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**Phase behaviour and electro-optical response of systems composed of
nematic liquid crystals and poly (2-ethylhexylacrylate)**

Running title: Properties of LC/poly(2-ethylhexylacrylate) systems

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Abstract

Experimental studies of phase diagram and morphology of mixtures composed of linear poly(2-ethylhexylacrylate) (poly-2EHA) of molecular weight $M_w=92000\text{g/mol}$ and E7, an eutectic blend of nematic liquid crystals (LCs), were performed. The latter consists of four cyanoparaphenylenes i.e. 4-cyano-4'-n-pentyl-biphenyl (5CB), 4-cyano-4'-n-heptyl- biphenyl (7CB), 4-cyano-4'-n-oxyoctyl-biphenyl (8OCB), and 4-cyano-4''-n-pentyl-p-biphenyl (5CT). Thermal properties of the poly-2EHA/E7 system were studied by differential scanning calorimetry and the sample morphologies were investigated by optical microscopy. Phase diagram analysis revealed an increase of the nematic-isotropic transition temperature when E7 was added to poly-2EHA, compared to pure E7. This effect, related to a preferential miscibility phenomenon of E7 components towards poly-2EHA, was evidenced by gas chromatography analysis coupled to mass spectrometry (GC-MS), allowing to qualify and quantify the content of phase separated LC domains.

Thermograms of model LC mixtures including 5CB, 7CB, 8OCB and 5CT, which correspond to their composition in segregated LC domains of poly-2EHA/E7, present strong deviations from eutectic behavior. In order to access the impact of such variations for practical applications, such a model LC mixture was introduced in photochemically crosslinked 2-EHA (polycross-2EHA). Surprisingly, the electro-optical response of the obtained polycross-2EHA/LC films was considerably improved compared to the original polycross-2EHA/E7 system.

Keywords: eutectic liquid crystal; poly(2-ethylhexylacrylate); phase behavior; morphology; photopolymerization; electro-optical response.

1. Introduction:

Polymer Dispersed Liquid Crystal (PDLC) film consists generally of micron-sized nematic liquid crystalline (LC) domain dispersed in a polymer matrix [1–5]. They have been subject of intensive studies [6–8], because of both fundamental interest and potential applications in the field of smart windows, optical shutters, active display devices, sensors, microlenses and smart food packaging. Their unique electro-optical properties make them suitable for a large range of opto-electronical to biomedical devices [9–18]. In the field off-state, the PDLC film scatters light due to mismatch between the effective refractive index (n_{eff}) of the LC and that of the polymer (n_p). In the field on-state, LCs of positive anisotropy tend to align with their nematic director parallel to the field direction. In such a state, refractive index matching occurs and the PDLC film becomes transparent.

Generally, PDLC materials can be obtained by different methods [19]: thermally induced phase separation (TIPS), solvent evaporation induced phase separation (SIPS), polymerization/crosslinking induced phase separation (PIPS) and emulsion or encapsulation [20]. The choice of one of these methods can lead to specific features of PDLC films [21]. In many applications, commercial multicomponent LC mixtures like the well-known eutectic nematic E7 are used, since they possess high anisotropy over a large temperature range. As an example, E7 exhibits a single nematic to isotropic transition temperature at $T_{\text{NI}}=61^\circ\text{C}$ and a glass transition temperature at $T_g=-62^\circ\text{C}$, providing a large nematic range of approximately 120°C . In most cases these transition temperatures seems to remain identical in the presence of a polymer, however some authors report about exceptions which were explained by preferential solubility effects of the constituents of these eutectic LC blends towards the polymer. A short overview of the literature shows that this phenomenon was obtained with several polymer/LC systems like UV curable resin NOA65/E7 [22] and NOA65/E44 [23], for which the phase behavior of the LC-rich domains deviate remarkably from those of pure

eutectic LC mixtures. For the first system [22], gas chromatographic (GC) analysis showed an important deviation compared to the original composition of E7. In the second system NOA65/E44, the heterogeneity of LC domains formed after photopolymerization, compared with results involving a pure LC (7CB), was attributed to different miscibilities of the E44 compounds towards NOA65.

Other systems were concerned by large shifts of phase transition temperatures in polymer/LC films; for example thermo-optical studies of poly(methylmethacrylate)/E7 [24] showed an increase of T_{NI} , indicating preferential solubility during the phase-separation process. The same effect was observed on poly(methylphenylsiloxane) (PMPS)/E7 phase diagrams [25,26], by varying the molecular weight of the polymer. It has been noticed in the case of the molecular weight of 60000g/mol that the nematic–isotropic transition temperature increased by nearly 20°C when adding 80weight% of polymer to E7. In a study of the phase behavior and morphology of poly(n-butylacrylate) (polyABu)/E7 blends, High Performance Liquid Chromatography (HPLC) analysis of the separated LC domains revealed relatively high solubility of 5CB with polyAbu, compared with PMPS [27,28].

In the present work, the range of investigated polymeric systems was extended to poly (2-ethylhexylacrylate) (poly-2EHA), and analysis of the preferential solubility phenomenon was conducted by several techniques, such as Polarizing Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). In addition, GC coupled with Mass Spectrometry (GC-MS) was employed as promising method for the determination of the content of segregated LC domains from the poly-2EHA/E7 system.

To the best of our knowledge, no data are currently available in literature describing the consequences of the phenomenon of preferential solubility on electro-optical properties of corresponding PDLC films. Generally, electro-optical characteristics of PDLC films were examined by varying various parameters such as nature, architecture and concentration of LC

and polymer, film thickness, and morphology [29], [30]. In this report the electro-optical performance of photochemically crosslinked poly-2EHA (polycross-2EHA)/LC films will be analyzed, using model LC blends prepared according to the compositional results obtained from GC-MS results.

