

Polymer Dispersed Liquid Crystals Based on Poly(styrene-*b*-ethylene oxide), Poly(bisphenol a carbonate) or Poly(methylphenylsiloxane), and 4'-(Hexyloxy)-4-biphenyl-carbonitrile: Analysis of Phase Diagrams and Morphologies Generated

Agnieszka Tercjak, Elena Serrano, Maider Larrañaga, Iñaki Mondragon

Departamento de Ingeniería Química y Medio Ambiente, Escuela Politécnica, Universidad del País Vasco/Euskal Herriko Unibertsitatea, Plaza Europa, 1 20018 Donostia/San Sebastián, Spain

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ABSTRACT: Thermodynamic phase behavior was studied for polymer dispersed liquid crystal (PDLC) films consisting of blends of different thermoplastics such as poly (bisphenol A carbonate) (PC), poly(methylphenylsiloxane) (PMPLSi), poly(styrene-*b*-ethylene oxide) (PSEO) block copolymer, and low-molecular weight 4'-(hexyloxy)-4-biphenyl-carbonitrile (HOBC) liquid crystals. The phase diagrams of these PDLC systems were built up using thermal transitions determined by differential scanning calorimetry (DSC), transmission optical microscopy (TOM), and dynamic mechanical analysis (DMA). Final morphology of these PDLC films generated by tempera-

ture induced phase separation was monitored by TOM. The final morphology of HOBC blends with PC, PSEO, or PMPLSi could be modified by controlling the relative compositions resulting in PDLC systems with small and narrow size-distribution of nematic droplets, suitable for use in thermo-optical devices. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1116–1125, 2008

Key words: miscibility; phase separation; polymer dispersed liquid crystal; thermal properties; thermally reversible materials

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) composite films constitute a novel class of optical materials, because of their potential uses in thermo- and electro-optical devices^{1–12} such as optical switches (light shutters), transmittance (transparency) windows, and reflective displays. They usually consist of few micron ($\sim 5 \mu\text{m}$ or less) size droplets of a low-molecular mass liquid crystal (LC) dispersed in an optically transparent polymer matrix.^{1,7,13–15} PDLC films have considerable potential for large area LC display devices and light control applications. Since these composite systems exhibit the anisotropic optical and dielectric properties of nematic LCs, by choosing appropriate combinations of LCs and polymer materials they can be optically switched from highly light scattering

state (OFF-state) to transparent state (ON-state) due to mismatching and matching of the refractive indices of the polymer and the oriented LC by applying external field (thermal gradient or relatively small electrical voltage).^{4,16–20} In the OFF-state, surface anchoring causes a nonuniform director field within the droplets, and the film scatters light due to the mismatching between the effective refractive index, n_{eff} , of the LC and the refractive index, n_p , of the polymer.²¹ In the field ON-state, the director is aligned along the field direction ($n_{\text{eff}} = n_o$) and for normal light incidence, the film becomes transparent if the ordinary refractive index n_o of the LC is equal to n_p .^{7,22,23} Both the threshold voltage, V_{th} , and the response times τ_R and τ_D (rise and decay times, respectively) at which the PDLC switches from whiteness to transparency and the optical contrast between the white and transparent state are controlled by the size, shape,^{24,25} and anchoring energy of the LC domains. It is well established that the morphology generated strongly affects the thermo- and electro-optical properties of PDLC materials.^{17,26–31} In general, the morphology is controlled by relative rates of phase separation, which depend on a number of factors such as type of LC and thermoplastic (TP) or block copolymer (BC), LC concentration, compatibility

Correspondence to: A. Tercjak (scptesza@sc.ehu.es)

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between the LC and TP or BC, and others. PDLCs have number of advantages over conventional low-molecular-mass LC displays. Some of the advantages are simple manufacturing and minimal fabrication cost, flexibility, a higher contrast ratio, and fast response time.

Although there are many studies reported on the phase behavior and the morphology of PDLC systems for many polymer/LC blends. However, the mixtures between polysiloxanes and a low-molecular-weight LC have seldom been examined except for the reports of Gogibus et al.^{32–34} These authors studied the phase behavior and morphology generated in binary blends of poly(methylphenylsiloxane) (PMPLSi) or poly(dimethylsiloxane) with two low-molecular-weight LCs (4-cyano-4'-*n*-pentyl-biphenyl and eutectic mixture of parafenylenes). They constructed phase diagrams, via transmission optical microscopy (TOM), where a relation between the Flory-Huggins theory of isotropic mixture and the Maier-Saupe theory of nematic order has been found to exist. They conclude that there was a good agreement between theory and experiments, and their results reveal a remarkable enhancement of the miscibility of PDLC with respect to similar systems involving poly(dimethylsiloxane). From the literature it should be noted that the knowledge of the phase diagram of a polymer/LC system is still prerequisite for any complete interpretation of the electro-optical characterization with respect to the film morphology of PDLC materials.

Apart from polysiloxane blends, mixtures of LC with BC have also not been the objective of many research investigations.³⁵ Taking into account that, one of the most promising results in the field of PDLC devices were obtained using polystyrene (PS) as the matrix,^{28,36–38} we consider that using BCs with PS as one of the copolymer blocks for preparation of PDLC films can provide an interesting variety of phase separated morphologies. Thus, controlling the morphology of LC/BCs blends may result in achieving new types of multifunctional materials including thermo- and electro-optical thin films. This is because both the polymer matrix and the low-molecular-weight LCs can respond to external stimuli (auto-assembly of BC and alignment of LC). It is essential to establish the phase diagram of PDLC and the corresponding morphologies before attempting to any study on the dynamics of polymerization-induced phase separation in the thermosetting system modified with PDLCs, which is one of our ongoing goals.

In our previous study,^{38,39–41} we have reported preparation, thermo-optical properties, and generated morphologies of TP/thermoset systems modified by nematic LCs. The main objective of this article is the preparation of binary TP/nematic LC blends, to analyze the thermo-optical behavior as a

function of generated morphology. Such PDLC systems can be used to prepare meso/nano multifunctional thermosetting materials especially in case BC blends, which will be the subject of our further study.

