

Preferential solvation of the eutectic mixture of liquid crystals E7 in a polysiloxane

Lamia Bedjaoui^a, Nicolas Gogibus^b, Bernd Ewen^b, Tadeusz Pakula^b, Xavier Coqueret^c,
Mustapha Benmouna^a, Ulrich Maschke^{c,*}

^aLaboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Aboubakr Belkaïd, BP 119, 13000 Tlemcen, Algeria

^bMax-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

^cLaboratoire de Chimie Macromoléculaire, CNRS (UMR No 8009), Bâtiment C 6, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France

Received 26 January 2004; received in revised form 14 June 2004; accepted 16 July 2004

Abstract

Blends of the nematic liquid crystal E7 and poly(methylphenylsiloxane) (PMPS) with molecular weight 120,000 g/mol are investigated by high performance liquid chromatography (HPLC) measurements. This study was prompted by observations made recently while analyzing the phase behavior of poly(siloxane)/E7 and poly(acrylate)/E7 systems. A remarkable increase of the nematic to isotropic transition temperature T_{NI} was found when polymer was added to the liquid crystal. Surprisingly, the increase of T_{NI} was enhanced with the polymer concentration up to 80 wt%, where it reached its highest value. This behavior could be interpreted by invoking a preferential solvation of the constituents of E7 towards the polymer. The present investigation provides an evidence of this phenomenon using HPLC data.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Polymer physical chemistry; Polymer science and technology; Polymer composite materials

1. Introduction

The mixture of liquid crystals (LC) commonly known as E7 is made of four cyano substituted polyphenyls at a given composition [1,2]. E7 is an eutectic mixture that is widely used in polymer dispersed liquid crystal (PDLC) materials working in normal mode conditions because it offers a wide range of operating temperatures for applications in display devices, privacy windows, optical shutters etc. [3–6]. Indeed, E7 exhibits a single nematic to isotropic (NI) transition at nearly $T_{NI}=61$ °C and no other transitions between +61 and –62 °C, where it shows a glass transition T_g . In the majority of cases reported in the literature by us [7, 8] and other groups [9,10], these transition temperatures are hardly modified in the presence of a polymer. There are, however, some exceptions which remain to be elucidated

involving a phase separation of the constituents of the multi-component mixture E7 in the presence of certain polymers [1,11–13]. A possible interpretation of this phase separation is given by the preferential solvation of the constituents of E7 towards the polymer under certain conditions. The purpose of the present paper is to give evidence of this phenomenon for the poly(methylphenylsiloxane) (PMPS)/E7 system.

Several investigations were reported in the literature leading to the observation of compositional fractionation of E7. To the best of our knowledge, Nolan et al. [1] were the first to make the observation of a preferential solvation of the components of E7 in the UV-cured 40 wt% NOA65/60 wt% E7 system. The analysis of the LC composition inside the droplets by gas chromatography showed important deviations compared to the original composition of E7 due to the presence of different interactions between each of the LC and the polymer. Indeed, the percentage of 4-cyano-4'-n-pentylbiphenyl (5CB) drops by several percent (6%) while that of

* Corresponding author. Tel.: +33-3-20-33-63-81; fax: +33-3-20-43-43-45.

E-mail address: maschke@univ-lille1.fr (U. Maschke).

4-cyano-4'-*n*-heptyl-biphenyl (7CB), 4-cyano-4'-*n*-oxyoctyl-biphenyl (8OCB), and 4-cyano-4''-*n*-pentyl-*p*-terphenyl (5CT) increases significantly. The immediate consequence of these compositional changes was a shift in the NI transition temperature which is found to increase from 61 to 65.6 °C. This effect can be explained by the growing percentage of 8OCB and in particular 5CT in the droplets, compared to the two other LC. Recall that pure 5CT shows a high NI transition temperature $T_{NI}=240$ °C explaining the increase of T_{NI} of the LC droplets if preferential solvation takes place (see Table 1). Even a small compositional change of E7 involving 5CT leads therefore to a pronounced effect on T_{NI} which can be easily detected experimentally by polarized optical microscopy (POM), differential scanning calorimetry, and light scattering (LS) measurements.