2. Experimental

2.1 Materials

The monofunctional monomer 2-Ethyl Hexyl Acrylate (2EHA) (Figure 1a) was obtained from Sigma-Aldrich, the difunctional isotropic crosslinking agent hexanedioldiacrylate (HDDA) (Figure 1b) was supplied by Cray Valley and the photo-initiator 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) was obtained from Ciba-Geigy. The poly (2-Ethyl Hexyl Acrylate) (poly-2EHA) had an average molecular weight $M_w=92.000\text{g/mol}$ and was supplied from Sigma Aldrich. The polydispersity of this polymer was determined by gel permeation chromatography (GPC) performed in tetrahydrofuran (THF) at room temperature yielding $M_w/M_n=3$. E7 represents a commercially available eutectic LC mixture and was purchased from Synthon GmbH, Germany. It contains 51wt.-% of 4-cyano-4'-n-pentyl-biphenyl (5CB), 25wt.-% of 4-cyano-4'-n-heptyl-biphenyl (7CB), 16wt.-% of 4-cyano-4'-n-oxyoctyl-biphenyl (8OCB) and 8wt.-% of 4-cyano-4''-n-pentyl-p-biphenyl (5CT) [31]. E7 exhibits a single T_{NI} at 61°C and a glass transition temperature T_g at -62°C . The refractive indices of E7 at $T=20^\circ\text{C}$ are given as $n_o=1.5183$; $n_e=1.7378$ ($\lambda=632.8\text{ nm}$), leading to a birefringence of $\Delta n=n_e-n_o=0.2195$ [32]. The details of the chemical structures of LC molecules involved in E7 were presented in Figure 1c. The LC 4-cyano-4'-n-butyl-biphenyl (4CB) supplied by Merck was used as a standard to establish the calibration curves needed for GC-MS analysis; its chemical structure is illustrated in Figure 1d.

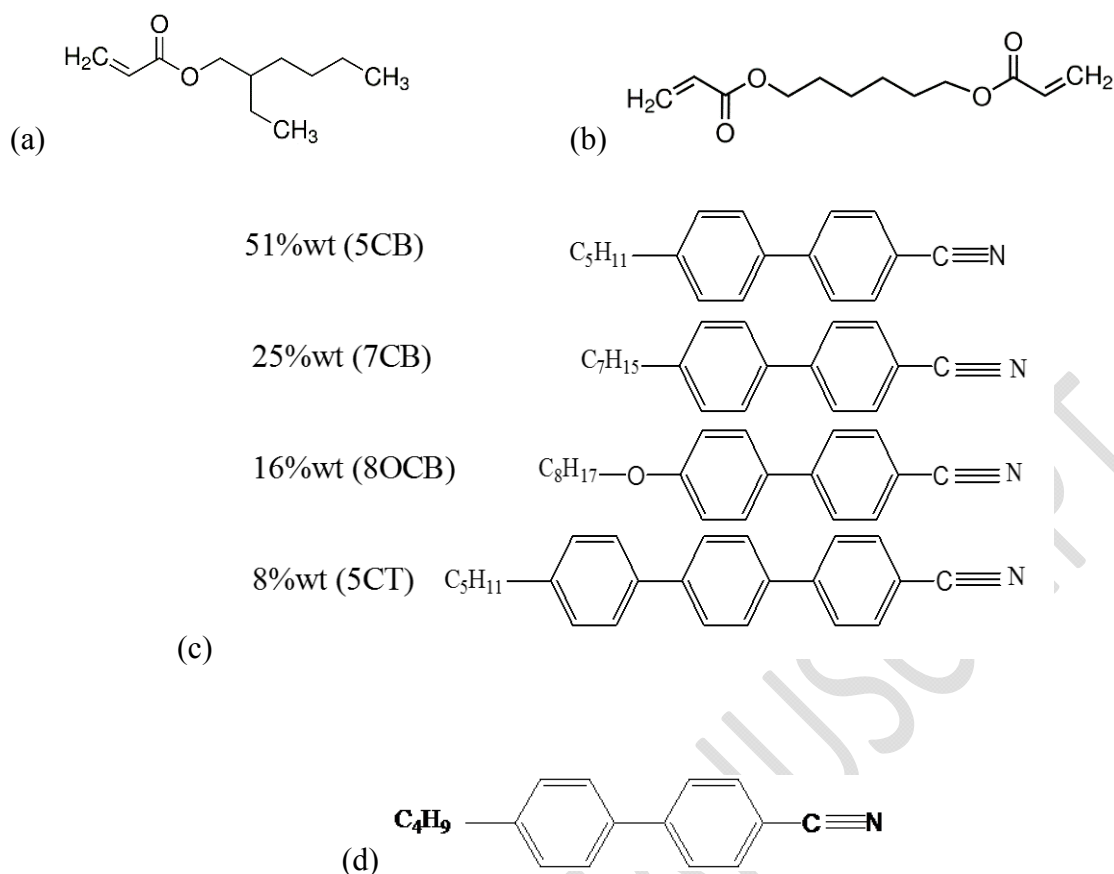


Figure 1) Chemical structures of (a) 2-Ethylhexylacrylate (2EHA) monomer, (b) Hexanedioldiacrylate (HDDA), (c) nematic LC E7, and (d) 4-cyano-4'-n-butyl-biphenyl (4CB).

