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Synthesis, Preparation, and Characterization of Liquid Crystal/Organo-Montmorillonite Nanocomposites

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A new chiral calamitic liquid crystal 4'-((S)-3,7-dimethyloctyloxy)phenyl 4-(10-undecen-1-yloxy)benzoate (DOPUB) has been synthesized and characterized by spectroscopic methods (¹H-NMR and ¹³C-NMR). The focus is on the preparation of the nanocomposites of new chiral calamitic liquid crystal DOPUB/Organo-montmorillonite clay (OMMT) by solution intercalation method addition with OMMT contents 2.5, 5, and 7.5 wt% and determination of the morphology, thermal behavior, and crystalline properties of liquid crystal DOPUB/OMMT. Montmorillonite (MMT) modified by cationic surfactant cetyltrimethylammonium bromide (CTAB) for increasing the interaction of clay with DOPUB liquid crystal. The characterization of clay minerals and nanocomposites was investigated by X-ray diffraction. The mesomorphic behavior of liquid crystal (DOPUB) and the nanocomposites was investigated by differential scanning calorimetry (DSC) and optical polarizing microscopy (PM).

Keywords Liquid crystal; montmorillonite; nanocomposites

Introduction

In the recent years, polymer-inorganic nanocomposites have attracted a great deal of interest due to their enhanced chemical, thermal, mechanical properties can be improved and new high quality compounds [1–3]. In these nanocomposites, inorganic particles are dispersed at a nanometer inside polymer matrix allows to obtain a product with improved performances [4]. Nanocomposites materials exhibit hybrid properties derived from the polymer matrix and inorganic particles. This hybrid technique should be able to be applied not only polymer nanocomposites systems but also low molecular weight liquid crystals have a big potential properties [5]. They have excellent properties leading to a various applications such as opto-electronic devices, photonic crystal, depolarizers, scattering displays [6, 7].

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The inorganic particles as a nanofillers generally used are clay minerals [8]. Among the layered silicates, montmorillonite (MMT) is particularly effective as reinforcement for the liquid crystal/clay hybrids systems because of their high surface area, low cost, and especially high cation exchangeable capacity (CEC) [9]. In order to achieve good dispersion of the MMT in the liquid crystal, the surface of MMT was modified by a suitable approach in order to make them more organophilic and increase the interlayer distance of the MMT, thus, liquid crystal are able to insert between the layers [4–10]. There are many exchangeable cations on the surface and interlayer of MMT such as Na^+ , Mg^{+2} , K^+ . So cationic surfactants are generally used as modifiers such as alkyl ammonium salt [10]. The product consisted of modification of MMT was so-called organo-montmorillonite (OMMT).

In this study, firstly we synthesized and characterized a new chiral calamitic liquid crystal 4'-((S)-3,7-dimethyloctyloxy)phenyl 4-(10-undecen-1-yloxy)benzoate (DOPUB) and then we prepared the nanocomposites of DOPUB/OMMT by solution intercalation method with loading OMMT content (2.5, 5, and 7.5 wt%). The effect of modification of the montmorillonite clay mineral with organic surfactant on the DOPUB/OMMT nanocomposites was studied.