Nwabunma and Kyu [11] investigated the phase diagram of uncured NOA 65 and eutectic mixture of LCs E44 similar to E7, and compared the results with those involving the single component K21 (or 7CB) [14,15]. The analysis of the morphology by POM and static LS revealed a bimodal size distribution of LC droplets in the E44 case, whereas these authors reported a single size distribution for the K21 system. It was assumed that such observations could be explained by a selective solvation of the components of E44 towards the polymer. In this case, one might expect the existence of a nematic phase above the NI transition temperature of the uncured NOA65/E44 system as it was found in PBA/E7 and PMPS/E7. The phase diagram reported in Ref. [11] gives data describing the cloud point curve but no analysis of the (N+I₂)/(I₁+I₂) nematic— isotropic transition was presented.

Bouchaour et al. [12] performed a study of the phase behavior and morphology of a poly(*n*-butylacrylate) (PBA)/E7 system covering a wide range of temperature and composition. They observed the existence of a nematic + isotropic phase at temperatures higher than the NI transition temperature T_{NI} of pure E7 upon adding polymer to bulk LC as shown in Fig. 1 of Ref. [12]. The increase of T_{NI} versus polymer concentration subsists practically through a LC concentration as low as 40 wt%, where a NI transition temperature 10 °C higher than T_{NI} of pure E7 was found. In

Table 1

Description of the low molecular weight LC compounds included in the nematic mixture E7

Liquid crystal	Liquid crystal (short name)	T_{NI} [°C]
Nematic LC mixture	E7	61
4-Cyano-4'- <i>n</i> -pentyl-biphenyl	5CB	35.3
4-Cyano-4'- <i>n</i> -heptyl-biphenyl	7CB	42.8
4-Cyano-4'- <i>n</i> -oxyoctyl-biphenyl	8OCB	80
4-Cyano-4''- <i>n</i> -pentyl- <i>p</i> -terphenyl	5CT	240

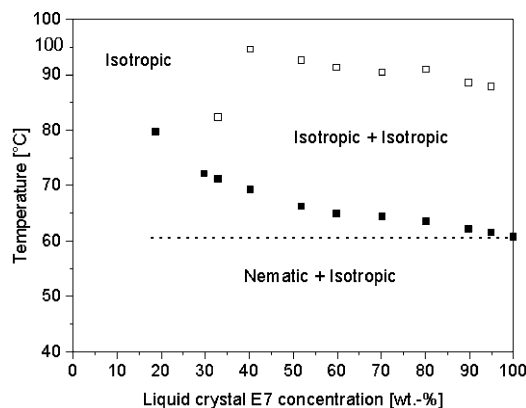


Fig. 1. Experimental phase diagram of PMPS ($M_w=60,000$ g/mol)/E7 system (see Ref. [13]). Filled squares represent the transition temperatures from the nematic + isotropic to the isotropic + isotropic regions, whereas open squares stand for the transition temperatures from isotropic + isotropic to isotropic phases. The dotted line displays the nematic— isotropic transition temperature of pure E7.

particular, analysis of the experimental results within the theoretical models of Flory–Huggins for isotropic mixing combined with the Maier–Saupe theory for nematic ordering did not yield consistent results. The observed phenomenon was explained by the occurrence of a preferential solvation of some of the constituents of E7 in the polymer but only recently evidence could be obtained experimentally by performing high performance liquid chromatography (HPLC) measurements [16].

