Liquid Crystals

Solubility effects of multicomponent liquid crystal blends towards poly (n-butyl-acrylate)

Lamia Bedjaoui-Alachaher [a] [b] , Hassiba Bensaid [a] , Claudia Gordin [a] & Ulrich Maschke [a]

[a] Unité Matériaux et Transformations (UMET), UMR N° 8207 CNRS, Université de Lille 1 – Sciences et Technologies, Villeneuve d'Ascq, France

[b] Laboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Aboubakr Belkaïd, Pôle Chetouane, Tlemcen, Algeria

Available online: 04 Oct 2011

PLEASE SCROLL DOWN FOR ARTICLE

Solubility effects of multicomponent liquid crystal blends towards poly (*n*-butyl-acrylate)

Lamia Bedjaoui-Alachaher[a,b], Hassiba Bensaid[a], Claudia Gordin[a] and Ulrich Maschke[a]*

[a]*Unité Matériaux et Transformations (UMET), UMR N° 8207 CNRS, Université de Lille 1 – Sciences et Technologies, Villeneuve d'Ascq, France;* [b]*Laboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Aboubakr Belkaïd, Pôle Chetouane, Tlemcen, Algeria*

Blends composed of isotropic linear poly (*n*-butylacrylate) of molecular weight $M_w = 112,000$ g mol^{-1} and the commercial four-component nematic low molecular weight liquid crystal (LC) mixture E7 exhibit a strong shift of the single nematic–isotropic transition temperature T_{NI} compared to that of the pure LCs, which was evidenced by using two complementary experimental techniques: differential scanning calorimetry (DSC) and high-performance liquid chromatography. The first one provides direct information about phase behaviour and variation of T_{NI} of the polymer/LC blends, whereas the second one consists of analysing qualitatively and quantitatively the composition of millimetre-sized segregated LC domains in the two-phase region of the phase diagram.

In order to understand the origin of the unusual phase behaviour, several LC blends were prepared by modifying the concentration of the four single LC components that are present in the eutectic E7 mixture, following the results from the previous chromatographic analysis. These model blends were investigated by DSC measurements, showing that the variation, particularly of the terphenyl LC compound concentration, plays a determining role for the phase behaviour of the LC mixture and the shift of T_{NI}.

Keywords: polyacrylate; liquid crystal; phase behaviour; miscibility; high-performance liquid chromatography; differential scanning calorimetry

1. Introduction

Liquid crystal (LC)/polymer systems continue to attract many researchers, since extensive investigations were made in the last decade (1–7). These systems have been widely studied from fundamental and experimental points of view for their potential applications, such as electrically controllable light shutters, reflective displays, communication technologies and holographic gratings (8, 9). Most applications on LC/polymer systems rely on the specific nature of the employed LC mixture, which should remain constant while adding it to the polymer.

Among low molecular weight LC compounds, the commercial multicomponent nematic mixture E7 from Merck has been widely used for a large number of applications due to its high optical anisotropy (10) and a large temperature range, in which it maintains anisotropic characteristics. E7 represents an eutectic LC blend composed of 51 weight-% (wt%) 4-cyano-4'-*n*-pentyl-biphenyl (5CB), 25 wt% 4-cyano-4'-*n*-heptyl-biphenyl (7CB), 16 wt% 4-cyano-4'-oxyoctyl-biphenyl (8OCB), and 8 wt% 4-cyano-4''-*n*-pentyl-*p*-terphenyl (5CT). Its single nematic–isotropic phase transition temperature (T_{NI}) appears at 59.4°C, and at room temperature it still exhibits a nematic phase. These liquid crystalline properties are extended down to the glass transition temperature (T_g) at –62.5°C.