2.2 Sample preparation

The poly-2EHA/E7 blends were prepared by the TIPS process. x wt.-% of E7 ($x=10; 20; \dots; 90$) and $(100-x)$ wt.-% of poly-2EHA were mixed together at room temperature for several hours. The phase behavior of poly-2EHA/E7 mixtures was already established experimentally by POM [33-34] and will thus be analyzed by DSC. To investigate the electro-optical performance of polymer/LC systems, PDLC films were prepared by the PIPS technique. Blends of (2EHA/HDDA/Darocur 1173) (96/2/2wt.-%) together with a LC mixture, either E7 or a model blend, were polymerized/crosslinked under UV-visible irradiation for 30min. The

LC concentration of the precursor blends was kept at 70wt.-% to achieve a homogeneous thermodynamic state. The photopolymerization/crosslinking process was carried out by irradiating the sample cells under a Philips TL08 UV light source, possessing a maximum output at a wavelength of $\lambda=365\text{nm}$, and a dose rate of $0.5\text{mJ}/\text{cm}^2$. The cells were assembled using two 1mm thick plane parallel glass plates, which were coated inside with thin transparent conductive layers of indium tin oxide (ITO). The size of the cells was $1\text{cm}\times 1\text{cm}$.

2.2.1 Polarized optical microscopy

For polarized optical microscopy (POM) experiments, an Olympus BX41 apparatus, equipped with a Linkam heating/cooling stage LTS350 together with a temperature-controlling unit TMS 94, was used. The samples were placed between two micro glass slides, then heated up until they became optically clear, and then cooled down slowly to ambient temperature. The heating and cooling rates were $0.5^\circ\text{C}/\text{min}$. The same heating/cooling procedures were repeated three times for each sample to minimize experimental uncertainties.

2.2.2 Thermal characterization

Thermal properties like determination of phase transition temperatures and enthalpies of polymer/LC blends were investigated by DSC (Perkin-Elmer model 8000). Samples were prepared by introducing about 8-10mg of the initial mixture into aluminum DSC pans, to avoid evaporation effects during the temperature treatment. A rate of $10^\circ\text{C}/\text{min}$ (heating-cooling cycle) was used in the temperature range from 72°C to $+100^\circ\text{C}$. The program consisted first in cooling the sample, followed by three heating and cooling cycles to take into account eventual thermal events related to the sample preparation history. A Pyris computer software from Perkin-Elmer was used to determine the onset temperature of the various phase transitions. Only thermograms from the second heating scan were considered for the analysis.

The DSC apparatus was calibrated using indium and zinc as standards at a heating rate of 10°C/ min.

2.2.3 GC-MS analysis

GC-MS analysis was carried out on a Perkin Elmer Turbo Mass Spectrophotometer (Norwalk, USA) which includes a Perkin Elmer Auto sampler XLGC. The column used was a Perkin Elmer Elite-5 capillary column measuring 30m×0.25mm with a film thickness of 0.25mm composed of 95% Dimethylpolysiloxane. The carrier gas used was Helium at a flow rate of 2.5mL/min. Injection volumes of 0.4µL were used per sample. The oven temperature program was as follows: temperature was kept at 100°C for 15min and then increased to 150°C with a rate of 10°C/min followed by an isotherm period of 10min.; then temperature was increased to 240°C (10°C/min) followed by another isothermal period of 10min. Injection port and transfer line temperatures were set at 300°C and 180°C, respectively. GC-MS analysis was carried out using electron impact ionization at 70eV and data were evaluated using total ion count (TIC) for compound identification and quantification. The spectra of the components were compared with known components stored in the GC-MS database. Measurement of peak areas and data processing were carried out by Turbo Mass-OCPTVS-Demo SPL software. To establish the calibration curves, the internal calibration method was chosen by adding 4CB as standard. This standard was added to the LC sample to be analyzed with a constant concentration of 1mg/mL.

2.2.4 Electro-optical measurements

For electro-optical measurements, the collimated beam from a He/Ne laser ($\lambda=632.8\text{nm}$) passed through the sample cell at an angle of 90° compared to the cell surface, and the transmitted light was collected by a photodiode. Using a standard frequency and function

generator together with a voltage amplifier, an electric field was applied across the samples (1kHz-sinusoidal). Optical transmission curves were thus obtained as function of the applied voltage, allowing to extract characteristic parameters such as V_{10} , representing the voltage corresponding to 10% of transmitted light. T_{OFF} and T_{ON} correspond to the light transmitted in the OFF and ON states, respectively.

3. Results and discussion

Thermograms of the poly-2EHA/E7 system obtained from DSC measurements are displayed in Figure 2.