Gogibus et al. [13,17,18] reported an investigation of the morphology and phase behavior of various linear poly (siloxane) and low molecular weight LC systems. In particular, they considered systems involving the polymers poly(dimethylsiloxane) (PDMS) [17,18] and PMPS [13], and the LCs 5CB and E7. Trends similar to those of the PBA/E7 system were also observed on the PMPS/E7 system as presented in Fig. 1 which shows the phase diagram of this system, where the polymer exhibits a molecular mass of 60,000 g/mol. This phase diagram shows clearly three different regions including a nematic + isotropic and an isotropic + isotropic biphasic region, and a wide region exhibiting a single isotropic phase. The isotropic polymer and the LC are not miscible at low temperatures. The filled squares in Fig. 1 represent the transition temperatures from the nematic + isotropic to the isotropic + isotropic region. Using optical microscopy, it was possible to observe the transition temperatures from the isotropic + isotropic region to the single isotropic phase shown by open squares. Above this temperature only one isotropic phase does exist.

Fig. 1 shows that the transition temperatures from the nematic + isotropic to the isotropic + isotropic region deviate from the NI transition temperature of the pure LC. A first slow and then nearly exponential increase was observed by increasing the concentration of PMPS. This effect is much more pronounced than in the case of the PBA/E7 system. An increase of nearly 20 °C was found in the presence of

80 wt% PMPS which was attributed to the preferential solvation of E7 but no evidence of this phenomenon was given so far for poly(siloxane) systems. However, corresponding phase diagrams of PMPS/5CB systems do not show such a behaviour, although the PMPS was characterized by the same molecular weight [13]. Indeed, the NI transition temperature was found to remain constant at 35 °C throughout the whole phase diagram. These findings indicate the absence of other phenomena than the nature of the LC used.

In the present work, we report a chromatographic analysis of the composition of the LC inside droplets of a PMPS/E7 system to validate the hypothesis of preferential solvation of E7 invoked in Ref. [13] from the phase behavior of this polymer/LC system.

2. Experimental section

2.1. Materials

The low molecular weight LC E7 as well as the single compounds 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*-terphenyl (5CT) were purchased from Merck KGaA, Darmstadt (Germany). E7 is an eutectic mixture containing 51 wt% of 5CB, 25 wt% of 7CB, 16 wt% of 8OCB, and 8 wt% of 5CT (see Table 1). In spite of its multicomponent nature, E7 exhibits a single nematic-isotropic transition temperature $T_{NI} = 61$ °C and a glass transition temperature at $T_g = -62$ °C.

The PMPS was prepared by anionic living polymerization using *n*-butyllithium as initiating species and trimethylchlorosilane as end-capper. The obtained product was purified and characterized by gel permeation chromatography using a PMPS calibration curve. The molecular weight was $M_w = 120,000$ g/mol and the degree of polydispersity (M_w/M_n) = 1.3.

2.2. Sample preparation

Sample preparation was made by solvent induced phase separation. The polymer and LC were dissolved in a common organic solvent (tetrahydrofuran, THF) at 30 wt% 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 several days. After total evaporation of the THF, large size distributions of the LC droplets were found, spanning the range from micrometers to millimeters depending on the blend composition. Extraction of the LC from the droplets for HPLC measurements was made using a 25 μ l 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.

2.3. HPLC characterization

HPLC analysis was carried out using a Waters 510 model equipped with an UV-detector model 481. A standard Versapak C18 μ column from Alltech was employed with a flow of 1 ml/min. A mixture consisting of 25% water and 75% methanol (both HPLC grade solvents) was used 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. The extracted LC as mentioned above was diluted in THF to recover the corresponding concentration.

3. Results and discussion

Prior to the analysis of the content of the LC droplets of PMPS/LC samples, extensive work was performed to calibrate the results obtained from HPLC measurements. In this calibration, standards were prepared in the laboratory by mixing pure 5CB, 7CB, 8OCB and 5CT in a wide range of composition to determine the relationship between the obtained peak areas or heights and the corresponding concentration of each LC. Samples were also prepared in various concentrations from the different single components allowing to identify clearly all four LC, depending on their retention times. The following order of appearance was found as a function of retention time: 5CB, 7CB, 8OCB, and 5CT. This order can be explained by the decreasing affinity of these LC with the column material under the given experimental conditions.