The phase diagrams and morphology of LC/polymer mixtures based on nematic LCs and polyacrylates have been investigated by several techniques, such as polarising optical microscopy (POM), differential scanning calorimetry (DSC) and light scattering (LS), in a wide range of temperature and composition (see, for example, Mucha (4)). For acrylate-based systems it has been found, generally, that low molecular weight LC molecules remain dissolved in the polymer for a small number of LCs. The limit of miscibility of LCs in the polymer is generally reached at about 30–35 wt% LC concentration. At higher LC concentrations, a phase-separation process occurs, and a heterogeneous polymer/LC system will be obtained consisting of a homogenous polymeric phase with dissolved LCs, and additional phase-separated LC domains of sizes varying from nano- to millimetres.

The number of LCs dissolved in the polymer-rich phase may lead to a drastic decrease of the glass transition temperature of the amorphous polymer. This behaviour, known as the plasticising effect, occurs in many polymeric systems, even with a single LC component. If the latter will be replaced by a multicomponent LC blend, such as E7, the phase-separated LC might show a variation of T_{NI} compared to that of the pure LC mixture. Such a change of T_{NI} of E7

*Corresponding author. Email: ulrich.maschke@univ-lille1.fr

can strongly affect the properties of polymer/LC systems, since the miscibility of each LC component of E7 towards the polymer is not identical, so that the LC composition in segregated domains changes its optical, electro-optical and dielectrical properties, as well as the optical and mechanical behaviour of the polymer matrix.

Such a variation of the LC composition inside phase-separated domains can be explained by the preferential miscibility, which has been observed in polymeric systems using a eutectic mixture as the nematic solvent (11–16). Indeed, some preliminary results have been already obtained for poly (*n*-butylacrylate) (PABu)/E7 blends, showing the particular interest of this system. Bouchaour *et al.* (12) performed a study of the phase behaviour and morphology of a PABu/E7 system covering a wide range of temperature and composition by POM. Surprisingly, they observed the existence of a nematic–isotropic phase transition at temperatures higher than T_{NI} of pure E7 upon adding polymer to bulk LC (12).

Nolan *et al.* (11) found a preferential miscibility effect of the E7 components in the UV-cured 40 wt% NOA65/60 wt% E7 system. The analysis of the LC composition inside phase-separated domains by gas chromatography revealed an important variation compared to the initial composition of E7.

Nwabunma and Kyu (13) investigated the phase diagram of uncured NOA65 with two different LCs: E44, which represents another commercial eutectic mixture of low molecular weight LCs, and the single LC component K21 (7CB), which is included in E44. The analysis by POM and static LS showed bimodal size distribution of LC domains in the E44 case, whereas a single size distribution for the K21 system is reported. It was assumed that such observations are due to a selective solubility of the components of E44 towards the polymer.

Gogibus *et al.* (14) established phase diagrams of various linear poly (methylphenylsiloxane) (PMPS) and low molecular weight LCs. An increase of T_{NI} of nearly 20°C was found in the presence of 80 wt% PMPS, exhibiting a molecular weight of 60,000 g mol^{-1}. The evidence that the preferential miscibility occurs in this system was explained experimentally by performing high-performance liquid chromatography (HPLC) measurements (17). The analysis of the LC composition inside the phase-separated LC domains by HPLC showed important deviation compared to the original composition of E7, due to the presence of different interactions between each of the LC components of E7 and the PMPS. Indeed, the percentage of 5CB in the domains drops by 4.9% and that of 7CB by 5.6% in the case of the 40 wt% PABu system, while the percentage of 8OCB and 5CT increase by 7.5%

and 33.8%, respectively. The increase of T_{NI} can be explained by the growing percentage of 8OCB and in particular of 5CT in the LC domains, compared to the two other LCs. 5CT possesses the highest value of T_{NI} among the four single LCs considered here, explaining thus the increase of T_{NI} in the PMPS/E7 system.

Recently, the HPLC technique accompanied by analytical ultraviolet (UV) analysis was also applied by Bras *et al.* (18, 19), allowing the identification of each of the E7 components and the determination of E7 solubility in supercritical carbon dioxide (ScCO$_2$). The relative mass fraction of each E7 component in the CO$_2$-rich phase was determined to evaluate the ability of CO$_2$ to fractionate this LC blend towards its components. This approach is important for the design and development of polymer-dispersed LCs using supercritical fluid technology.