The main aim of this study was to establish the equilibrium phase diagrams of mixtures of a TP such as poly(bisphenol A carbonate) (PC), PMPLSi, poly(styrene-*b*-ethylene oxide) (PSEO) BC, and a low-molecular-weight liquid crystal (4'-(hexyloxy)-4-biphenyl-carbonitrile) (HOBC) as well as to analyze the phase behavior of PDLC systems during heating/cooling process using TOM, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). Further, the morphology changes generated *in situ* during switching from opaque (OFF-state) to transparent state (ON-state) was analyzed. The influence of the cooling intervals on the distribution of the particles sizes in the final morphology of PDLC systems has also been studied by TOM.

EXPERIMENTAL

Materials

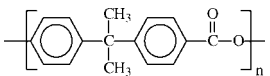
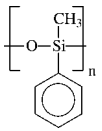
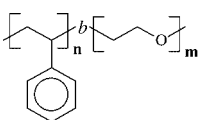
In this study, two different thermoplastics (TP), poly(bisphenol A carbonate) (PC) and poly(methylphenylsiloxane) (PMPLSi), both supplied by Sigma-Aldrich (Spain), as well as a polystyrene-*block*-poly(ethylene oxide) (PSEO) diblock copolymer, supplied by Polymer Source, have been used. Their chemical structures, molecular weight, and refractive index are shown in Table I. Here, it should be noted that different molecular weight of the TP is partially responsible for miscibility between components and consequently for different final properties of generated PDLC. Nonetheless, different chemical structure of investigated materials is taken into account, this aspect cannot be discussed in this article.

The nematic LC used was 4'-(hexyloxy)-4-biphenyl carbonitrile (HOBC), supplied by Sigma-Aldrich (Spain), and it was used without further purification. The chemical structure and properties of this LC are shown in Table II.

Sample preparation

Binary blends of PC, PMPLSi, or PSEO with HOC in the whole range of compositions were prepared in the same following way: first, both components were dissolved in tetrahydrofuran to make a 10–15 wt % solution. The resultant solutions were stirred mechanically for 24 h at room temperature under the same conditions. Then, the temperature was raised to 130°C and the solvent was allowed to completely evaporate for 24 h. The pure components

TABLE I
Characteristics of the TPs and the BC

Name	Chemical structure	M_n^a (g mol ⁻¹)	M_w/M_n^b	n_d^c
PC		17,300	-	1.586
PMPLSi		720	-	1.609
PSEO		PS = 125,000 PEO = 16,100	1.4	1.568

^a Number-average molecular weight (from supplier).

^b Polydispersity index (from supplier).

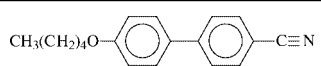
^c TexLoc Refractive Index of Polymers.

films have been obtained in the same way as the polymer or block copolymer/LC blends.

Techniques

Thermo-optical behavior of both TP/LC binary blends was investigated by using a transmission optical microscope (TOM) (Nikon Eclipse E600) equipped with a hot stage (HS) (Mettler FP 82HT) using crossed polarizers. For microscopy measurements, a small quantity of the mixture was cast on a clean glass slide at 130°C, and after heating, following the standard procedure of sample preparation, the glass slide was sandwiched by another one. The thickness of the samples was controlled by using a 0.5-mm aluminum spacer. This procedure was repeated to have at least two independently prepared samples of the same composition. To get changes in transmission light when the external gradient of temperature was applied, the thin film placed between two microscope slides was heated/cooled/heated from 30 to 80°C at a rate of 1°C min⁻¹.

TABLE II
Characteristic of the LC

Name	Chemical structure	T_{CN}^a (°C)	T_{NI}^b (°C)
HOBC		59	76

^a Crystal-nematic (T_{CN}) transition.

^b Nematic-isotropic (T_{NI}) transition temperatures as determined by DSC (see Fig. 1).

The morphological features of binary blends were investigated by optical microscopy with crossed polarizers. The images were captured every 15 s and the thickness of the samples was controlled. Additionally, direct representation of morphologies during switching between opaque to transparent state were recorded with and without crossed polarizers.

The miscibility between TPs and nematic crystals was analyzed on a Mettler Toledo DSC 822 differential scanning calorimeter. Nitrogen was used as purge gas (10 mL min⁻¹). Temperature and enthalpy were calibrated by using an indium standard. Measurements were performed in sealed aluminum pans containing a sample weight of around 7 mg. To ensure comparable thermal history, all samples were first heated to 150°C and maintained at that temperature for 10 min, then cooled down to -50°C, and reheated to 150°C. All scans were performed at a constant rate of 5°C min⁻¹. The DSC measurements allow determining the thermal transitions. The nematic-isotropic transition temperature (T_{N-I}) was defined at the end of the characteristic endothermic peak, corresponding to the temperature at which the last fraction of the LCs was melted. The resulting T_{N-I} is a point located in the isotropic-nematic equilibrium curve, obtained without the undercooling observed when decreasing the temperature from the isotropic region. The melting temperature of the LC phase was also determined at the end of the characteristic endothermic transition. Typical representative DSC endothermic curves used to determine both the nematic-isotropic transition temperature and the melting temperature obtained for PC/HOBC blends was shown in the Figure 1. Heating scans were performed after a storage period of a few days at room temperature to promote crystallization.

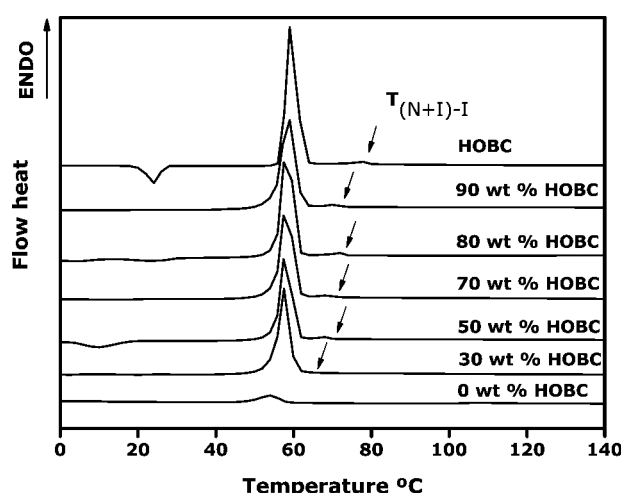


Figure 1 DSC thermograms for PC/HOBC system with different PC contents.