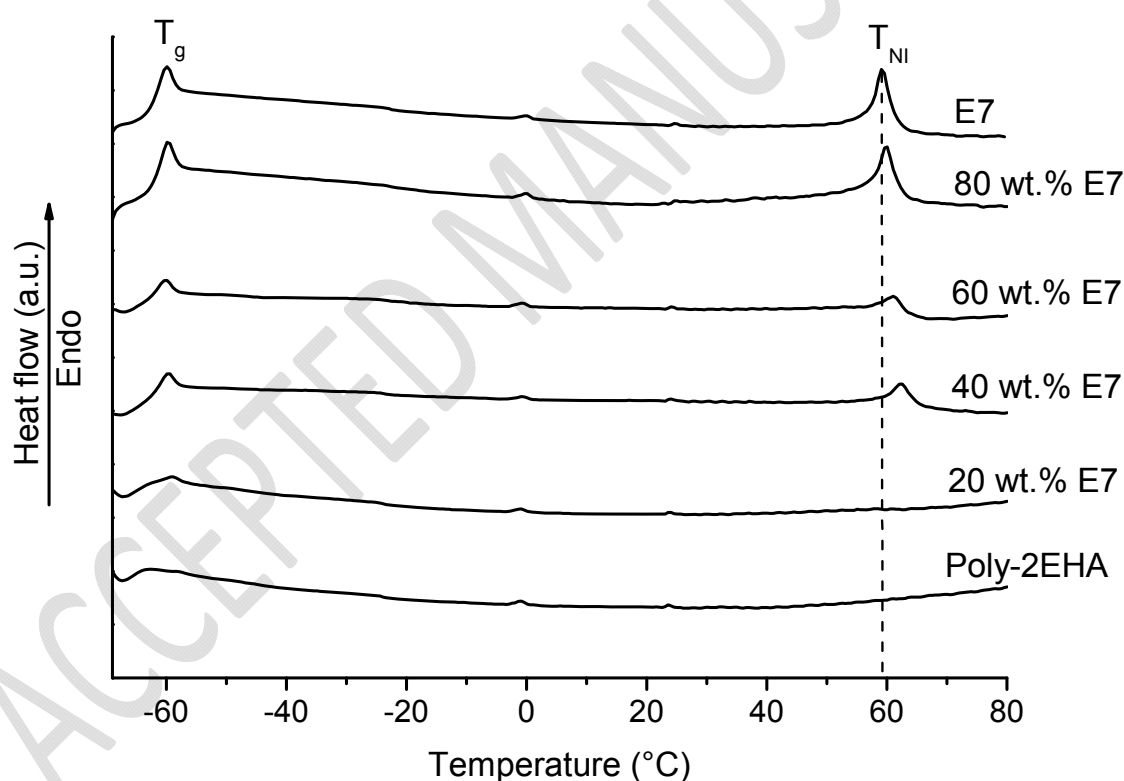
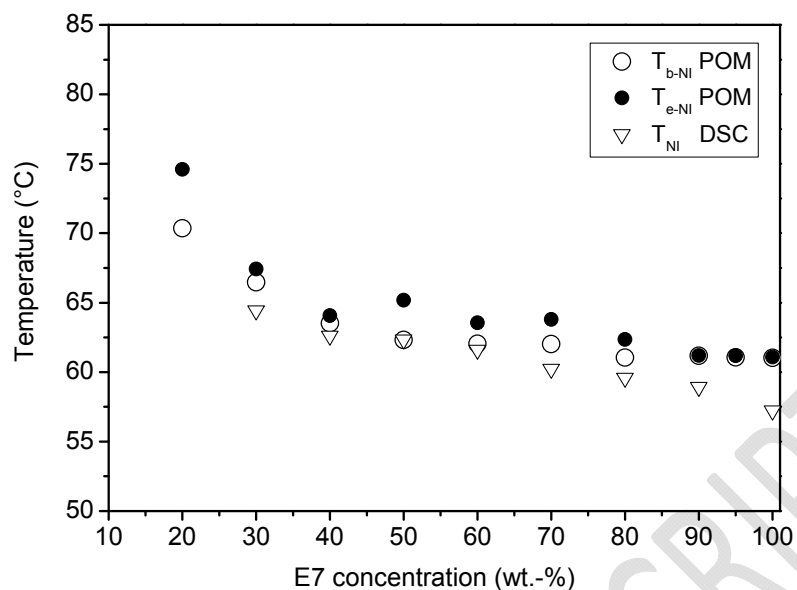


Figure 2) Thermograms obtained from DSC measurements (heating rate 10°C/min) for a series of poly-2EHA/E7 mixtures for LC concentrations ranging from 0 to 100 wt.-%. T_g represents the glass transition temperature and T_{NI} stands for the nematic to isotropic transition temperature.

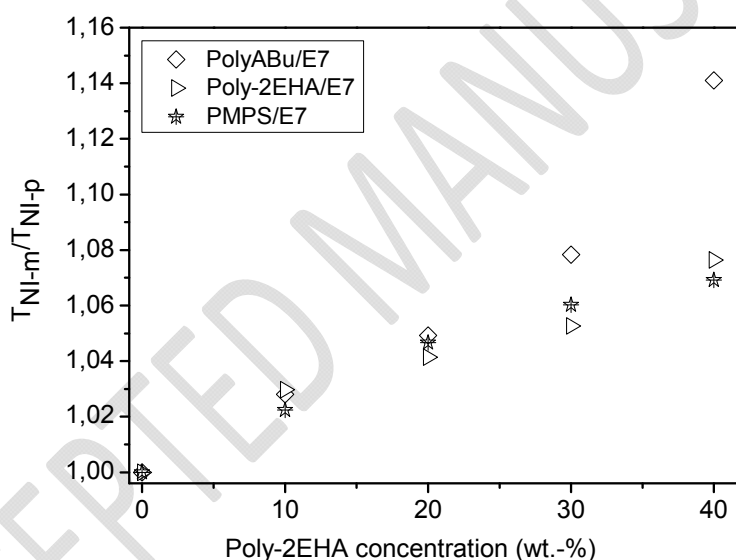
The poly-2EHA/E7 blends were analyzed using increments of 10wt.-% starting from pure poly-2EHA to pure E7. In Figure 2, the heat flow of each poly-2EHA/E7 mixture was represented as function of temperature, covering a wide range from -72°C up to $+100^{\circ}\text{C}$, which allows detection of various transition temperatures, such as T_{NI} of the LC and T_{g} of the polymer and LC. The pure LC E7 is characterized by two transition temperatures: a glass transition at low temperature ($T_{\text{g}}=-62^{\circ}\text{C}$) and a nematic-isotropic transition at higher temperature ($T_{\text{NI}}=+61^{\circ}\text{C}$). No other transition occurs, and the nematic phase covers a wide range of temperatures. Above T_{NI} , E7 adopts an isotropic phase. The glass transition temperature of poly-2EHA was about $T_{\text{g}}=-63^{\circ}\text{C}$ and was almost coincident with T_{g} of E7. By increasing the poly-2EHA concentration starting from pure E7, the nematic-isotropic transition shifts to higher temperatures, while the exothermic peak widens slightly.