Experimental

Materials and Instrumentation

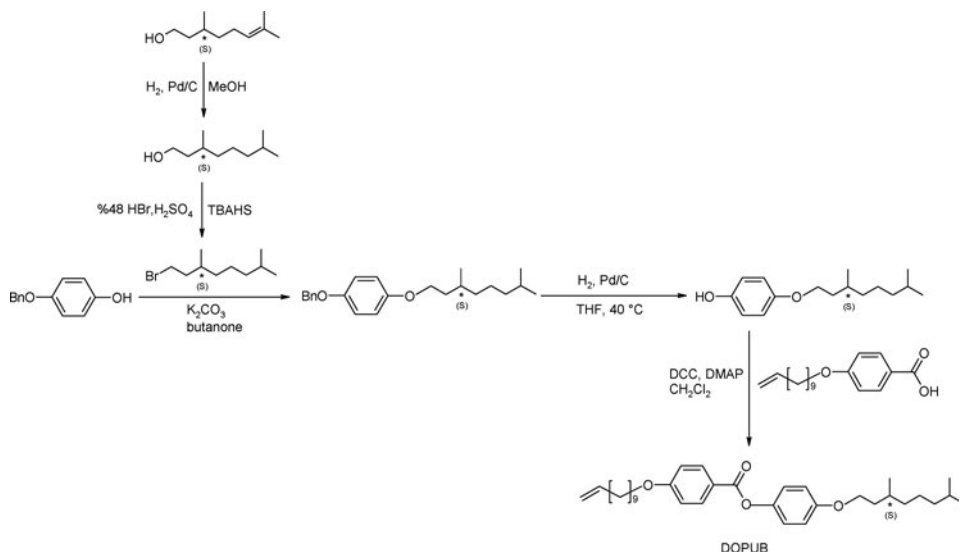
The montmorillonite clay was provided by Across Organics, surface area = 240 m²/g. The surfactant molecule is cetyltrimethylammonium bromide, of chemical formula $\text{C}_{19}\text{H}_{42}\text{NBr}$ (CTAB) was purchased by Merck. ((S)-3,7-dimethyloctyloxy chiral terminal group of DOPUB liquid crystal was introduced from starting with commercial material (S)-(-)- β -Citronellol (Aldrich, $\geq 99.0\%$, $[\alpha]_{\text{D}}^{20} = -5.3^\circ$, neat).

X-ray diffraction (XRD) patterns were obtained using an Analytical Philips X'Pert-Pro X-ray diffractometer with CuK_α radiation of wavelength ($\lambda = 0.154 \text{ nm}$) at the rate of $0.5^\circ/\text{min}$ in the range of $5\text{--}80^\circ$ (2θ) at room temperature. XRD analysis was carried out on the clay mineral powder and on the dispersion of the montmorillonite in the DOPUB. Mesomorphic properties were studied by optical microscopy using a Leica Polarizing Microscope, equipped with a Mettler FP-82 HT hot stage and control unit. Transition thermal analysis was conducted by a differential scanning calorimetry (DSC) under nitrogen atmosphere in a Perkin-Elmer calorimeter with a cooling system. About 8 (± 0.5) mg nanocomposites samples were crimped in an aluminum pan and heated at a rate $10^\circ\text{C}/\text{min}$ from room temperature to -20 to 100°C in a nitrogen atmosphere.

Synthesis, Characterization, and Liquid Crystalline Properties of DOPUB Liquid Crystal

The synthesis of 4'-((S)-3,7-dimethyloctyloxy)phenyl 4-(10-undecen-1-yloxy)benzoate (DOPUB) liquid crystal was carried out as shown in Scheme 1. (S)-(-)- β -Citronellol was reduced to (S)-3,7-dimethyl-1-octanol under catalytic hydrogenation conditions (H_2 , Pd/C in MeOH) [11] in the first reaction step of the DOPUB. Then, (S)-3,7-dimethyloctyl bromide which was prepared from corresponding starting alcohol ((S)-3,7-dimethyloctanol) as described by Jocelyn et al. [12] was used to introduce the chiral moiety at the terminal position of DOPUB. The (S)-3,7-dimethyloctyloxy group was attached to 4-benzyloxyphenol by etherification and then debenzoylation [13] was realized under catalytic

hydrogenation conditions to give 4-(S)-3,7-dimethyloctyloxyphenol. Finally, DOPUB liquid crystal was obtained by the esterification of 4-(S)-3,7-dimethyloctyloxyphenol with 4-(10-undecen-1-yloxy)benzoic acid [14] as procedures described previously [15].



Scheme 1. Synthesis of the new chiral calamitic liquid crystal DOPUB

The characterization of the DOPUB is based on ^1H -, ^{13}C -NMR (Bruker Avance III 500 spectrometer in CDCl_3 solutions, with tetramethylsilane as internal standard). The proposed structure is in full agreement with the spectroscopic data.