In this work, the composition of the LC inside phase-separated domains of a poly-*n*-butylacrylate/E7 system will be determined qualitatively and quantitatively by a combination of chromatographic (HPLC) and calorimetric (DSC) techniques. In particular, model LC blends will be elaborated on the basis of the four single LCs included in the commercial mixture E7, that is, 5CB, 7CB, 8OCB and 5CT. The individual LC concentrations were chosen following the results from the previous HPLC analysis. DSC measurements of these model blends allow one to investigate the phase behaviour and the transition temperatures.

2.   Experimental details

2.1   *Materials and sample preparation*

Poly(*n*-butylacrylate) was prepared by a radical polymerisation technique using 2,2'-azoisobutyronitrile (AIBN) as the initiating species, purified and characterised by gel permeation chromatography (GPC), yielding $M_w = 112,000$ g mol^{-1} and $M_w/M_n = 2.2$. The eutectic LC mixture E7 was purchased from Merck KGaA (Darmstadt, Germany), containing 51 wt% of 4-cyano-4'-*n*-pentyl-biphenyl (5CB), 25 wt% of 4-cyano-4'-*n*-heptyl-biphenyl (7CB), 16 wt% of 4-cyano-4'-*n*-oxyoctyl-biphenyl (8OCB) and 8 wt% of 4-cyano-4''-*n*-pentyl-*p*-terphenyl (5CT) (11, 20). E7 exhibits a nematic to isotropic transition temperature at $T_{NI} = +59.4$°C and a glass transition temperature at $T_g = -62$°C.

The four single low molecular weight LCs used, 5CB, 7CB, 8OCB and 5CT, were purchased from Synthon Chemicals GmbH (Wolfen, Germany). The characteristic transition temperatures of the LCs are given in Table 1. All LCs were used as received.

The preparation of polymer–LC samples was made by a solvent-induced phase-separation process (SIPS).

Table 1. Characteristic transition temperatures of the low molecular weight LCs used. T_{CrS}, T_{SN}, T_{CrN} and T_{NI} represent the crystalline–smectic, smectic–nematic, crystalline–nematic and nematic–isotropic transition temperatures, respectively. T_g is the glass transition temperature of E7.

LC	T_g (°C)	T_{CrS} (°C)	T_{SN} (°C)	T_{CrN} (°C)	T_{NI} (°C)
5CB				24	35.5
7CB				30	42.8
8OCB		54.5	67		80
5CT					240
E7	−62.5				59.4

Polymer and LCs were dissolved at room temperature, in a common organic solvent (tetrahydrofuran, THF) at 50 wt%. The resulting mixture was stirred mechanically for two hours, and a small quantity was cast on a clean glass slide, or into an aluminium pan, designated for HPLC investigations and DSC analysis, respectively. The samples were completely dried at room temperature for several days. After total evaporation of the solvent, phase-separated structures were found, exhibiting randomly dispersed LC domains.

2.2 Techniques and experimental procedures

2.2.1 DSC measurements

DSC measurements were performed on a Perkin Elmer Pyris Diamond calorimeter equipped with an Intracooler 2P system, allowing cooling experiments. Samples for calorimetric measurements were prepared by introducing approximately 8 mg of the film into aluminium DSC pans, which were sealed to avoid evaporation effects during the temperature treatment. A rate of $10°C \, min^{-1}$ (heating and cooling) was used in the temperature range from –72 to +120°C. The program consists 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. The thermograms presented in this work were obtained from the second heating ramps. In each case, at least five duplicate samples, having the same composition and prepared independently, were used to check the reproducibility of results. The glass transition temperatures were determined from the midpoint of the transition range of the thermograms.

2.2.2 HPLC characterisation

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 used with a flow of 1 ml min^{-1}. A mixture consisting of 30% water

and 70% methanol (both HPLC-grade solvents) was applied in the isocratic operation mode.

Chromatograms were obtained at a wavelength of 315 nm, because the absorption band of the aromatic groups of the LCs is located near this wavelength. Extraction of the LCs from the segregated LC domains for HPLC measurements was made using a capillary syringe under a POM. The extracted LCs were diluted in THF to recover the corresponding concentration.

