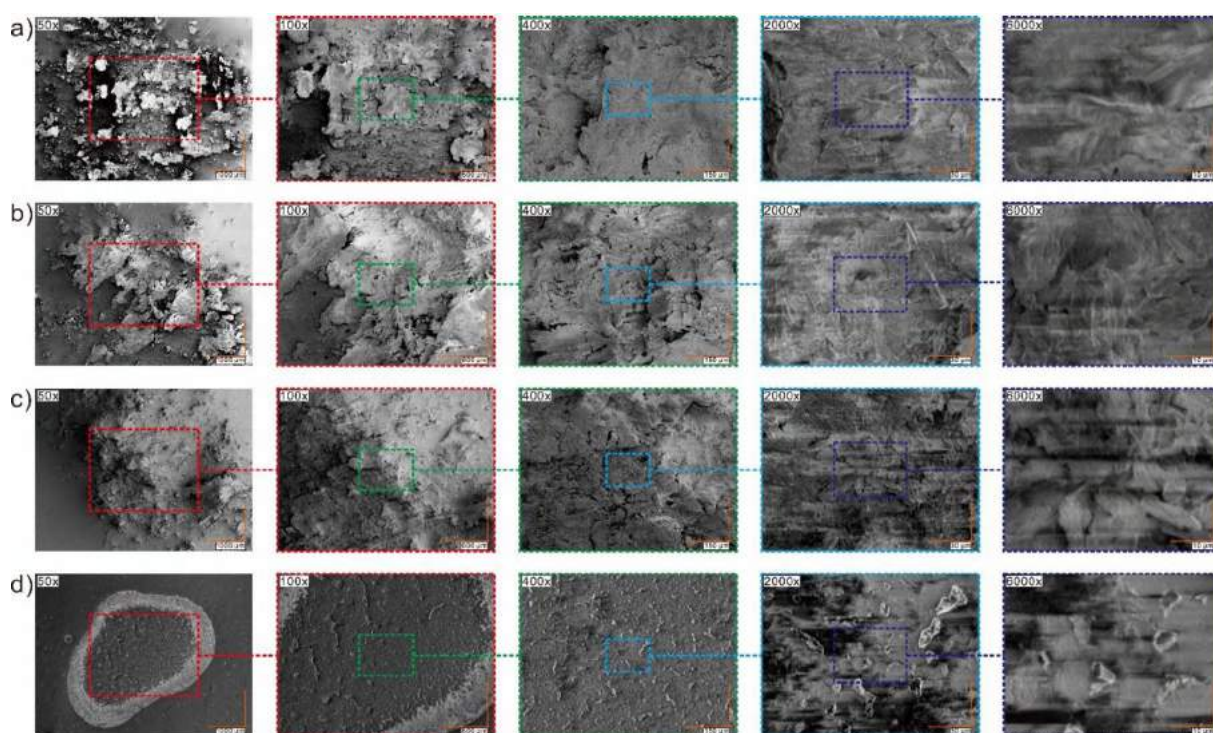


Figure S10. SEM images for Composite 1 (a), Composite 2 (b), Composite 3 (c) and Au nanoparticles (d). The colored dashed rectangles represent the enlarged areas.

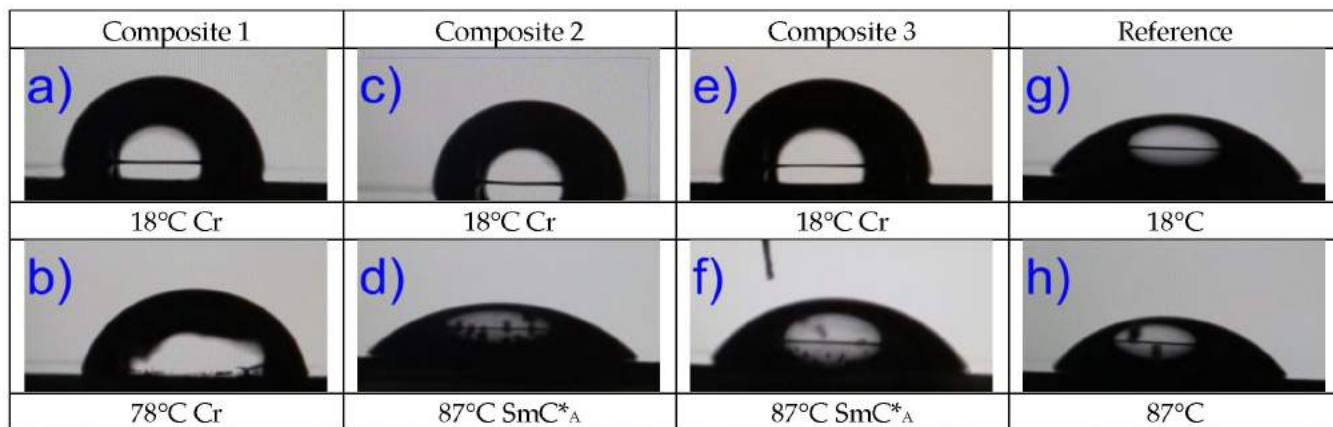


Figure S11. Images for the water droplet deposited on the thin layer of Composites 1-3 and pure silicon wafer (reference) at selected temperatures.