DMA of the specimens was carried out on binary blends with a Perkin–Elmer DMA7 in a one-point device to obtain glass transition temperatures (T_g). The temperature range studied was from 30 to 250°C at a heating rate of 5°C min⁻¹, using powder samples. During the scans the samples were subjected to a static force of 110 mN and a dynamic force of 100 mN, at a frequency of 1 Hz. The glass transition temperature of the mixtures was taken as temperature corresponding to the maximum of loss factor, $\tan \delta$, peak.

RESULTS AND DISCUSSION

Figure 2(a–c) shows the phase diagrams of PC/HOBC, PMPLSi/HOBC, and PSEO/HOBC systems, respectively. In all phase diagrams it can be observed that there is a critical concentration of LC for phase separation from glassy state of both components (G) to binary system, which has been carefully analyzed for each system below. Above this concentration, the equilibrium phase diagrams of both PC/HOBC and PSEO/HOBC blends show two phase transition lines separating three different regions, which are clearly identified on the diagrams. In the upper region, a single phase is obtained, thus the polymer and LC form an isotropic solution (denoted as I). In addition, both systems show two binary regions below the coexisting curves: nematic + isotropic liquid mainly containing polymer (N+I) and crystalline phase of HOBC + isotropic liquid mainly containing polymer (K+I).

In the same measurement conditions, the phase diagram of PMPLSi/HOBC, Figure 2(b), reveals the presence of the three binary phases observed for the other systems; that is, isotropic liquid (I), nematic + isotropic (N+I), and crystalline + isotropic (K+I). In addition, the formation of a nematic pure region of HOBC (denoted as N) at high concentrations of LC can be clearly observed. It should be noted that all transitions were observed by using optical microscopy but only two of them can be detected by DSC, the (K+I) to (N+I) and (K+I) to (I) transitions. As it was published in our previous article,³⁸ the typical DSC thermograms of these systems show distinctly the transitions from crystalline to nematic and from nematic to isotropic regions Figure 1.

For PC/HOBC systems [Fig. 2(a)], the (N+I) binary phase exists for HOBC contents higher than 10 wt %. The temperature of the (N+I) to (I) transition, $T_{(N+I)-(I)}$, of these PDLc samples increases with increasing HOBC content and finally $T_{(N+I)-(I)}$ for high HOBC content almost reaches the temperature of (N) to (I) transition of pure HOBC (entry T_{N-I} in Table II). From this phase diagram, it can be clearly seen that the range in which PDLc system

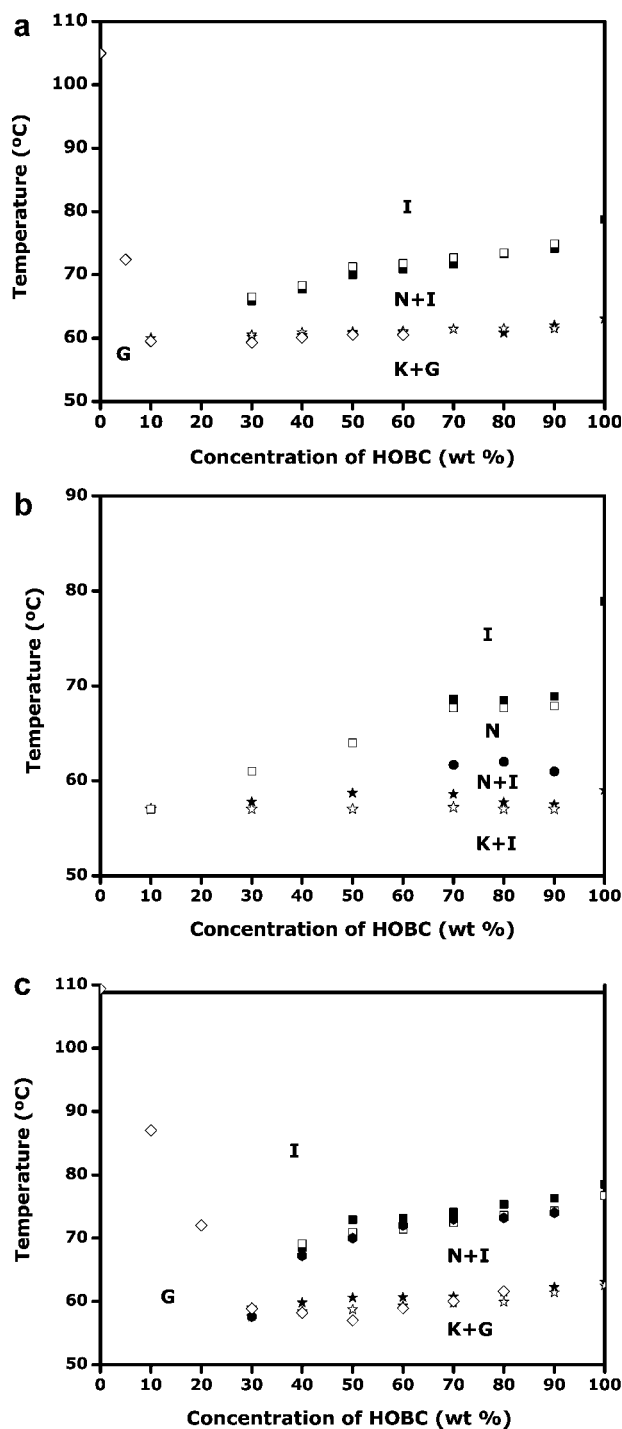


Figure 2 Equilibrium phase diagram of (a) PC/HOBC, (b) PMPLSi/HOBC, and (c) PSEO/HOBC systems. The symbols \star and \star represent the transition temperature from (K+G) to (N+I) state for TOM and DSC measurements, respectively; \square and \blacksquare represent the transition temperature from (N+I) to I state for TOM and DSC measurements, respectively; and \diamond represent the transition temperature from glassy to elastic state detected by DMA measurement.