The procedure for 4'-((S)-3,7-dimethyloctyloxy)phenyl 4-(10-undecen-1-yloxy)benzoate (DOPUB): To a solution of the 4-(10-undecen-1-yloxy)benzoic acid (4.8 mmol) and 4'-(S)-3,7-dimethyloctyloxyphenol (5.2 mmol) in 40 mL of dry dichloromethane, 5.9 mmol of dicyclohexylcarbodiimide (DCC) and 0.5 mmol of dimethylaminopyridine (DMAP) as catalyst were added and the reaction mixture was stirred at room temperature under an argon atmosphere for 24 h. The precipitate was filtered off on silica gel and washed with dichloromethane (DCM). The solvent was evaporated. The crude products were purified by column chromatography on silica gel using dichloromethane as eluent and recrystallized from ethanol. Yield: 0.99 g (40%) of white crystals. ^1H -NMR (500 MHz, CDCl_3) δ (ppm) = 8.13 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.09 (d, $J \approx 9.0$ Hz; 2 Ar-H), 6.96 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.92 (d, $J \approx 9.0$ Hz; 2 Ar-H), 5.86–5.77 (m; 1H, $\text{CH}_2=\text{CH}$), 5.02–4.92 (m; 2H, $\text{CH}_2=\text{CH}$), 4.04 (t; $J \approx 6.6$ Hz; 2H, OCH_2), 4.01–3.95 (m; 2H, OCH_2), 2.07–2.02 (m; 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 1.86–1.78 (m; 3H, CH_2 , CH), 1.69–1.43, 1.39–1.14 (2m; 21H, 1 CH, 10 CH_2), 0.95 (d; $J \approx 6.6$ Hz; 3H, CH_3), 0.87 (d; $J \approx 6.5$ Hz; 6H, 2 CH_3). ^{13}C -NMR (125 MHz, CDCl_3) δ (ppm) = 165.38 (CO), 163.44, 156.77, 144.35, 121.67 (Ar-C), 132.22, 122.48, 115.07, 114.24 (Ar-CH), 139.23 ($\text{CH}_2=\text{CH}$), 114.16 ($\text{CH}_2=\text{CH}$), 68.30, 66.73 (OCH_2), 37.29, 36.23 (CH), 39.25, 33.82, 29.84, 29.50, 29.42, 29.35, 29.12, 29.11, 28.93, 27.99, 25.99, 24.68 (CH_2), 22.74, 22.63, 19.66 (CH_3).

Sample Preparation

Modification of Montmorillonite

The organic clay was prepared by exchanging the inorganic cation reaction of montmorillonite with quaternary cetyltrimethylammonium bromide (CTAB). Montmorillonite clay was dispersed in dimethyl sulfoxide (DMSO) by stirring. Cetyltrimethylammonium bromide was added to the dispersion. The dispersion was stirring for 24 hr at 80°C. After modified clay was recovered by centrifugation, washed repeatedly with deionized water until supernatant solution was free of bromide ions was detected by addition of AgNO₃, and finally dried at 60°C. The organoclay with CTAB is symbolized here after by OMMT [16].

Preparation and Characterization of Liquid Crystal/Organo-Montmorillonite Nanocomposites

The Liquid Crystal/Organo-Montmorillonite nanocomposites were prepared by solution intercalation method using modified montmorillonite and new mesogen DOPUB. The DOPUB/OMMT nanocomposites were obtained by compounding the modified clay mineral OMMT with adding 2.5, 5, and 7.5 wt%. The organoclay was dispersed with chloroform by constant magnetic stirring for 24 hr. DOPUB was dissolved in chloroform at room temperature. Afterwards, two solutions were mixed and the dispersion was maintained by constant magnetic stirring at room temperature for 24 hr. The sample was dried at 25°C under vacuum for a week [17–18].

Results and Discussion

Liquid Crystalline Properties

The mesomorphic properties of the obtained new chiral calamitic liquid crystal DOPUB were investigated by optical polarizing microscopy and differential scanning calorimetry (DSC). The transition temperatures, corresponding enthalpy values and mesophase type observed for DOPUB are given in Fig. 1.