Linear dependencies between the peak areas and the LC concentration were found in all four cases studied here which makes data analysis a rather easy task. Fig. 2(a)–(d) show the calibration curves used to evaluate the concentration of the four components of the LC from corresponding peak areas of the chromatograms. In practice, peak areas were analyzed by weight using each time high quality white paper from the same company. Data evaluation was also performed by taking into account peak heights but the evaluation of peak areas was chosen here since the latter yields more reproducible results. The experiments were rather sensitive to slight variations of the temperature which might lead to enlargement of the peaks, becoming broader and less intense. Peak area calculations were therefore preferred and allowed furthermore to perform deconvolution of adjacent peaks as it was necessary to separate 7CB and 8OCB.

The chromatogram (a) in Fig. 3 corresponds to pure E7 which is shown here to confirm the composition of the bulk LC used in these experiments and to make a direct comparison with the samples corresponding to the presence of polymer at a finite concentration. Starting from the composition of the four LC of E7, the self-prepared E7 yielded exactly the same peak areas and heights as the E7

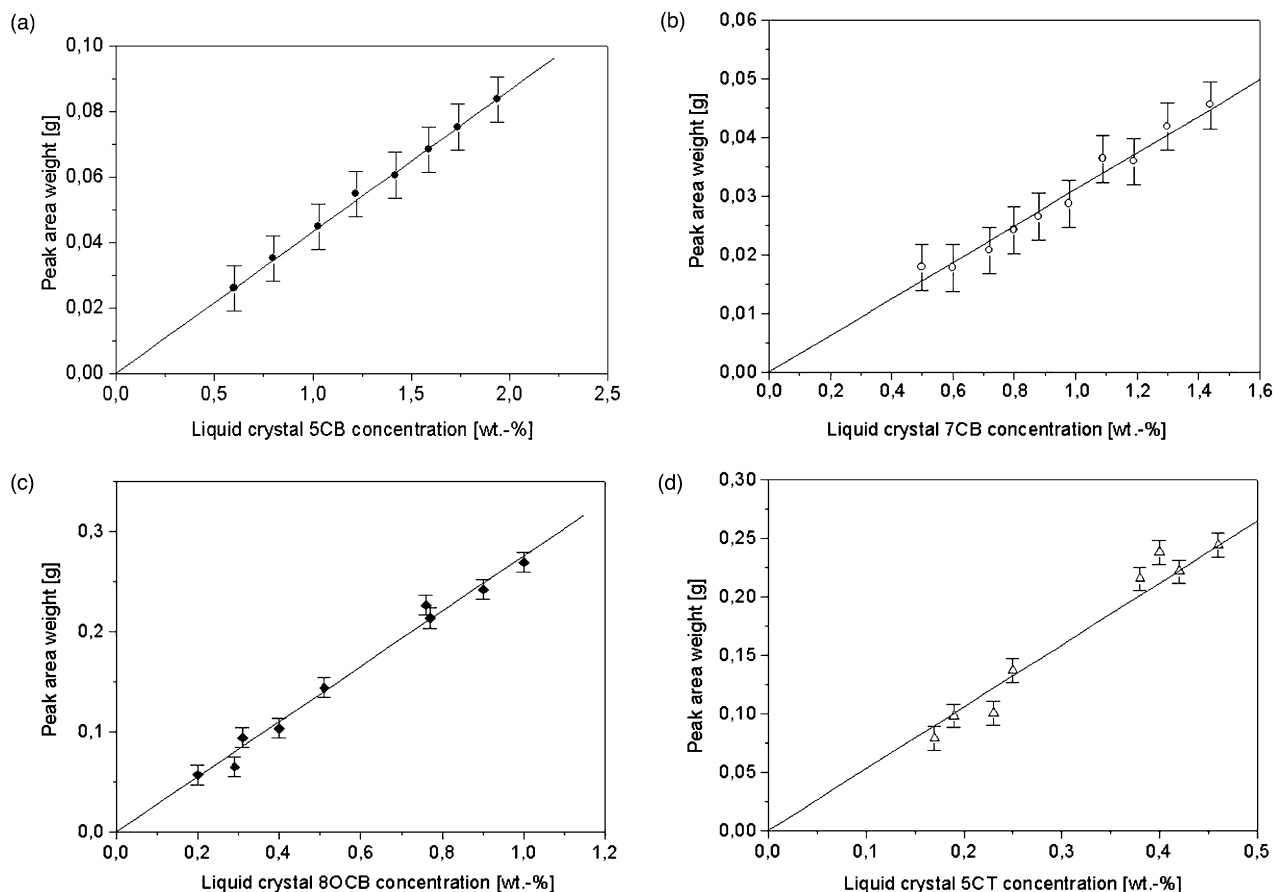


Fig. 2. Calibration curves in terms of the HPLC peak area weights for a large range of LC concentrations. (a) 5CB; (b) 7CB; (c) 8OCB; (d) 5CT. Straight lines were obtained by linear regression analysis.

purchased from Merck thus confirming the composition mentioned in the experimental part and in Table 2.

Fig. 3(b) shows the compositional changes of the LC as a result of the preferential affinity of 5CB and 7CB towards the polymer. The chromatogram presented in this figure was obtained from a 50 wt% E7/50 wt% PMPS sample showing clearly the increase of the peak areas and heights of 8OCB and 5CT and a slight decrease of the two other LC, compared to E7.

One has to keep in mind that the areas of the four LCs correspond to quite different quantities of the LC, i.e. the 5CT peak area is much more important than that of 5CB but the concentration of 5CT in E7 is more than 6 times lower than that of 5CB. The same general situation apply for the comparison of 5CB with 8OCB. This means that already a

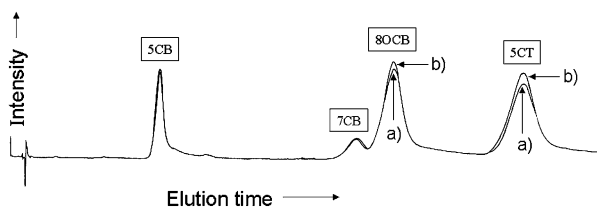


Fig. 3. HPLC chromatograms from the pure E7 mixture, curve (a), and from a blend of 50 wt% E7/50 wt% PMPS, curve (b).