maintains the (N+I) state becomes wider with increasing of HOBC content. Indeed, for 90 wt % of HOBC the nematic phase can be presented from 57

to 69°C, thus 10PC/90HOBC sample exhibits mesostable nematic phase of HOBC approximately in the same range that corresponds to the pure HOBC. This observation indicates that nematic phase is a pure LC phase. Moreover, it is also worth to note that the introduction of PC into the blends do not have any influence on the temperature of the (K+G) to (N+I) transition ($T_{(K+G)-(N+I)}$). However, the crystallization of HOBC in PC/HOBC systems was hindered by addition of PC. In fact, spherulites of HOBC phase in PDLC after cooling down from (N+I) region to room temperature were visually observed only after a few hours at 25°C, which is in agreement with the results obtained from DSC. It is well known that the crystallization of LC in PDLC systems at room temperature impedes their use for optical devices. Usually, eutectic mixtures of various LCs are used for these purposes, principally to avoid crystallization and to produce the desired matching of refractive indices. Although the PC/HOBC blends can be taken as model systems, from application point of view, and it is interesting to study the changes in morphologies on the addition of PC, which hinders crystallization of LC, which are discussed later in the article.

For PMPLSi/HOBC blends, the phase diagram is different from that for PC/HOBC, especially for the behavior of nematic phase of HOBC. Similar to PC/HOBC blends, the (N+I) binary phase exists when HOBC is higher than 10 wt %. However, the range in which PMPLSi/HOBC blends is in the (N+I) state is narrower. Additionally, as observed by TOM+HS, for HOBC concentration higher than 70 wt % the (N+I) binary region is divided into two regions. In the first one, nematic + isotropic binary phases exist and in the second one typical nematic + isotropic binary state is visible at higher temperature. These PDLC systems based on PMPLSi are interesting, from the point of view of application as optical devices, since the addition of PMPLSi delays the crystallization process in these systems as seen by us from the appearance of LC-spherulites after a few days while cooling down from the (N+I) or (N) region to room temperature. Additionally, it can be clearly seen that the addition of PMPLSi into the systems did not have any influence on the temperature in which PDLC systems change their state from the (K+I) one to the (N+I) and, after that, to typical Schlieren nematic phase (N). Here again, DSC results obtained for PMPLSi/HOBC systems are in good agreement with those obtained by TOM+HS. A similar phase diagram for PMPLSi/HOBC was reported by Gogibus et al.^{32–34} for the blends of PMPLSi or poly(dimethylsiloxane) with two different low-molecular-weight liquid crystals (4-cyano-4'-*n*-pentyl-biphenyl and eutectic mixture of paraphenylenes). The partial miscibility between different polysiloxane/LC systems has been confirmed in this study based on DSC and TOM results.

Figure 2(c) shows the phase diagram of PSEO/HOBC systems. The maximum solubility of HOBC with the BC (PSEO) is ~30 wt % HOBC. Higher mass fraction of HOBC leads to binary phase systems when cooling below the equilibrium curve, and it produces vitrification of a liquid phase with 30 wt % HOBC at around 57–60°C, thus building the boundary of the K+G region. Here, it should be noted that, in contradiction to the results for PC/HOBC and PMPLSi/HOBC systems, increasing PSEO content slightly decreases the temperature in which the system comes from the (K+G) state to the (N+I) state. On the other hand, as for the PC/HOBC systems, introducing PSEO into the PDLC hinders crystallization of HOBC phase, which means that HOBC spherulites appear after a few hours at room temperature if cooling down from the (N+I) region. For HOBC content higher than 30 wt % at about 57–60°C, the HOBC crystals are completely transformed into a nematic phase. When the (N+I) region is attained during heating, nematic domains begin to dissolve, increasing the HOBC concentration in the liquid phase along the equilibrium curve, and thus separating the (I) region from the (N+I) one. When the equilibrium curve is reached, the nematic domains are completely dissolved leading to a single isotropic liquid. Here again, DSC results obtained for PSEO/HOBC systems are in good agreement with the data obtained by TOM+HS measurements. PSEO/HOBC blends were not annealed in this study, either for DSC or for TOM+HS measurements. Moreover, the phase diagram established for PSEO/HOBC system is quite similar to the diagrams reported by Hoppe et al.^{28,37} for two different molecular weights PS with *N*-4-ethoxybenzylidene-4'-butylaniline (EBBA), where partial miscibility between components was confirmed by decreasing of the T_g of the PS with addition of small amount of LC to the PDLC blends. The maximum solubility of EBBA in the PS was around 23 wt %, similar to the solubility of the HOBC in the PSEO reported in present work.

Thermo-optical properties of binary blends were also studied by hot-stage cross-polarized optical microscopy. Thermo-optical curves in the isotropization region of PC/HOBC and PSEO/HOBC with 90, 70, 50, and 30 wt % HOBC contents are plotted in Figure 3(a,b), respectively. The corresponding curves for PMPLSi/HOBC with 90 wt % HOBC systems are shown in Figure 3(c). From the results obtained for PC/HOBC and PSEO/HOBC blends with different HOBC contents, it can be concluded that there is a threshold percentage of around 30 wt % HOBC in the blends where nematic-isotropic transition, T_{N-I} , was still detected. The threshold HOBC concentration for PMPLSi containing blends was also 30 wt %. It is worth to note that the addition of PC, PMPLSi,