The superposition of the variation of the nematic-isotropic transition temperatures, depending on the sample composition, is presented in Figure 3a. These data were obtained by POM and DSC. Results from DSC correspond to the peak maxima of the thermograms and those obtained by POM represent onset (beginning) and end of the transition. An increase of the nematic-isotropic transition temperatures was observed with decreasing LC amount in the poly-2EHA/E7 mixture. These results show a good correlation between the two characterization methods. This increase can be explained by a preferential solubility phenomenon between the different components of E7 and poly-2EHA.

Investigations were carried out earlier on different systems such as PMPS/E7 [25] and PABu/E7 [35], to analyse the phenomenon of preferential solubility between the polymer and the LC. In Figure 3b, an attempt was made to correlate the results of all these systems in terms of the temperature ratio $T_{\text{NI-m}}/T_{\text{NI-p}}$, as a function of the polymer composition.



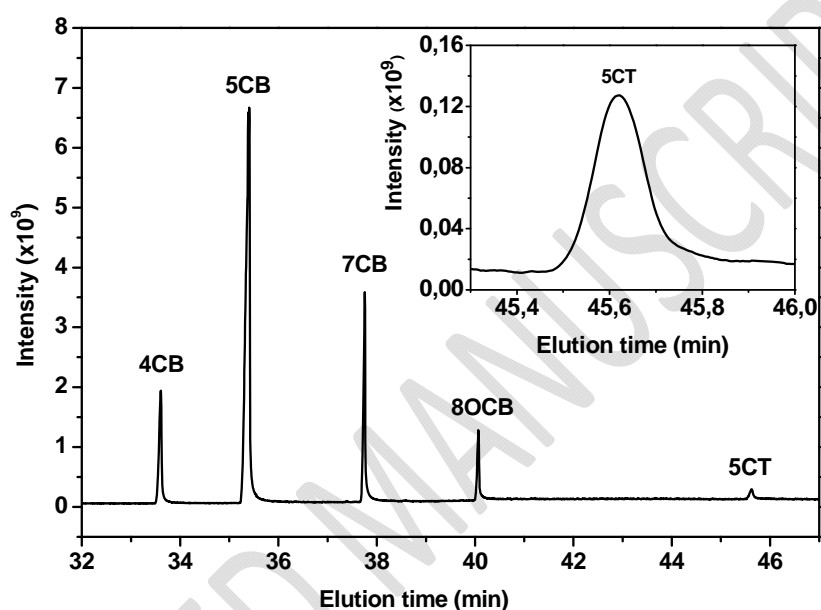
(a)



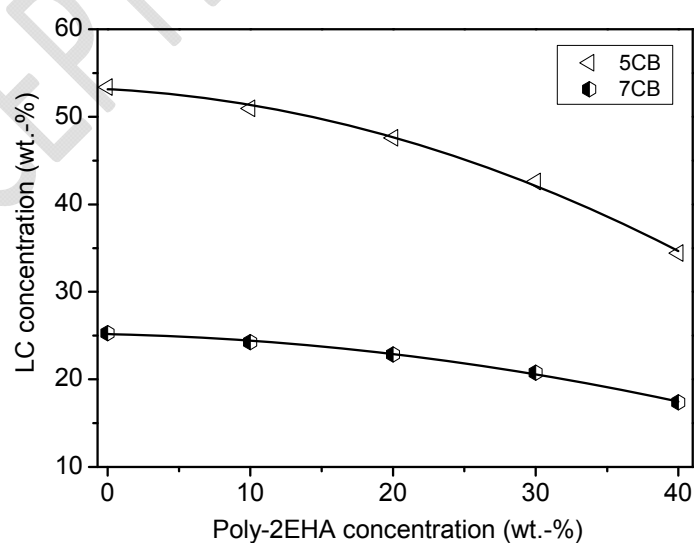
(b)

Figure 3) (a) Superposition of T_{NI} data obtained by POM and DSC of the poly-2EHA/E7 system. T_{b-NI} and T_{e-NI} correspond to beginning and end of appearance of the T_{NI} transition observed by POM, respectively. (b) Variation of T_{NI-m}/T_{NI-p} of polymer/E7 systems versus polymer concentration obtained from POM. T_{NI-m} corresponds to the nematic-isotropic transition temperatures of LC of polymer/E7 mixtures (PMPS/E7 [25], PABu/E7 [35]). T_{NI-p} represents T_{NI} of pure LC E7.