Data evaluation was performed by taking into account peak areas from chromatograms. Pure 5CB, 7CB, 8OCB and 5CT samples were employed in various concentrations to identify the peaks corresponding to these LCs, which appear in the following order: 5CB, 7CB, 8OCB and 5CT. More details of the calibration procedure are given by Bedjaoui *et al.* (17).

3. Results and discussion

Figure 1 shows thermograms of the PABu/E7 system obtained from DSC measurements. PABu/E7 blends were analysed using increments of 10 wt% starting from pure PABu to pure E7. In this figure, the heat flow of each PABu/E7 mixture is represented as function of temperature, covering a wide range from –72°C up to +120°C, which allows detection of various transition temperatures, such as T_{NI} of the LCs and T_g of the polymer and the LCs.

The pure LC E7 is characterised by two transition temperatures: a glass transition at low temperature ($T_g = -62.5°C$) and a nematic–isotropic transition at higher temperature ($T_{NI} = +59.4°C$). Between these two temperatures, no other transition occurs, and the nematic phase covers a wide range of temperatures. Above T_{NI}, E7 adopts an isotropic phase.

The pure poly (*n*-butyl acrylate) shows a single glass transition in the whole range of temperatures explored, which can be determined as $T_g = -55°C$.

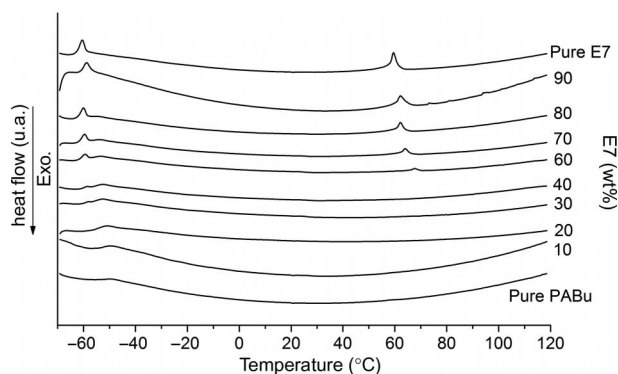Figure 1. DSC thermograms of the PABu/E7 system for several compositions, starting from pure PABu and E7 in a temperature range from –70°C to +120°C.

The LC glass transition temperature appears in the thermograms for mixtures with LC composition higher than 20 wt%. A decrease of T_g of the polymer was found by adding a small number of LCs, revealing a plasticising effect of the LCs towards the polymer matrix. This decrease can be explained by the fact that small LC molecules are dissolved in the polymer matrix and act like a plasticiser, thus influencing mechanical, optical, dielectrical and, eventually, electro-optical properties in the case of polymer-dispersed LC materials (21, 22). A further increase of the LC content leads to a constant value of T_g of the polymer. The LC glass transition appears at $-62.5°C$ for samples with 30 or 40 wt% E7, whereas no other transition was observed at higher temperatures. In the concentration range from 60 to 90 wt%, the thermograms essentially show two transitions: T_g (LC) and T_{NI}, which appear independently. Clearly, the upper part of the right-hand side of Figure 1 shows that T_{NI} undergoes an evolution depending on the LC concentration.

In order to understand the solubility behaviour of a single LC (taking part of E7) towards PABu, DSC thermograms of the PABu/5CB system for various compositions are collected on the left-hand side of Figure 2, presenting only the temperature range around T_{NI} of 5CB at 35.5°C. To compare with PABu/E7, the corresponding thermograms are shown on the right-hand side of Figure 2. Indeed, this figure allows one to follow the dependence of T_{NI} of both systems as a function of temperature and composition. It was observed that the T_{NI} of 5CB remains constant and that of E7 increases strongly with polymer concentration.