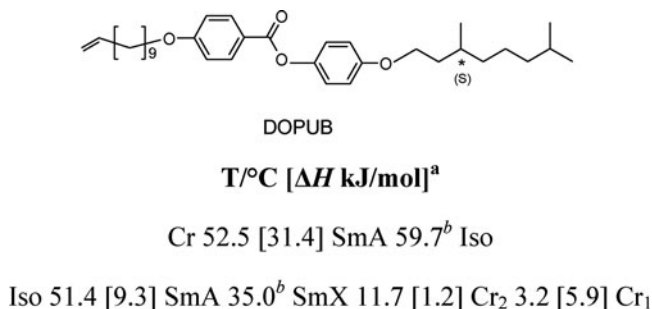


Figure 1. The chemical structure and phase transition temperatures of the DOPUB. (a) Perkin–Elmer DSC-6; heating (top lines)/cooling (bottom lines) rates were 10°C/min; enthalpy values are given in square parentheses. Abbreviations: Cr = crystalline, Sm = smectic, Iso = isotropic liquid phase; (b) Transition was detected by polarizing microscopy.

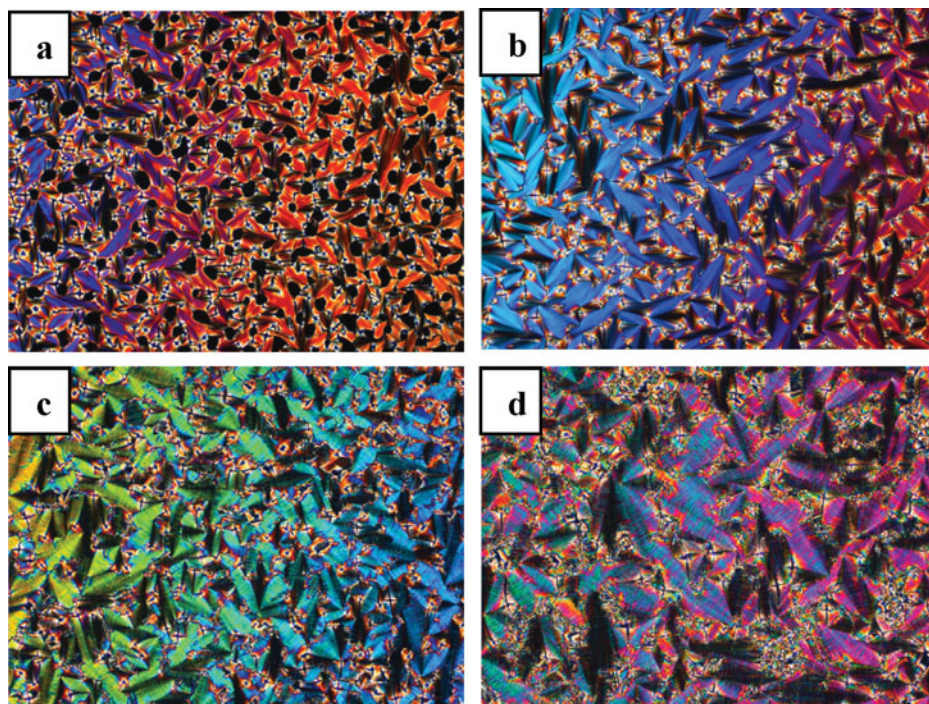


Figure 2. The textures obtained between crossed polarizers as observed for the smectic phases of DOPUB (a) SmA phase on heating; (b) fan-shaped texture of the SmA phase at 46.0°C on cooling; (c) texture of the SmX phase at 33.0°C on cooling; (d) the SmX phase at 30°C on cooling.

The chiral calamitic liquid crystal compound DOPUB exhibits smectic mesophases at low temperatures. On heating, the typical fan-like texture of the smectic A mesophase of compound DOPUB is appeared as shown in Fig. 2. Although this phase transition is not associated with a calculable peak in the DSC thermogram, a small detectable hump is observed at around 58°C in the heating curve (see Fig. 5). On cooling from the isotropic liquid, SmA mesophase first develops a fan-shaped texture in planar alignment and homeotropically aligned regions appearing completely dark. With decreasing temperature, at 35°C, the fan-shaped texture of the mesophase does not change but some lines on fans starts appearing, which becomes sharper as the temperature is reduced further. This mesophase is assigned as SmX phase. No peak is observed for this transition in the DSC cooling curve. On further cooling, optically there is no change, only a strong increase of the viscosity is observed at lower temperatures. The typical textures of the smectic mesophases of compound DOPUB are shown in Fig. 2.