small diminution of the peak area of 5CB corresponds to a considerable amount of this LC soluble in the polymer since 5CB represents the major constituent of E7.

On the other hand, peak area changes are very sensitive to even small variations of 8OCB and 5CT concentrations in the droplets, whereas the peak areas of 7CB are generally too small to allow accurate analysis.

Table 2 gives the composition of LC in the bulk and inside droplets for films corresponding to 20 and 60 wt% PMPS. The last column on the right hand side of this table summarizes the tendencies by giving the direction and percentage of changes of the four cyano substituted polyphenyls at this polymer concentration. 5CB is practically the only component whose concentration decreases in the droplets meaning that it prefers to remain dissolved in the polymer due to its higher affinity compared to the other components. The percentage is somewhat low but since 5CB is the major constituent of E7, this corresponds to a significant amount of LC remaining in the vicinity of the polymer. On the other hand, although the concentration of 5CT in the droplets undergoes an increase of 34%, since the original concentration is low, the additional amount of 5CT resulting from its low affinity with the polymer is relatively small.

Table 2

Composition of bulk E7 and of polymer/E7 samples with 20 and 60 wt% PMPS as well as the changes of the latter composition compared to pure E7, expressed in percentages of the corresponding LC

LC constituents	Composition of LC in E7 [wt%]	LC content in blend with 20 wt% PMPS [wt%]	LC content in blend with 60 wt% PMPS [wt%]	Variation of the LC content compared to pure E7 [%] (sample with 60 wt% PMPS)
5CB	51	50.1	48.5	−4.9
7CB	25	24.9	23.6	−5.6
8OCB	16	16.2	17.2	+7.5
5CT	8	8.8	10.7	+33.8

Variations of the concentration of each component of E7 in terms of the polymer concentration are displayed in Fig. 4(a)–(d) to show how the affinity of this LC evolves with the polymer concentration. Symbols represent averaged values of at least 5 data for each point and the solid lines are guides for the eyes. Linear relationships between LC concentration in the droplets and PMPS composition were found in all four cases reported here. As expected, the concentration of 5CB decreases with increasing PMPS content, whereas that of 7CB decreases only slightly which means that 7CB does not exhibit a preferential solvation with the polymer. The concentrations of 8OCB and 5CT in the droplets increase by adding PMPS to pure E7 as shown in Fig. 4(c) and

(d). Experimental evidence is thus given for the phenomenon of preferential solubility.