Figure 3 shows the dependence of the ratio of temperatures T_{NI-m}/T_{NI-p} as a function of PABu
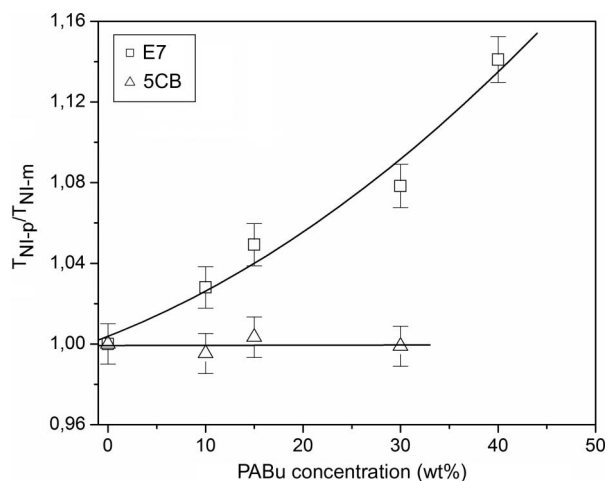
Figure 3. Variation of T_{NI-m}/T_{NI-p} of PABu/E7 and PABu/5CB systems versus PABu concentration. T_{NI-m} represents the nematic–isotropic transition temperatures of 5CB and E7 from DSC thermograms of PABu/LC mixtures. T_{NI-p} corresponds to the nematic–isotropic transition temperatures of pure LCs 5CB and E7, which were also obtained from DSC thermograms.

composition, combining both systems investigated. This ratio was calculated by taking into account the nematic–isotropic transition temperature T_{NI-m} calculated for each mixture of both systems and T_{NI-p}, the nematic–isotropic transition temperatures of pure LCs (5CB and E7).

The ratio T_{NI-m}/T_{NI-p} of the PABu/5CB system remains unchanged according to the polymer concentration. The pure LC does not contribute to the observation of the shift of T_{NI}, although 5CB represents a certain miscibility with PABu. In the case of the PABu/E7 system, T_{NI-m}/T_{NI-p} seems to increase following a second-order polynomial relationship. The error made between theoretical and experimental ratios is between 0.2% and 1.5%. As an example, the ratio T_{NI-m}/T_{NI-p} of 1.05 (corresponding to $T_{NI} = 62.37°C$) was found for 15 wt% PABu and a value of 1.14 (corresponding to $T_{NI} = 67.72°C$) was obtained for 40 wt% PABu. It would be interesting to know why such significant variation of T_{NI-m}/T_{NI-p} was observed, and how it would be possible to qualify and quantify this effect.

Since E7 is composed of four cyanobiphenyl derivatives possessing nearly the same chemical structure and similar affinity to organic solvents, separation of these compounds by analytical means remains a difficult task. It has been shown that HPLC could be an adequate technique allowing one to qualify and to quantify single LCs present in LC mixtures (17).

In order to understand the compositional changes of the LC mixture towards the polymer, the content of millimetre-sized phase-separated LC domains of
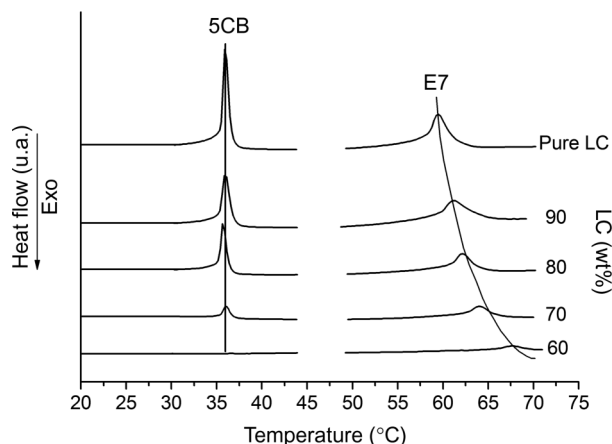

Figure 2. Thermograms obtained from DSC measurements of PABu/5CB and PABu/E7 systems in a limited temperature range around the nematic–isotropic transition temperatures of 5CB (35.5°C) and E7 (59.4°C), respectively.