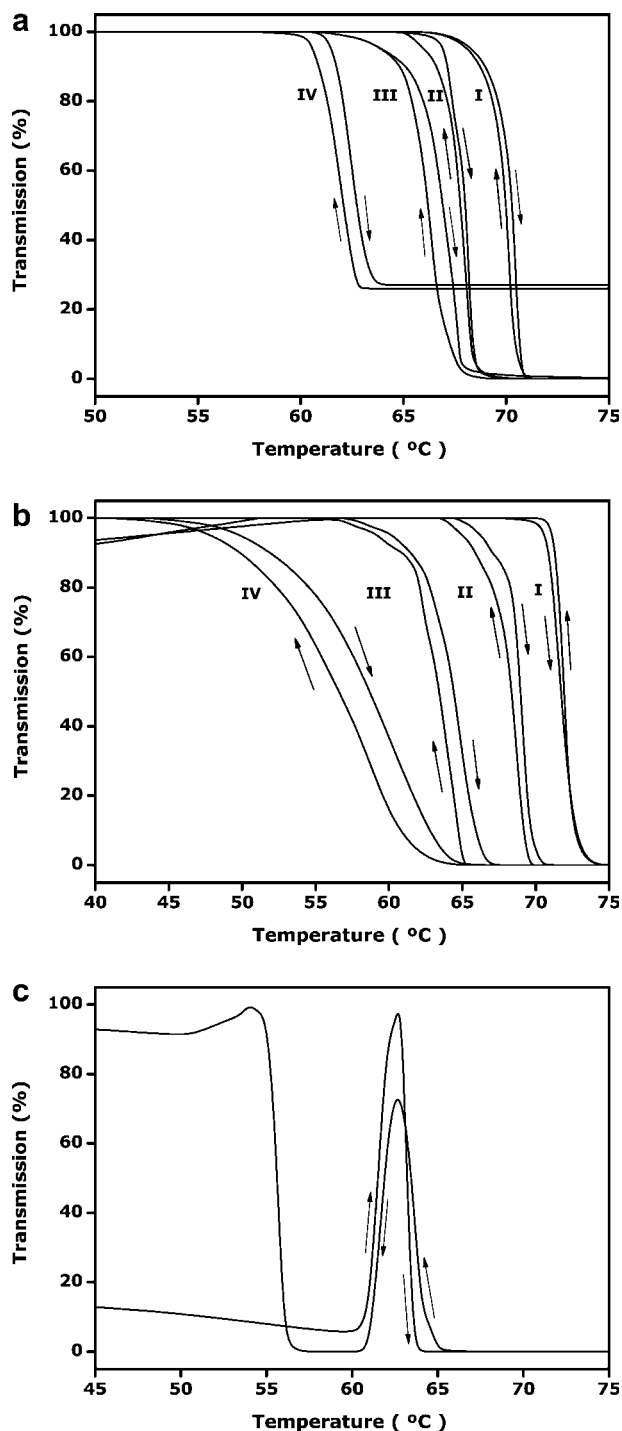


Figure 3 Thermooptical curves in isotropization region of (a) PC/HOBC and (b) PSEO/HOBC blends with HOBC content of: (I) 90 wt %, (II) 70 wt %, (III) 50 wt %, and (IV) 30 wt %. While (c) shows isotropization region of PMPLSi/HOBC blends with 90 wt % HOBC.

or PSEO leads to broader temperature range in which mesophase of LC is in its mesostable nematic state. The addition of PC into PC/HOBC blends has been found to significantly shift the temperature of T_{N-I} to lower temperatures for all the samples and show thermoreversibility. Similar results obtained by

Mucha et al.⁴² for polyacrylic acid modified with benzoyl peroxide allowed him to conclude that obtained materials have good thermo-optical properties. Moreover, Hoppe et al.⁴³ performed the some measurement for thermosetting system modified with EBBA and PS as third component concluding that these PDLC films might be employed as temperature sensors, as thermoreversible recording materials, or as active elements in thermal memory optical devices.

The range of the nematic-isotropic transition is broader for 30 wt % LC samples to compare with samples having higher LC contents in PC/HOBC systems. It is well known, that the narrower range of the nematic-isotropic transition indicates a shorter time for OFF- to ON-state, which suggests that the PC/HOBC with 90 wt % HOBC blend can be a better material for application in optical devices than blends with higher PC content. Furthermore, it may be noted that for the blends containing less than 30 wt % of HOBC, no T_{N-I} was detected neither using DSC nor TOM.

Returning to PSEO/HOBC system, it exhibits a similar behavior to the PC/HOBC blends. In this case, the addition of PSEO to the PDLC systems has stronger influence on the shifting of the temperature in which nematic-isotropic transition takes place. For less than 50 wt % PSEO, the samples show a narrow nematic-isotropic transition of LC. Consequently, PDLC containing less than 50 wt % PSEO has potential application as optical thermoreversible devices, especially the addition of PSEO hinders HOBC crystallization at room temperature. Moreover, both shifting to low temperature of T_{N-I} and hindering of crystallization of HOBC with increasing PSEO content confirm partial miscibility in the systems.

For PMPLSi/HOBC systems [Fig. 3(c)] the thermo-optical curves in the isotropization region are slightly different and show "atypical" behavior during switching from strong scatter light (OFF-state) to transparent state (ON-state). During heating process, the 10 wt % PMPLSi/HOBC blends switch from opaque to transparent state at around 57°C (thermo-optical curve taken with cross-polarizer fell down from 100% transmission to 0%, thus the sample become optically transparent) similar to the typical behavior of neat HOBC. However, after switching, the thermo-optical curve of this blend undergoes additional peak with the maximum at 100% transmission. This "atypical" behavior can be easily understood by following the changes of *in situ* generated morphology during switching process, as shown in Figure 4. Upon heating the PMPLSi/HOBC with 90 wt % HOBC blend from (K+I) phase [30°C; Fig. 4(a)] to the I region [80°C; Fig. 4(j)], birefringent droplets of HOBC appears around 55.5°C [compare Fig. 4(b,c)], suggesting (N+I) phase separation. At around 60°C [Fig. 4(e,f)] nematic droplets