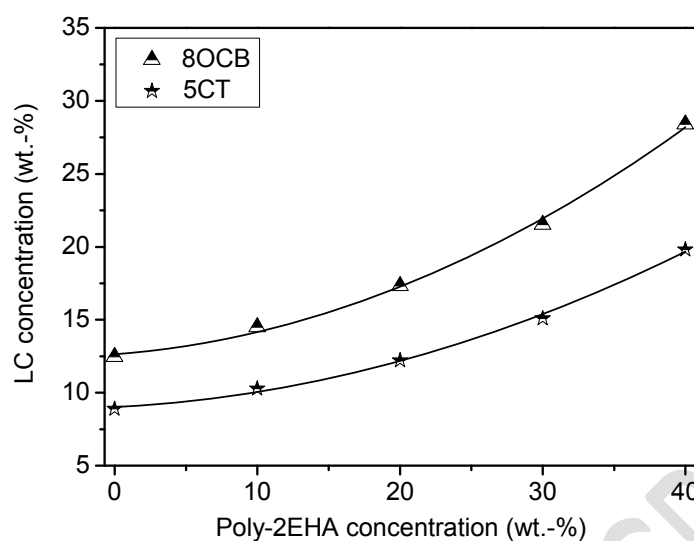
This ratio was calculated by taking into account the nematic-isotropic transition temperatures T_{NI-m} , corresponding to the LC part of polymer/E7 mixtures, and T_{NI-p} , representing the nematic-isotropic transition temperature of pure LC E7. In all cases considered here, these transition temperatures show an increase with the polymer concentration. Results from PMPS/E7 and poly-EHA/E7 were found to be similar, whereas the PABu/E7 system presents a more pronounced effect on T_{NI} .



(a)



(b)



(c)

Figure 4) (a) Chromatogram of LC E7 obtained by GC, (b) and (c): Variation of the concentration of E7 components (5CB, 7CB, 8OCB and 5CT) depending on poly-2EHA content of the initial poly-2EHA/E7 mixtures, obtained from GC-MS data.

The combination between GC and MS represents a powerful method to identify and quantify LC compounds included in LC mixtures like E7. Calibration curves were established for each component relative to an added internal standard which was 4CB. Figure 4a shows the result of the separation of pure E7 by GC-MS, and Figures 4b and 4c display the outcome of the analysis of phase separated LC domains in poly-2EHA/E7 mixtures in terms of the variation of the concentrations of 5CB, 7CB, 8OCB, and 5CT. The x-axis of Figure 4b and 4c correspond to the poly-2EHA concentration of the examined poly-2EHA/E7 blends. Similar results as for PMPS/E7 and PABu/E7 were found, i.e. 5CB and 7CB concentrations decrease with increasing poly-2EHA concentration, whereas 8OCB and 5CT display opposite behavior. The dependences presented in Figures 4b and 4c show that 5CB and 7CB are miscible to some extent with poly-2EHA while 8OCB and 5CT show poor affinity with the polymer. The variation of the 5CT concentration reveals to be quite important, and can lead to

a strong increase of T_{NI} of the segregated LC domains due to its high nematic-isotropic transition temperature which corresponds to 240°C. The results are consistent with the hypothesis proposed that the LC composition from separate domains varies depending on the polymer concentration, due to preferential miscibility phenomenon. It can be concluded that GC-MS data were helpful to qualify and quantify this effect observed by POM and DSC.

To confirm the obtained GC-MS results, DSC measurements were performed on samples made from four individual LC mixtures that correspond to the composition of the single LC compounds from segregated domains of poly-2EHA/E7 blends, which contain 10–40 wt.-% poly-2EHA. The concentration data of these LC mixtures are reported in Table 1, and these LC-compositions were analyzed by DSC and POM.

LC	5CB (wt.-%)	7CB (wt.-%)	8OCB (wt.-%)	5CT (wt.-%)
E7	51	25	16	8
E7 (1)	50,9	24,3	14,5	10,3
E7 (2)	47,6	22,8	17,3	12,3
E7 (3)	42,6	20,8	21,5	15,1
E7 (4)	34,4	17,4	28,4	19,8

Table 1: Composition of individual LC mixtures denoted E7 (1), E7 (2), E7 (3), and E7 (4), corresponding to the results from GC-MS measurements of segregated domains of the poly-2EHA/E7 system.

Figure 5 gathers the thermograms of these four LC mixtures, showing a single glass transition and a single nematic-isotropic transition together with a large nematic region for E7 (1) and E7 (2). On the other hand, E7 (3) and E7 (4) present additional transitions at temperatures

below room temperature, related to crystallization and melting effects, meaning that these mixtures cannot be furthermore considered as eutectic blends. These results clearly confirm the presence of a preferential miscibility effect of the poly-2EHA/E7 system and show an important impact for practical applications.