the PABu/E7 system was analysed at room temperature. Details of this procedure, as well as calibration curves, are given elsewhere (17). The concentrations of 5CB, 7CB, 8OCB and 5CT in the phase-separated domains as a function of the corresponding PABu concentration are given in Figure 4(a) and (b), exhibiting linear relationships in all cases considered here. Figure 4(a) shows that 5CB and 7CB concentrations decrease as a function of the polymer concentration, whereas Figure 4(b) represents an increase of 8OCB and 5CT concentrations with increasing PABu content. As a result, we can see that important variations of the LC content in segregated domains have already taken place for low polymer concentrations. For example, the sample with 20 wt% PABu reveals a decrease of 20% and 6% of 5CB and 7CB, respectively, whereas

8OCB and 5CT concentrations increase about 6% and 40%, respectively. Although the variation of 5CT concentration appears nearly negligible, a slight change of this compound can already lead to a strong increase of T_{NI} of the LC domains, due to the relatively high T_{NI} of the pure 5CT, corresponding to 240°C.

These dependencies prove that 5CB and 7CB are miscible to some extent with PABu, whereas 8OCB and 5CT show a low affinity with this polymer. The results are in agreement with the assumption proposed that the composition of the LC from the segregated domains varies according to the polymer concentration, due to the preferential miscibility phenomenon.

To confirm the HPLC results, DSC measurements were performed on samples made from LC mixtures that correspond to the composition of the LCs from the segregated domains of PABu/E7 blends, which contain 10–40 wt% PABu. The concentration data of these LC mixtures are reported in Table 2, and these compositions were analysed by DSC.

Figure 5 gathers thermograms of four LC mixtures, which correspond to the compositions of the LCs from the segregated domains, obtained from HPLC analysis. These mixtures provide, as shown in Figure 5, two different transitions: the glass transition T_g and the nematic–isotropic transition T_{NI}. It should be
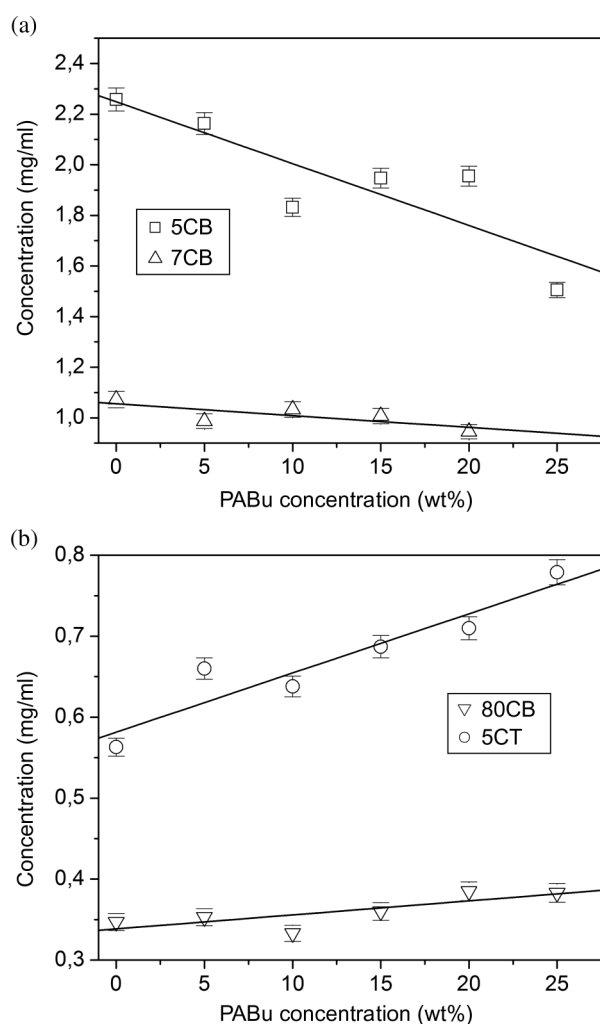

Figure 4. HPLC results from phase-separated domains of the PABu/E7 system: variation of the concentration of the four constituents of E7, (a) 5CB and 7CB, (b) 8OCB and 5CT, versus PABu concentration. Symbols represent averaged values of at least five data points and solid lines correspond to a fit made by linear regression analysis.