Organo-montmorillonite and Nanocomposites Properties

The X-ray diffraction patterns at room temperature of purified MMT, modified OMMT and adding 2.5, 5, and 7.5 wt% DOPUB/OMMT nanocomposites in the region $2\theta = 5\text{--}50^\circ$ was investigated. The pattern of purified MMT exhibits a strong diffraction peak with the mean interlayer spacing of the (001) plane, d001, given in Fig. 3. A typical diffraction peak of purified MMT is $2\theta = 8.921^\circ$, responding to a basal spacing (d-spacing) of 9.90 Å. Montmorillonite is a smectite group with layered structure composed of silicate layers.

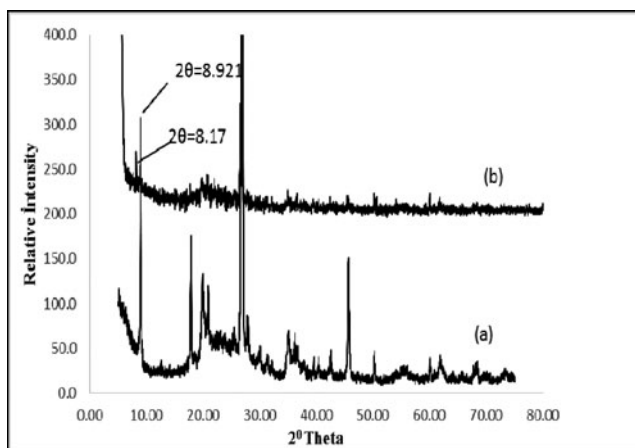


Figure 3. XRD of patterns of MMT (a) and OMMT (b).

These silicate layers are filled exchangeable cations such as Mg^{+2} , Ca^{+2} , Na^{+} , and water molecules. In this study, the exchangeable cations of montmorillonite exchanged with cetyltrimethylammonium bromide (CTAB). The pattern of modified OMMT was a peak at $2\theta = 8.17^\circ$, responding to a basal spacing of 10.81 \AA , given in Fig. 3. OMMT the d001 reflection broadened and shifted to lower angles, that is larger d-spacing, compared to unmodified MMT, indicating the exchange of inorganic cations in between the MMT layers with organic cations. As a result of modification of MMT with CTAB, OMMT of interlayered silicate layers expanded. The X-ray diffraction pattern of DOPUB/OMMT nanocomposites showed that Fig. 4.

It was observed that there were XRD characteristic peaks for DOPUB liquid crystal in the range of $2\theta = 14\text{--}26^\circ$. It was found that the diffraction peak positions are only slightly changed. The pattern of DOPUB exhibit a diffraction peaks are $2\theta = 17.98^\circ$ and 23.36° , responding to a basal spacing of 4.93 \AA and 3.80 \AA , respectively. The patterns of DOPUB/OMMT nanocomposites exhibit a diffraction peak are observed with DOPUB

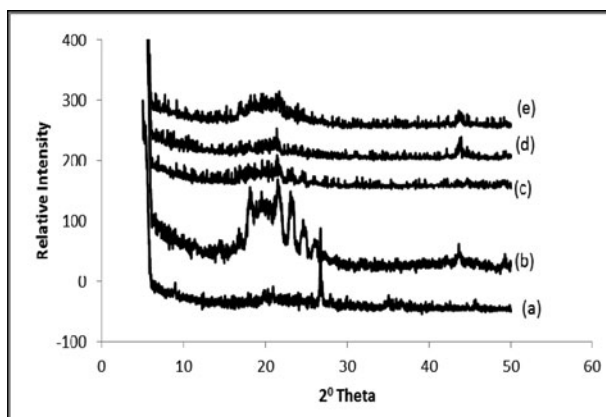


Figure 4. XRD of patterns of OMMT (a), DOPUB (b), DOPUB/OMMT nanocomposites in the ratio 2.5 wt% (c), 5 wt% (d), and 7.5 wt% (e).