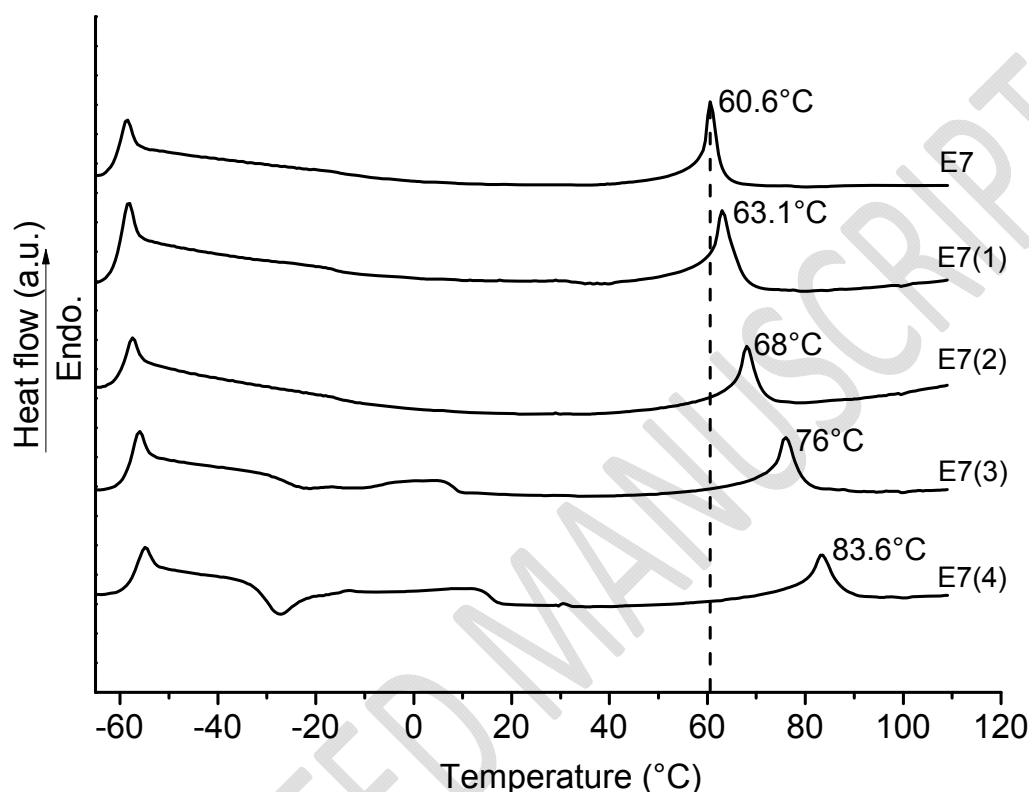


Figure 5) DSC thermograms of model LC mixtures composed of 5CB, 7CB, 8OCB and 5CT, which correspond to the compositions of the LCs from the segregated domains of the poly-2EHA/E7 system, obtained from GC-MS investigations. The temperatures given on the thermograms correspond to the peak maxima of the T_{NI} transition.

The results obtained from DSC thermograms were confirmed by POM observations. Figures 6a and 6b represent typical nematic LC morphologies at $T=25^{\circ}\text{C}$ for pure E7 and model LC mixture E7 (4), respectively, showing both Schlieren textures exhibiting some differences in size and number of micro-domains. This change in morphology was particularly observed at

the beginning of the nematic-isotropic phase transition showing that the micro-domains of E7 (4) possess larger sizes compared to those of the commercial E7. The texture of E7 (4) remains in the nematic state at $T=70^{\circ}\text{C}$ (Figure 6 (d)), while that of pure E7 presents an isotropic phase at the same temperature (Figure 6 (c)).

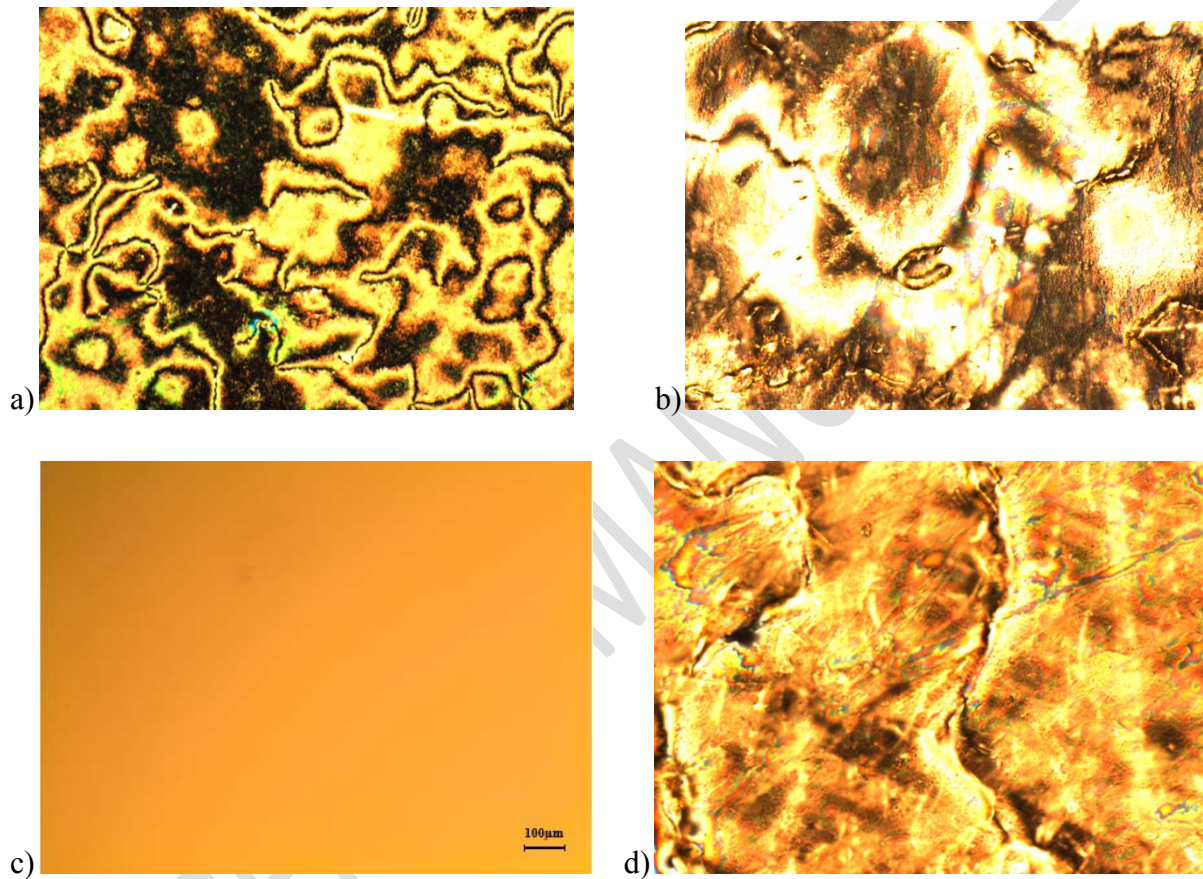
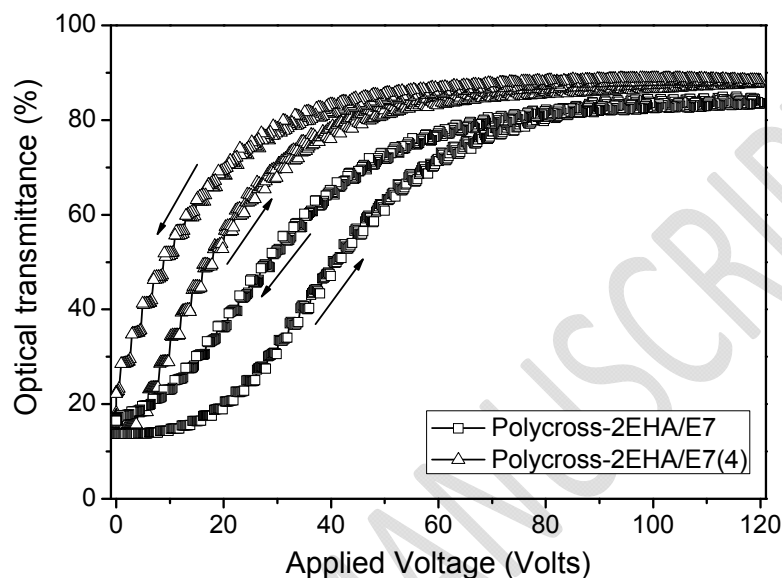


