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Selective solubility of E7 components in poly (n-butylacrylate)

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Abstract

Recently, the phase diagram of poly (n-butyl acrylate) and the nematic liquid crystal (LC) mixture E7 has revealed an anomalous behaviour that was attributed to the multicomponent nature of the LC which is made of four cyanoparaphenylenes. The anomalous emergence of a nematic phase at relatively low LC concentration above 60°C cannot be rationalized in terms of standard meanfield models commonly used to calculate phase diagrams of analogous systems. It was then suspected that the only possibility to explain this observation is to invoke the hypothesis of a selective solubility of the LC components with respect to the polymer. A detailed analysis of the composition of the LC within droplets as a function of the E7 concentration in the samples was made by HPLC. The corresponding measurements indicate unambiguously that E7 undergoes a phase separation in the presence of poly (n-butylacrylate) and exhibits a selective miscibility that is reminiscent of the preferential solvation phenomenon. HPLC chromatograms exhibit peaks that correspond to the four single compounds included in the E7 mixture and can precisely identify those present in the sample droplets. We find that both nature of components and composition depend upon samples under consideration. The overall analysis of data enables us to understand the anomalies revealed by the complete phase diagram obtained by polarized optical microscopy (POM).

PACS: Type pacs here, separated by semicolons ;

Keywords: Polymer; liquid crystal; HPLC; phase diagram; POM.

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1. Introduction

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials made generally of multicomponent mixtures that are the subject of active research from both theoretical and experimental points of view. These systems consist of micron-sized LC inclusions dispersed in a solid polymer matrix. They can be used in display devices, light control equipments and communication technologies [1-4].

Most applications rely on the specific nature of electro-optical response functions together with the possibility to control the phase behavior and thermophysical properties of these systems. A rigorous assessment of the relationship

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between electro-optical properties and phase behaviour requires further research efforts. In view of the importance of this relationship, a precise knowledge of the phase diagram is necessary prior to any further investigation. Peculiarities in the phase diagrams of certain systems involving the eutectic LC mixture E7 have been reported by us [5-7] and by others [8, 9]. Since E7 is a standard LC often used in applications of PDLC systems, it is important to investigate these peculiarities which might be in relation to a preferential solvation phenomenon in the presence of certain polymers due to its multicomponent nature. This idea is supported by the fact that similar tendencies were not found in single component LCs such as 4-cyano-4'-n-pentyl-biphenyl (5CB) [10] and 4-cyano-4'-n-octyl-biphenyl (8CB) [11]. In particular such an effect was found in the case of poly (n-butyl-acrylate)/E7 by analyzing the composition of the LC inside droplets in various domains of the phase diagram in the temperature – composition frame [5].

The experimental phase diagram of the poly (n-butyl-acrylate)/E7 system is established using Polarizing Optical Microscopy (POM) and Light Scattering (LS). This combination of techniques is used to make sure that the phenomenon is reproducible. A direct method is employed to assess the preferential solvation phenomenon. It consists of analyzing the composition of LC within droplets in different regions of the phase diagram using HPLC characterization.

2. Experimental part

2.1. Materials and sample preparation

Poly(n-butylacrylate) was prepared by a radical polymerization technique using 2,2'-Azoisobutyronitrile as initiating species, purified and characterized by gel permeation chromatography (GPC) yielding M_w=112 000 g/mol and M_w/M_n=2.2. The eutectic LC mixture E7 was purchased from Merck Eurolab (Darmstadt, Germany), containing 51 weight percent (wt.-%) 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-terphenyl (5CT). E7 exhibits a nematic to isotropic transition temperature at T_{NI}=60°C.

Sample preparation was made following a combination of solvent induced phase separation (SIPS) and thermally induced phase separation (TIPS). The polymer and LC were dissolved in a common organic solvent (tetrahydrofuran, THF) at 50wt.-% and room temperature. The resulting mixture was stirred mechanically overnight and a small quantity was cast on a clean glass slide. The samples were completely dried at room temperature for two days in a vacuum chamber. After total evaporation of the THF, another glass slide was put on top of the first one. Samples with pure components have been prepared in a similar way to the polymer / LC blends. The phase behaviour is the same as in the case where THF was used.

2.2. Techniques and experimental procedures

2.2.1. Polarizing Optical Microscopy

The thermo-optical studies were performed on a POM Jenapol, equipped with a heating/cooling stage Linkam THMS 600 and a Linkam TMS 92 temperature control unit. We adopted the same procedure as in earlier studies for all samples considered [5]. Samples were first heated at a rate of 100°C/min to 70°C and more (depending on the composition) to ensure that a homogenous isotropic state has been reached. After 5min, the samples were quenched at a rate of 100°C/min to a lower temperature selected for observation of the texture. The same procedure was repeated few times (depending on the composition) with a quench made from the isotropic state to a temperature different from the preceding quench. At low temperatures, steps of 10°C were selected and in the vicinity of the transition temperature, steps of 1°C were used.