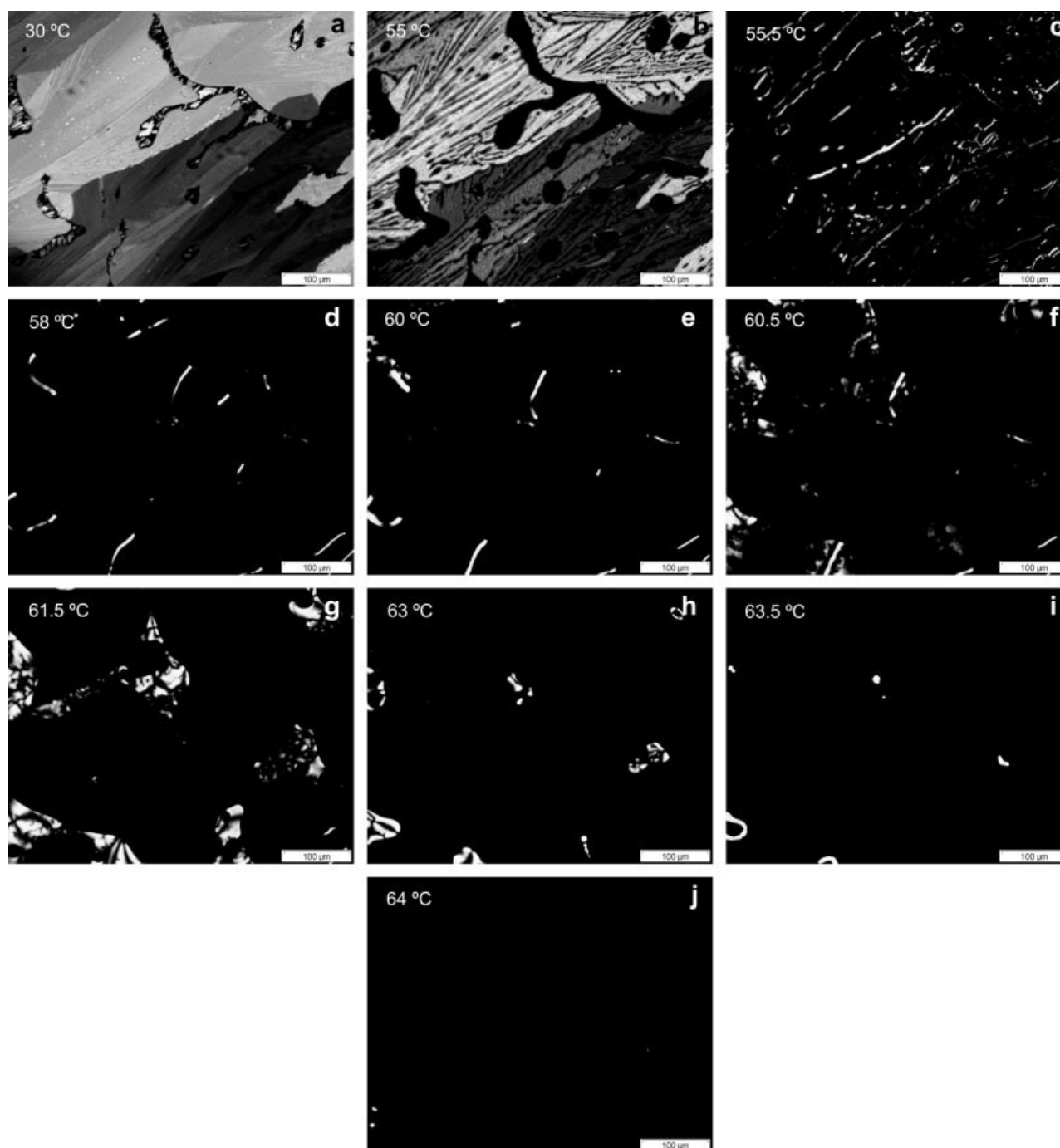


Figure 4 TOM micrographs with crossed polarizers of PMPLSi/HOBC with 90 wt % HOBC blend during cooling at $1^{\circ}\text{C min}^{-1}$. Bar scale is 100 μm .

of HOBC start to grow via coalescence, while exhibiting a Schlieren texture. When PMPLSi/HOBC with 90 wt % HOBC system reach 61.5°C the Schlieren texture becomes smaller upon heating, and at 64°C HOBC phase becomes isotropic. Visualization of *in situ* morphology generated during heating/cooling of PMPLSi/HOBC with 90 wt % HOBC system allows to better understand the “atypical” behavior of this system in the isotropization region.

The morphology of PC/HOBC, PMPLSi/HOBC, and PSEO/HOBC blends, for 50, 70, and 90 wt % HOBC contents is shown in Figures 5–7, respectively. The samples were obtained after quenching from 150°C to room temperature. The morphology generated after this treatment was observed using optical microscopy with crosses-polarizers at room temperature before any crystallization took place. The observed morphologies correspond to a disper-

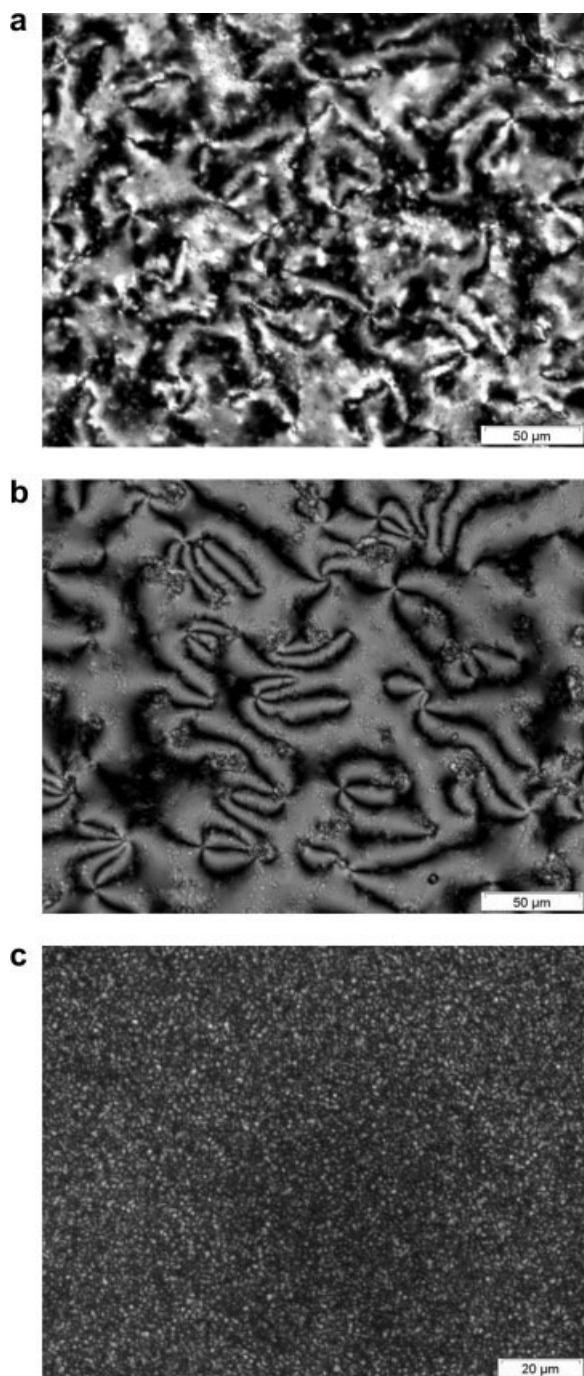


Figure 5 TOM micrographs of PC/HOBC blends, with crossed polarizers, containing: (a) 10 wt %, (b) 30 wt %, and (c) 50 wt % HOBC.