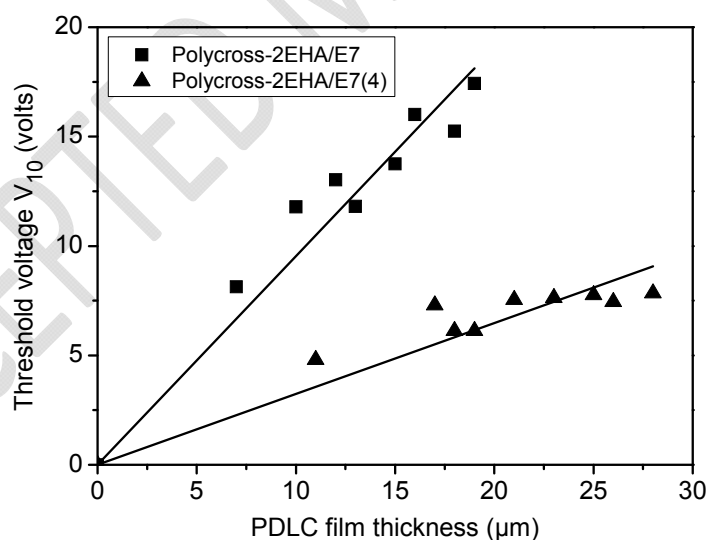
Figure 6) (a) and (c): POM pictures of LC E7 taken at $T=25^{\circ}\text{C}$ and $T=70^{\circ}\text{C}$, respectively; (b) and (d): Images from POM of model LC mixture E7 (4) obtained at $T=25^{\circ}\text{C}$ and $T=70^{\circ}\text{C}$, respectively. All observations were made during the heating cycle using the same magnification (representative scale bar for all images displayed on Figure 6 (c)).

An electro-optical investigation was undertaken to compare the electro-optical performance of poly-EHA systems including the commercial LC E7 with a LC composition that underwent a preferential miscibility phenomenon. The choice was focused on E7 (4) since this mixture

should yield the most important effect on the electro-optical properties compared with the other model LC blends. DSC as well as POM results revealed a nematic-isotropic transition temperature around 83°C for this mixture together with a nematic phase present at room temperature necessary to be able to perform electro-optical studies.



(a)



(b)

Figure 7) (a) Electro-optical responses of 19µm thick 30wt.-% Poly (EHA/HDDA)/70wt.-% E7 (pure) and 30wt.-% Poly (EHA/HDDA)/70wt.-% E7 (4) PDLC films, (b) Influence of the PDLC film thickness on threshold voltage (V_{10}).

Figure 7a shows the superposition of electro-optical responses obtained for PDLC films based on photochemically crosslinked poly-2EHA (polycross-2EHA)/LC films exhibiting both a thickness of 19 μ m. An important improvement of the electro-optical response of the film prepared with E7 (4) was observed with respect to that of the commercial LC E7. In particular, the E7 (4) based film required much lower voltages to achieve the transparent state. Note also that the hysteresis effect was lower, and a slightly higher transmittance T_{ON} was found compared to the film containing E7.

A certain number of parameters can be applied to evaluate more in detail the electro-optical properties of PDLC films, such as the threshold voltage (V_{10}) [36]. V_{10} is defined as the electric voltage required to obtain a transmittance of 10% of the PDLC film, and was found to be determined by the balance between surface anchoring and electric forces [37]. As shown in Figure 7b, V_{10} increases with increasing PDLC film thickness. Moreover, the films prepared with the modified LC present significantly lower V_{10} values compared to those based on the pure LC E7. The presence of E7 (4) leads thus to a significant enhancement of the electro-optical properties.

4. Conclusions

The phase behavior of a poly-2EHA/E7 system was examined by two different techniques POM and DSC, exhibiting a strong increase of the nematic-isotropic transition temperature when increasing the poly-2EHA concentration, which can be explained by preferential miscibility effects and phase-separation phenomena involving the polymer, as well as the different LC constituents. The GC-MS analysis allowed to obtain qualitative and quantitative data of the LC content confined in phase separated domains, and revealed thus the change of LC composition within these regions, compared to pure E7. Interestingly, the electro-optical response obtained for PDLC films elaborated with a model LC blend, E7 (4), chosen as a

result from substantial preferential miscibility phenomenon, shows a significant improvement of the electro-optical properties compared to the films prepared with pure E7.

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