4. Conclusions

A HPLC investigation of the PMPS/E7 system enabled us to determine the LC composition of droplets in terms of the polymer concentration. This composition shifts clearly from that of bulk LC and the shift is enhanced as the polymer concentration increases through 80% by weight. The content of 5CB and 7CB in the droplets decreases by roughly 5% in both cases, which is rather significant knowing that these LCs are the major components of E7.

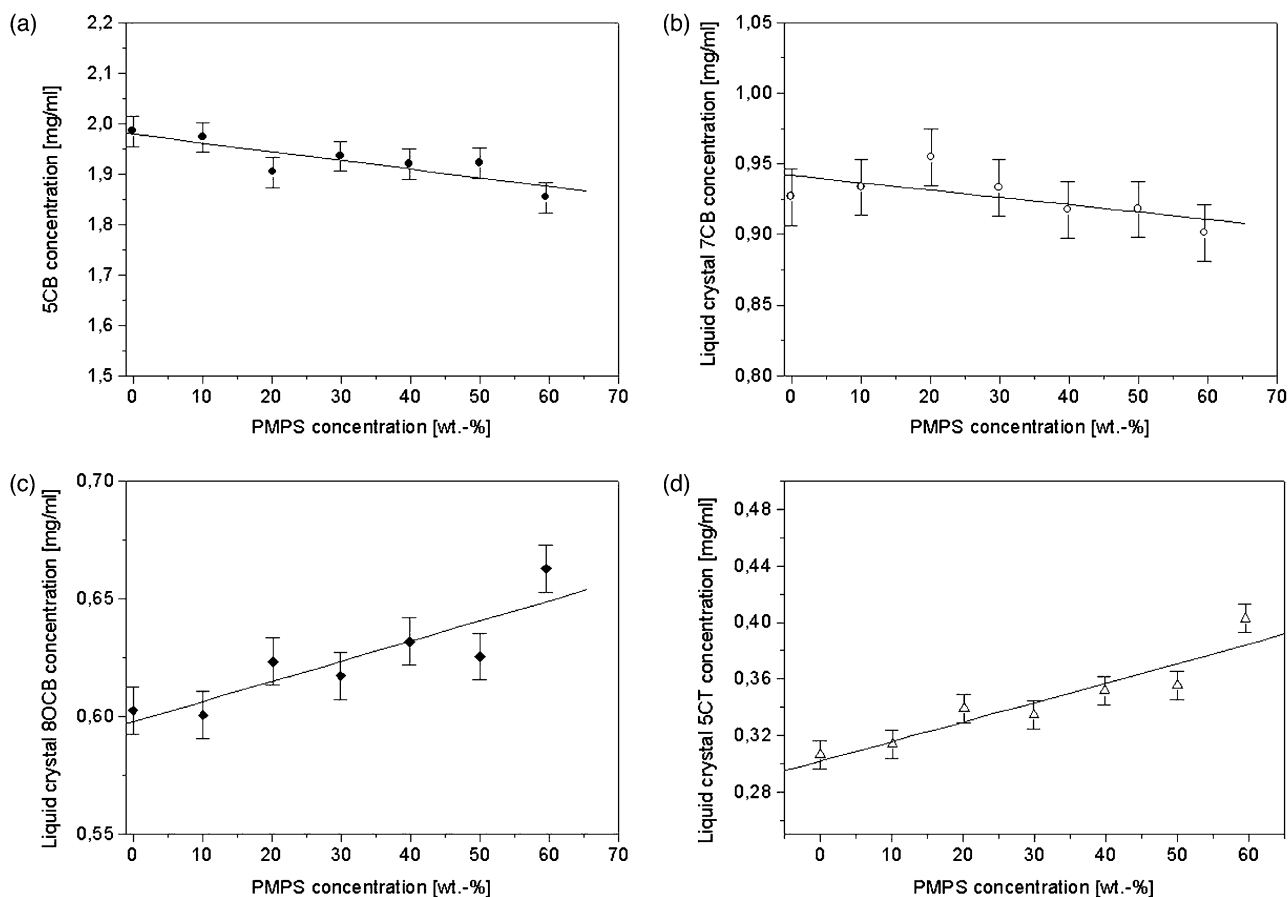


Fig. 4. Variation of the concentration of the constituents of E7 as a function of the PMPS concentration obtained from HPLC chromatograms (a) 5CB, (b) 7CB, (c) 8OCB, (d) 5CT. Each data point corresponds to an average of at least 5 individually determined values.

The other compositions increase from 7.5% (8OCB) to 34% (5CT). These results are consistent with the observations made recently on similar and other systems investigating the phase behavior of PDLC systems involving the mixture of low molecular weight LC E7. The present study validates the hypothesis of preferential solvation of constituents of this LC towards the polymer invoked to justify the increase of the NI transition temperature observed in the phase diagram.

Acknowledgements

M. Benmouna thanks the CNRS for kind invitation and the Laboratoire de Chimie Macromoléculaire for hospitality.

References

- [1] Nolan P, Tillin M, Coates D. *Mol Cryst Liq Cryst Lett* 1992;8:129.
- [2] Technical data sheet for E7 from Merck KGaA, Darmstadt, Germany.