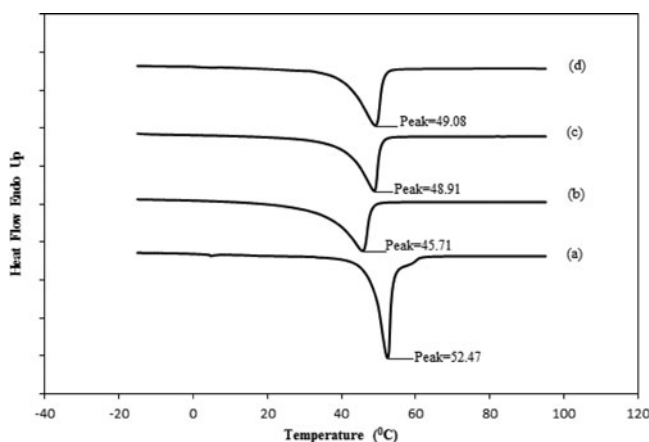


Figure 5. DSC scans of compound DOPUB (a), DOPUB/OMMT nanocomposites in the ratio 2.5% (b) 5% (c), and 7.5% (d) during the heating process (heating rates 10°C/min).

liquid crystal in the same characteristics peaks. However, the presence of the characteristic reflection of modified clay in the liquid crystal indicates that layered silicate is not observed within all the DOPUB/OMMT nanocomposites. The OMMT peak is dispersed within the DOPUB/OMMT nanocomposites, indicating that intercalation of the new chiral liquid crystal DOPUB within the modified clay OMMT occurs. As a result, exfoliated DOPUB/OMMT nanocomposites (2.5, 5, and 7.5 wt%) could be prepared.

The thermotropic behavior of DOPUB/OMMT nanocomposites were also investigated by POM and DSC. As seen from DSC, the heating and cooling curves in Figs. 5 and 6 of DOPUB, OMMT modified clay and DOPUB/OMMT nanocomposites in the ratio 2.5 wt%, 5 wt%, 7.5 wt%, DOPUB/OMMT nanocomposites show only a monotropic smectic A phase at lower temperatures, as indicated by small exotherms in the DSC cooling curves. Whereas an additional mesophase (SmX) occurs in the phase sequence of DOPUB at 35°C on cooling, any textural transformations are not observed (compare textures in Fig. 7) before

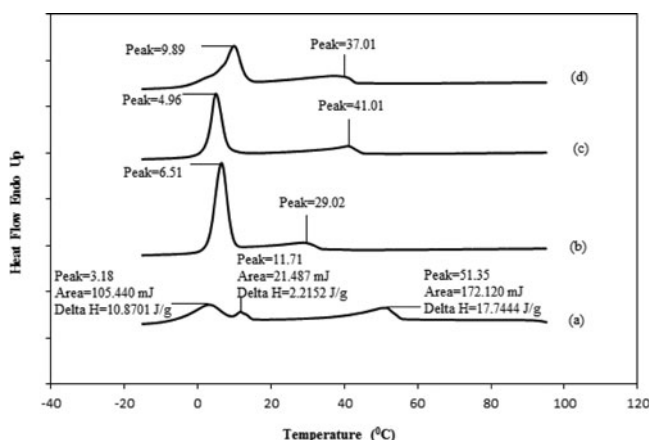


Figure 6. DSC scans of compound DOPUB (a), DOPUB/OMMT nanocomposites in the ratio 2.5% (b) 5% (c), and 7.5% (d) during the cooling process (cooling rates 10°C/min).