In the first stage, the switching times τ behavior to the amplitude of the alternating electric field was checked at two selected temperatures the SmC*_A phase, namely 117 and 105°C. Measurements were made on completely disordered samples and after each measurement series, the samples were heated to the isotropic liquid and subsequently cooled down to the next measuring temperature. Fig. S10 presents the dependence $\tau(U)$ for all composites at 105°C and $f = 50\text{Hz}$. As can be seen, with the U value increase, the τ decrease, which was to be expected, because the higher the electric field E causes the electric dipole moments to experience a higher force moment (the faster reorientation). The uncertainties related to the experimental points have different sizes, which results from the fact that during the data collection the time base on the oscilloscope was changing. Up to 120V, it can be observed that Au nanoparticles do no influence on τ values. Above 120V, it can be seen the Au nanoparticles lower the τ values and for 150V they are equal to: 22, 30, 31 μs for Composite 3, Composite 1, and Composite 2, respectively. The downward trend is much more noticeable for Composite 3 than for Composite 2. Only for Composite 3 above 120V, there is a continuous decrease in the τ value, while for Composite 2 at 150V there was a subtle increase. In addition, as the alternating voltage amplitude increased, the sample response during the change in signal polarity became narrower in the time domain. The wide sample responses at low U are because the molecules respond to a change in signal polarity, however, their reorientation time distribution is large. This behavior was observed for all samples. The inserts in Fig. S10 show the dependencies of $\tau(U)$ at 117°C for the two selected frequencies, namely 50 and 100Hz. For both frequencies under consideration, at low U values up to about 110V for 50Hz and 100V for 100Hz, plateau regions are observed for τ . Only above these U values we can see a higher times variability. In the frequency of 50Hz above 120V the shortest times are characterized by Composite 2 (about 25 μs) and the longest by Composite 1 (about 35 μs), while for frequencies of 100Hz and above 120V the shortest times are shown by Composite 3 (around 22.5 μs) and the longest for Composite 2 (around 35 μs). Moreover, in the 120-150V range with both frequencies only Composite 3 shows a plateau, while Composite 1 shows a typical downward trend. For Composite 2, sharp jumps in the τ values at 120V and 140V for 50 and 100Hz, respectively, were recorded in this range. The decrease in τ value for Composite 3 by about 7 μs and the increase for Composite 2 by about 7 μs with increasing frequency are not fully understood by us. However, this behavior is very promising for the use of these Composites 2-3 as electrical switches whose frequency dependency depends on the dopant concentration.

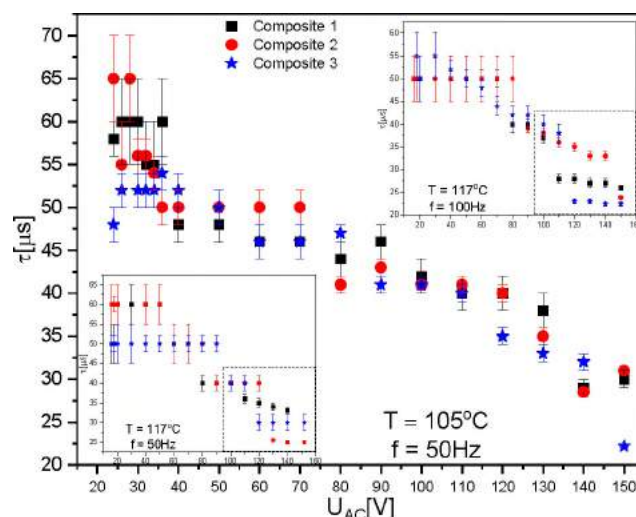


Figure S12. Amplitude dependence of reorientation times τ for $f = 50\text{Hz}$ at 105°C . The upper inset presents results for $f = 100\text{Hz}$ at 117°C . The bottom inset presents results for $f = 50\text{Hz}$ at 117°C . The dashed rectangular at insets have been shown the amplitude range where the changes are the highest.

In turn, although nanoparticles are decorated with aliphatic chains, which are the deliberate procedure to eliminate aggregation processes, we can't completely exclude this parasitic process. Let the typical (covalent) atomic radius for gold be $r \sim 135\text{pm}$. The nanoparticles considered in this article are spherical clusters with a diameter 2-4nm, therefore with radii $R \sim 1\text{-}2\text{nm}$. The single atom volume is proportional to r , like $\sim r^3$, while the volume of the whole nanoparticle with radius $R = 1.5\text{nm}$, like $\sim R^3$. Thus, the nanoparticles with radius R consist of $N \sim (R/r)^3 \approx 1372$ gold atoms. In turn, the number of atoms on the nanoparticle surface is $N - N' = N - ((R-r)/r)^3 \approx 338$. Therefore, theoretically each nanoparticle with a radius of 1.5nm has 338 Au atoms on the surface and each such Au atom can chemically bond through a strong covalent bond with the sulfur atom which is the surfactant part. Obviously, for steric reasons, not every Au atom can be bounded. It is possible that with the increasing Au concentration, adjacent nanoparticles will contact metallic cores at certain points or the metallic cores will be very close to each other. The more such cases there are, the Θ will be modified.