Table 2. Composition of LC mixtures that corresponds to the results from HPLC measurements of the segregated domains of the PABu-E7 system.

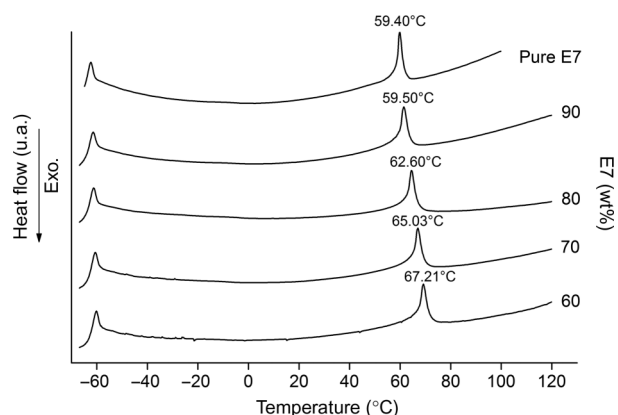| PABu (wt%)	5CB (wt%)	7CB (wt%)	8OCB (wt%)	5CT (wt%)
(10)	49.86	25.08	16.18	8.87
(20)	46.08	24.85	19.41	9.64
(30)	41.85	24.60	23.04	10.50
(40)	37.07	24.31	27.13	11.47

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, obtained from HPLC investigations.

pointed out that the thermograms of the model LC blends shown in Figure 5 reveal a eutectic character, since their composition is relatively close to E7. The experiments showed a single glass transition and a single nematic–isotropic transition, and a large nematic phase for all LC mixtures employed.

The evolution of the ratio of temperature T_{NI-m}/T_{NI-p}, as a function of PABu composition combining PABu/E7 blends and LC mixtures, is nearly identical for the two cases, as shown in Figure 6. Only a slight deviation was observed at higher PABu concentrations. These results clearly confirm the presence of a preferential miscibility effect of the PABu system and show an important impact for practical applications.

4.   Conclusions

The phase behaviour of PABu/E7, PABu/5CB and several LC mixtures was studied on a wide range of temperatures and composition by using simultaneously HPLC and DSC techniques. The nematic–isotropic transition temperature T_{NI} of the PABu/E7 system showed a shift upwards by increasing the PABu concentration, whereas the T_{NI} remained unchanged for the PABu/5CB system. The increase of T_{NI} for the PABu/E7 system can be explained by preferential miscibility effects and phase-separation phenomena involving the polymer, as well as the different LC constituents. In particular, HPLC analysis allowed qualitative and quantitative analysis of the LC content confined in domains, and revealed the change of LC composition within these phase-separated domains, compared to pure E7.

With this study we would like to emphasise the fact that mixing a polymer with an originally eutectic LC mixture could lead to phase-separation phenomena between different species in such multicomponent blends (E7 was taken here as an example, more complicated LC systems used for various applications might consist of more than 10 single LC components). As a result, refractive indices, optical and electro-optical response functions, dielectric and electrical properties, as well as thermodynamical and other physico-chemical properties of polymer/LC mixtures, might change compared to the situation, where only pure eutectic LC is present in the phase-separated dispersed LC domains.