sion of mesostable nematic state of HOBC domains in the matrix. The procedure chosen was mostly taken from the work by Hoppe et al.,²⁸ who have reported that a fast cooling leads to high nucleation rate followed by a limited growth/coalescence of dispersed nematic domains embedded into polymer matrix. Consequently, controlling of the final morphology by changing the cooling rate can lead to thermoreversible materials. Hoppe et al.^{28,37} and

Sumana et al.^{15,18} based on similar observation considered the PS/EBBA PDLC blends or E7 liquid crystal/polydimethyl siloxanes PDLC blends as thermoreversible materials with opto-electronic application.

As expected, among the difference in molecular mass of the three TPs, the average size of nematic domains decreases with increasing PC, PSEO, or PMPLSi content in the systems. Instead of PSEO/

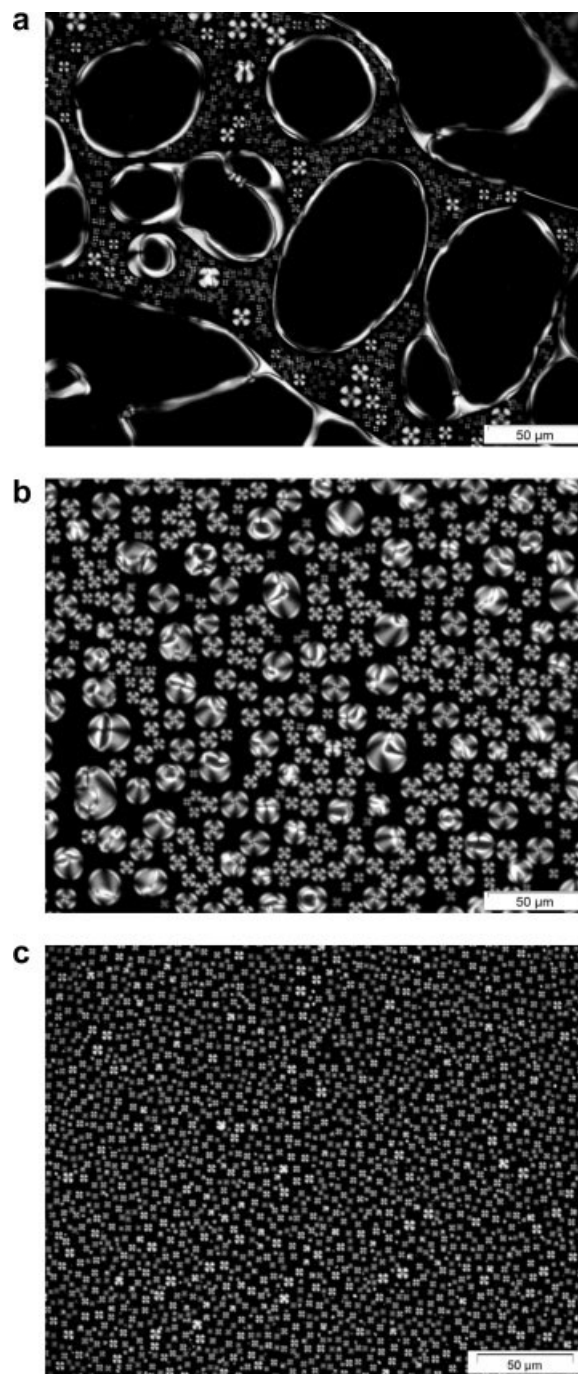


Figure 6 TOM micrographs of PMPLSi/HOBC blends, with crossed polarizers, containing: (a) 10 wt %, (b) 30 wt %, and (c) 50 wt % HOBC.

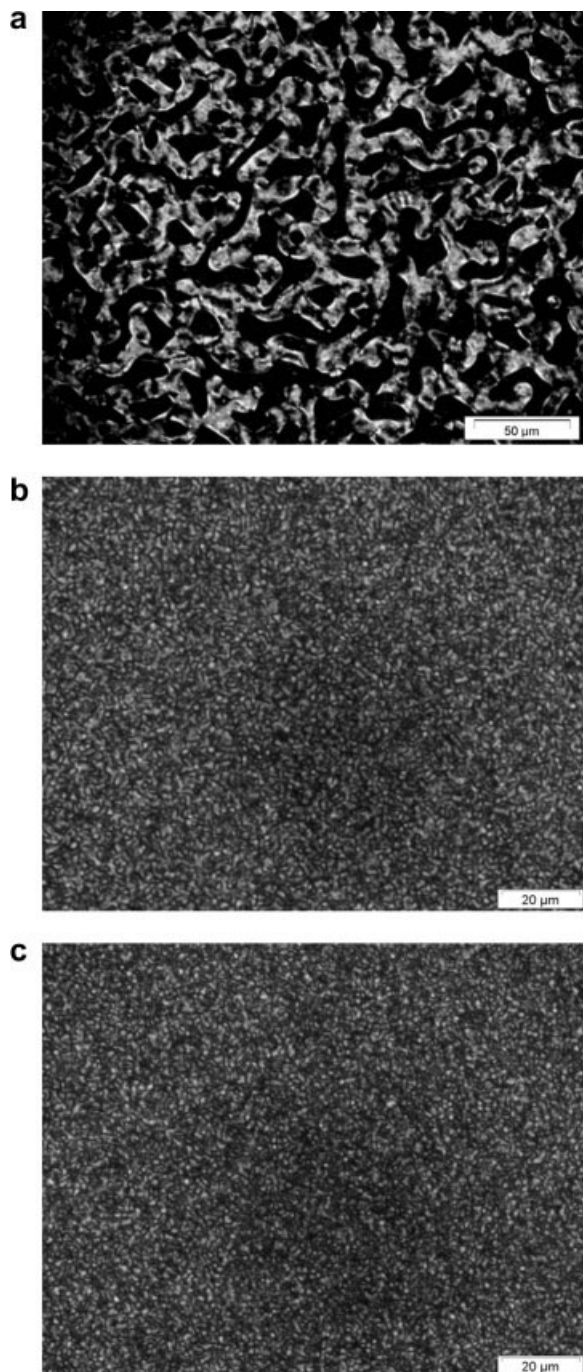


Figure 7 TOM micrographs of PSEO/HOBC blends, with crossed polarizers, containing: (a) 10 wt %, (b) 30 wt %, (c) 50 wt % HOBC.