2.2.2. HPLC characterization

HPLC analysis was carried out using a Waters 510 model equipped with an UV-detector model 481 and an automatic gradient controller. A standard Versapack C18µ column from Alltech was employed with a flow of 1ml/min. A mixture consisting of 30% water and 70% methanol (both HPLC grade solvents) was used in the isocratic operation mode. Chromatograms were obtained at a wavelength of 315nm because the absorption band of the aromatic groups of the liquid crystals is located near this wavelength. Extraction of the LC from the droplets for HPLC measurements was made using a 25µl syringe under an optical microscope. In fact samples used for this operation exhibited at room temperature large phase separated domains that could be seen even with the naked eye. The extracted LC was diluted in THF to recover the corresponding concentration.

2.2.3. Light scattering (LS)

Light scattering (LS) measurements were performed using the classical setup illustrated in Figure 1 of ref. [12]. The He-Ne Laser (λ=632.8 nm) was polarized linearly, perpendicular to the scattering plane. The scattered intensity was measured in the VV mode (I_{vv}), where the analyzer axis is parallel to the polarization direction of the incident beam. The scattering pattern was recorded by a CCD camera. No anisotropic effects were found on the intensity pattern performing radial averages of the scattered intensity. The samples already used for POM measurements were submitted to the same heating/cooling cycle as described in the previous section. In the isotropic state at temperatures above 70°C, the scattering intensity was constant exhibiting low values. The temperature at which the scattering intensity undergoes a sharp or discontinuous increase was taken as the onset of phase separation.

3. RESULTS AND DISCUSSION

Figure 1 shows the equilibrium phase diagram obtained by different techniques such as POM and LS[5]. Consistent data are obtained with different techniques giving firm evidence to the existence of the anomalous behaviour. Below the data points, two phases are in equilibrium: An isotropic (I) polymer phase is coexisting with a nearly pure LC phase that exhibits nematic order (N). At room temperature (20°C), the solubility limit of E7 in poly (n-butylacrylate) is near 30% while at sufficiently high temperatures, the polymer/E7 mixture shows a single isotropic phase. Interestingly, this diagram does not contain a miscibility gap of the type (Isotropic+Isotropic), probably because the critical temperature for isotropic mixing is too low and the nematic interaction dominates in the temperature and composition range shown in this diagram. The theoretical phase diagram corresponding to this system was calculated using standard approximations based on mean field arguments. The solid line in Figure 1 represents the output of such calculations and was already reported in more details in reference 5. The remarkable observation that should be underlined is that the miscibility gap (N+I) extends to a temperature range exceeding the nematic-isotropic transition temperature T_{NI} of the pure LC. As it is well known, E7 is a mixture of 4 distinct LC constituents with different solubilities towards poly (n-butylacrylate). To confirm the existence of preferential solvation phenomenon, HPLC characterization was carried out to analyze the LC composition within droplets.

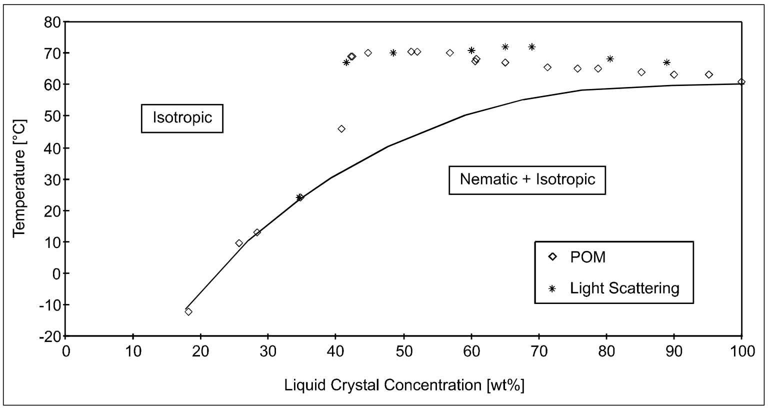

Fig.1. Equilibrium phase diagram of poly (n-butylacrylate)/E7. The symbols are POM and LS data and the solid line represents the calculed phase diagram [5].