- [3] Drzaic PS. *Liquid crystal dispersions*. Singapore: World Scientific; 1995.
- [4] Higgins DA. *Adv Mat* 2000;12:251.
- [5] Maschke U, Benmouna M, Coqueret X. *Macromol Rapid Commun* 2002;23:159.
- [6] Mucha M. *Prog Polym Sci* 2003;28:837.
- [7] Kara Slimane S, Maschke U, Benmouna F, Bacquet M, Roussel F, Buisine JM, Coqueret X, Benmouna M. *Eur Polym J* 2002;38:461.
- [8] Roussel F, Maschke U, Buisine JM, Coqueret X. *Phys Rev E* 2000;62:2310.
- [9] Kyu T, Illies I, Shen C, Zhou ZL. *Liquid crystalline polymer systems*. In: Isayev AI, Kyu T, Cheng SDZ, editors. *Technological advances*. Washington, DC: ACS Symposium Series 632 1996. Chapter 13.
- [10] Carpaneto L, Ristagno A, Stagnaro P, Valenti B. *Mol Cryst Liq Cryst* 1996;290:213.
- [11] Nwabunma D, Kyu T. *Polymer* 2001;42:801.
- [12] Bouchaour T, Benmouna F, Leclercq L, Ewen B, Coqueret X, Benmouna M, Maschke U. *Liq Cryst* 2000;27:413.
- [13] Gogibus N, Benmouna F, Ewen B, Pakula T, Coqueret X, Benmouna M, Maschke U. *J Polym Sci, Part B: Polym Phys* 2003;41:39.
- [14] Nwabunma D, Chiu HW, Kyu T. *Macromolecules* 2000;33:1416.
- [15] Nwabunma D, Kyu T. *Macromolecules* 1999;32:664.
- [16] Bedjaoui L, Bouchaour T, Benmouna M, Coqueret X, Maschke U. *Mol Cryst Liq Cryst* 2004;411:537.
- [17] Gogibus N, Maschke U, Benmouna F, Ewen B, Coqueret X, Benmouna M. *J Polym Sci, Part B: Polym Phys* 2001;39:581.
- [18] Gogibus N, Maschke U, Benmouna F, Ewen B, Coqueret X, Benmouna M. *Eur Polym J* 2001;37:1079.