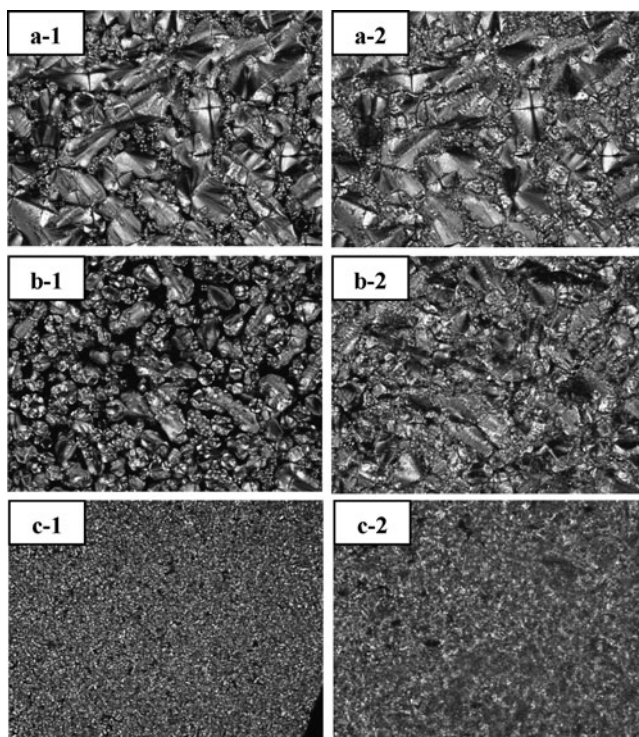


Figure 7. The textures obtained between crossed polarizers as observed for the smectic phase at (1) 36°C and (2) 25°C of DOPUB/OMMT nanocomposites in the ratio 2.5% (a) 5% (b), and 7.5% (c), respectively.

crystallization point for DOPUB/OMMT nanocomposites. Comparing the mesomorphic properties of the DOPUB liquid crystal with the DOPUB/OMMT nanocomposites shows that mesophase type remains the same and mesophase transition temperatures decrease by adding OMMT in the different ratio.

As compared with 2.5 wt% DOPUB/OMMT nanocomposite, the clearing points and mesophase ranges of the DOPUB/OMMT nanocomposites in the ratio 5 wt% and 7.5 wt% increase with increasing ratio of the modified clay mineral OMMT leading to a stabilization of smectic mesophase. The SmA mesophase range of the nanocomposites 5 wt% and 7.5 wt% are slightly broader than 2.5 wt% DOPUB/OMMT nanocomposite (see Fig. 6). In addition, in the case of DOPUB/OMMT nanocomposites the transition from the isotropic liquid to the SmA phase is broadened due to the fact that an additional mesophase (SmX) occurs in the phase sequence of DOPUB liquid crystal at 35°C that is not observed for DOPUB/OMMT nanocomposites. Hence, the only mesophase of DOPUB/OMMT nanocomposites, SmA, shows a mesophase interval which is about 16°C wider than that observed for the DOPUB liquid crystal.

Conclusions

A new chiral calamitic liquid crystal DOPUB has been synthesized and investigated. The DOPUB exhibits enantiotropic SmA and monotropic SmX mesophases at low temperatures. The new chiral calamitic liquid crystal DOPUB/OMMT nanocomposites in the ratio

2.5 wt%, 5 wt%, 7.5 wt% have been prepared in order to investigate the dispersion of the liquid crystal in OMMT and compare the changes in the morphology, thermal behavior, and liquid crystalline properties of DOPUB/OMMT nanocomposites. MMT modified by CTAB for increasing the interaction of clay with DOPUB liquid crystal. By using the XRD analysis, we showed that the diffraction peak of purified MMT is $2\theta = 8.921^\circ$, responding to a basal spacing (d-spacing) of 9.90 Å. The pattern of organoclay OMMT was a peak at $2\theta = 8.17^\circ$, responding to a basal spacing of 10.81 Å. By the modification of MMT with CTAB, interlayered silicate layers of OMMT expanded. It was observed that there were XRD characteristic peaks of modified clay in the liquid crystal DOPUB indicates that layered silicate is not observed within all the DOPUB/OMMT nanocomposites. Comparing the mesomorphic properties of the DOPUB liquid crystal with the DOPUB/OMMT nanocomposites shows that the SmA mesophase only appears on cooling and the mesophase transition temperatures decreased by adding OMMT in the different ratio 2.5 wt%, 5 wt%, and 7.5 wt%. The SmA mesophase range of the nanocomposites in the ratio 5 wt% and 7.5 wt% are slightly broader than 2.5 wt% DOPUB/OMMT nanocomposite. It can be concluded that in DOPUB/OMMT nanocomposites there is a considerable effect of the insertion of OMMT in the different ratio on the mesophase stability compared to the pure liquid crystal.

Acknowledgments

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