Several measurements were made with an attempt to cover a large domain of the phase diagram and establish the evolution of the LC composition in the droplets as a function of composition. A typical example of a HPLC chromatogram is given in Figure 2, showing the bulk E7 system which is given to validate the method since we need to know precisely the composition of the bulk LC used in the preparation of the PDLC films. As expected, the chromatogram of Figure 2 exhibits peaks corresponding to 5CB, 7CB, 8OCB, and 5CT. Evidence of the attribution of the peaks to the different single LC components was found by measuring these LCs separately under the same conditions. The emergence of a shoulder near the peaks (clearly visible in the 5CB and 8OCB peaks) is probably due to solvent effects. The solubility of E7 in the present solvent mixture water (30%) / methanol (70%) is reduced allowing a separation of the four different LC components. As a consequence, the chromatograms exhibit shoulders corresponding to each of the molecular species. Note that E7 does not exhibit such shoulders in more miscible solvents such as THF. Analysis of the chromatograms obtained from other samples at different compositions yields the results shown in Figure 3 where the concentrations of 5CB and 7CB in the droplets normalized to that of 5CT are given in terms of the polymer concentration. This representation is chosen for convenience since the absolute concentration of 5CT remains essentially unchanged in the droplets. The data demonstrate that the component 5CT is quite incompatible with the polymer and remains within LC domains while 5CB exhibits a high miscibility inducing its migration towards polymer domains. One notes a net decrease of the content of 5CB in the droplets going from nearly 63% in bulk E7 to near 50% when adding 25 wt.-% polymer. Similar tendencies are found in the case of 7CB with a lesser extend since its composition decreases from 33 to 25% in the same range of polymer concentration. These results show unambiguously that the components of the eutectic mixture E7 exhibit a selective miscibility towards poly (n-butylacrylate). Other polymers such as polysiloxanes show similarities with the present system in the presence of E7 that are reminiscent of the preferential solvation phenomenon [7]. The present HPLC analysis will be extended to those systems to corroborate the results reported here. Work along these lines is under progress and the results will be the subject of future communications.

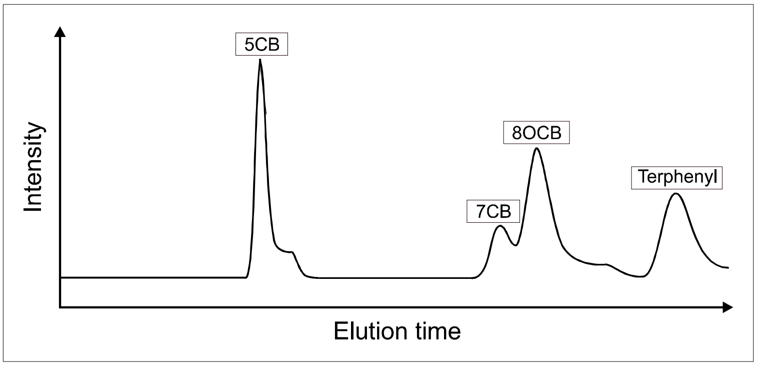

Fig.2. Typical HPLC chromatogram for pure E7 where its four cyanoparaphenylenes are clearly identified. This figure validates the HPLC method.

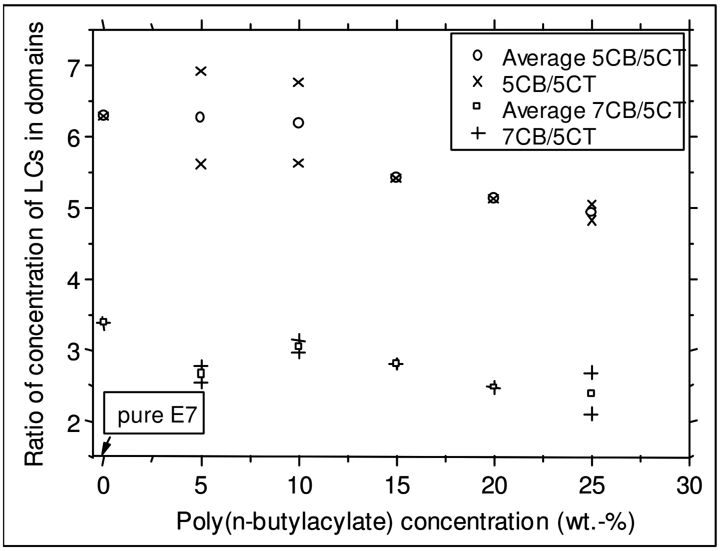

Fig. 3. Variations of the concentration of 5CB and 7CB in the droplets versus poly (n-butylacrylate) concentration. These variations are expressed as ratios of 5CB/5CT and 7CB/5CT ratios. Definition of the symbols are as indicated on the figure.

4. Conclusions

The phase diagram of poly (n-butylacrylate) and E7 mixtures exhibits a region where two coexisting (N+I) phases are observed even at temperatures higher than 60°C, the nematic to isotropic transition temperature of the bulk LC E7. This peculiar behaviour is explained as a preferential solubility of E7 constituents towards poly (n-butylacrylate). HPLC analysis is used to validate this interpretation. It is found that the composition of 5CB within droplets decreases with the polymer concentration showing that 5CB remains dissolved in the polymer matrix. A similar tendency is found for 7CB although more moderate. The component 5CT is less compatible with poly (butylacrylate) and its concentration within droplets remains practically unchanged when increasing the polymer concentration. To our knowledge this is the first evidence given by HPLC analysis to the phenomenon of preferential solvation in PDLC films involving E7. Work along these lines involving poly (n-butylacrylate), polysiloxanes and E7 is under progress and the results will be the subject of future communications.

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