References

(1) Kitzerow, H.S. *Liq. Cryst.* **1994**, *16*, 1–31.
(2) Higgins, D.A. *Adv. Mater.* **2000**, *12*, 251–264.
(3) Lampert, C.M. *Mater. Today* **2004**, *7*, 28–35.
(4) Mucha, M. *Prog. Polym. Sci.* **2003**, *28*, 837–873.
(5) Doane, J.W.; Vaz, N.A.; Wu, B.G.; Zumer, S. *Appl. Phys. Lett.* **1986**, *48*, 269–271.
(6) White, T.J.; Natarajan, L.V.; Bunning, T.J.; Guymon, C.A. *Liq. Cryst.* **2007**, *34*, 1377–1385.
(7) Chen, L.G.; Shanks R. *Liq. Cryst.* **2007**, *34*, 1349–1356.
(8) White, T.J.; Natarajan, L.V.; Tondiglia, V.P.; Lloyd, P.F.; Bunning, T.J.; Guymon, C.A. *Polymer* **2007**, *48*, 5979–5987.
(9) Harbour, S.; Kelly, J.V.; Galstian, T.; Sheridan, J.T. *Opt. Commun.* **2007**, *278*, 28–33.
(10) Leonard, S.W.; Mondia, J.P.; Van Driel, H.M.; Toader, O.; John, S.; Bush, K.; Birner, A.; Gösele, U.; Lehmann, V. *Phys. Rev. B Condens. Matter.* **2000**, *61*, 2389–2392.
(11) Nolan, P.; Tillin, M.; Coates, D. *Mol. Cryst. Liq. Cryst. Lett.* **1992**, *8*, 129–135.
(12) Bouchaour, T.; Benmouna, F.; Leclercq, L.; Ewen, B.; Coqueret, X.; Benmouna, M.; Maschke, U. *Liq. Cryst.* **2000**, *27*, 413–420.
(13) Nwabunma, D.; Kyu, T. *Polymer* **2001**, *42*, 801–806.
(14) Gogibus, N.; Benmouna, F.; Ewen, B.; Pakula, T.; Coqueret, X.; Benmouna, M.; Maschke, U. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 39–43.
(15) Kuschel, F.; Hartmann, L.; Bauer, M. *J. Appl. Polym. Sci.* **2010**, *117*, 1486–1492.
(16) Deshmukh, R.R.; Malik, M.K. *J. Appl. Polym. Sci.* **2008**, *109*, 627–637.
(17) Bedjaoui, L.; Gogibus, N.; Ewen, B.; Pakula, T.; Coqueret, X.; Benmouna, M.; Maschke, U. *Polymer* **2004**, *45*, 6555–6560.
(18) Bras, A.R.E.; Casimiro, T.; Caldeira, J.; Aguiar-Ricardo, A. *J. Chem. Eng. Data* **2005**, *50*, 1857–1860.
(19) Bras, A.R.E.; Henriques, S.; Casimiro, T.; Aguiar-Ricardo, A.; Sotomayor, J.; Caldeira, J.; Stos, C.; Dionisio, M. *Liq. Cryst.* **2007**, *34*, 591–597.
(20) Technical data sheet for E7 from Merck KgaA, Darmstadt, Germany.
(21) Drzaïc, P.S. *Liquid Crystal Dispersions*; World Scientific: Singapore, 1995; p 67; Chapter 2.
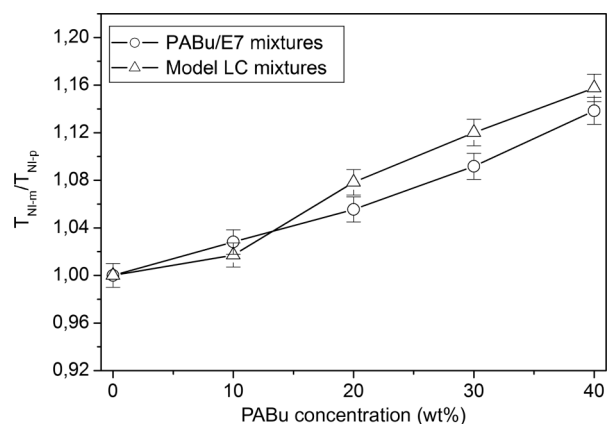(22) Smith, G.W.; Vaz, N.A. *Mol. Cryst. Liq. Cryst.* **1993**, *237*, 243–269.

Figure 6.   Comparison of T_{NI-m}/T_{NI-p} of PABu/E7 mixtures and the corresponding results for model LC blends. T_{NI-m} and T_{NI-p} represent the nematic–isotropic transition temperatures of mixtures and of pure E7, respectively, obtained from DSC thermograms.