HOBC and PMPLSi/HOBC systems, PC/HOBC blends containing less than 30 wt % of PC lead to rapid coalescence of the LC nematic droplets and, for the experiment conditions, they show typical Schlieren texture, which also is characteristic for neat HOBC systems prior to crystallization of LC (see Fig. 8). For more than 30 wt % PC, blends exhibit typical droplet-like morphology with the average size of the nematic domains of around $1.8 \pm 0.2 \mu\text{m}$. In the case

of PSEO/HOBC blends, for 10 wt % PSEO large coalesced droplets of HOBC were observed, which changed to droplet-like for contents higher than 10 wt % of PSEO. The average size of these blends decrease from $1.20 \pm 0.2 \mu\text{m}$ for 30 wt % of PSEO to $0.6 \pm 0.05 \mu\text{m}$ for 50 wt % PSEO. On the other hand, fast crystallization of PMPLSi/HOBC blends always led to droplet-like morphology, where average size decreased with increasing PMPLSi content. For less than 30 wt % PMPLSi, blends showed broader range of average size of nematic domains from $23 \pm 1 \mu\text{m}$ to $7 \pm 1 \mu\text{m}$. The addition of more than 30 wt % PMPLSi resulted in decreasing of average size of nematic domains to $11 \pm 0.8 \mu\text{m}$ or $7 \pm 0.5 \mu\text{m}$ for 50 wt % and 70 wt %, respectively. Moreover, under preparation conditions, any interface between two phases of investigated PSEO/HOBC, PMPLSi/HOBC, and PC/HOBC binary systems has been detected.

Taking into account the morphologies generated in the investigated blends, it can be concluded that fast cooling rate allows obtaining PDLC systems in which nematic domains are distributed in a narrow

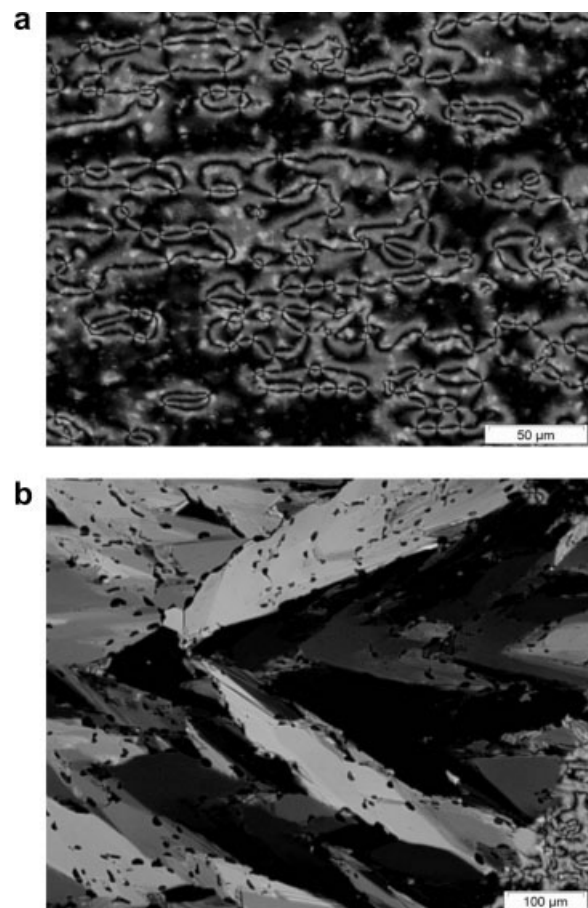


Figure 8 TOM micrographs of HOBC, with crossed polarizers, prior to fast crystallization after (a) 5 min, (b) 10 min at room temperature.

range of sizes (unimodal particle size). Moreover, it should be pointed out that in the respective blends and for contents higher than 30 wt % PC or 10 wt % PSEO, the sizes of the nematic domains were quite small. Both unimodal particle size and their small size obtained in some of the composition-dependent PDLC discussed above make them useful for applications in electro-optical devices. Both unimodal and small size of the particle allow to conclude that, dependently on the composition investigated, PDLC can be used in electro-optical devices. It can be especially concluded from the work by Sumana et al.,^{15,18} Malik et al.,⁴⁴ and Hoppe et al.²⁸

CONCLUSIONS

Phase diagrams of PC/HOBC, PSEO/HOBC, and PMPLSi/HOBC blends, based on DSC, DMA, and TOM at different temperatures, lead us to conclude that all of systems formed homogenous isotropic solution of the polymer and liquid crystal HOBC prior to switching from strong scatter light (OFF-state), thus opaque state, to transparent state (ON-state) of PDLC blends. None of the investigated systems exhibit a liquid-liquid demixing region. Only in the PSEO/HOBC blends, a partial miscibility was indicated between PS-block and HOBC, from the results showing the influence of PSEO addition on the temperature in which systems switched from nematic+isotropic to isotropic state.

Addition of PC, PSEO, or PMPLSi has been able to hinder crystallization of LC HOBC and it is one beyond a threshold percentage of ~ 30 wt % HOBC in the blends that its nematic-isotropic transition, T_{N-I} , is refined. Addition of the above blending polymers has also been found to change the range of temperature over which T_{N-I} exist. Thus suggest that these PDLC blends are better for application in thermo-optic devices.

Composition dependent morphological studies show that it is possible to obtain PDLC systems with small and narrow size-distribution of nematic droplets at a few selective compositions enhances their applications as thermo-optical materials.

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