

Equilibrium phase diagram of poly(2-phenoxyethylacrylate) and 5CB

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Abstract

The equilibrium phase diagram of mixtures of linear poly(2-phenoxyethylacrylate) of molecular weight $M_w = 181\,000$ g/mol, and the low molecular weight liquid crystal 4-cyano-4'-*n*-pentyl-biphenyl known as 5CB has been established using polarized optical microscopy and differential scanning calorimetry (DSC). The diagram exhibits an upper critical solution temperature and three main transitions: crystalline + isotropic (C + I) to nematic + isotropic (N + I), (N + I) to isotropic + isotropic (I + I), and (I + I) to isotropic (I). The (C + I) to (N + I) transition is observed by DSC, while the (N + I) to (I + I) transition is detected by optical microscopy and DSC, and the (I + I) to (I) transition only by optical microscopy. The results were successfully analyzed within a theoretical model combining the Flory–Huggins lattice theory for isotropic mixing and the Maier–Saupe theory of nematic ordering. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In recent years, the phase properties of mixtures of liquid crystals (LCs) and polymers have received a considerable attention from the fundamental point of view, due to its important applications [1,2]. For example, Polymer Dispersed Liquid Crystals (PDLCs) are systems used for display technology and light control devices like optical shutters [3–10]. Films made of PDLC can be switched electrically from a light scattering off-state to a highly transparent on-state. They consist generally of micron-sized droplets of low molecular weight LC (LMWLC) dispersed in a solid polymer matrix.

From the fundamental point of view, these systems are interesting as multi-component mixtures, where the individual species may have quite different thermodynamic properties. Mixing LC molecules with various ordered structures and a polymer matrix, gives rise to a variety of phase diagrams from which we can learn a lot on the state of matter and interaction between different species [11–14].

In this paper, the equilibrium phase diagram of poly(2-phenoxyethylacrylate) (PPEA) of molecular weight

$M_w = 181\,000$ g/mol and a LMWLC (4-cyano-4'-*n*-pentyl-biphenyl or 5CB) is obtained by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The pure LMWLC shows a crystalline phase below 23°C, a nematic phase between 23 and 35°C, and becomes isotropic above 35°C. Blends of PPEA and 5CB with various LC compositions were prepared by a combination of solvent induced and thermally induced phase separation processes [3,4]. The experimental phase diagram has been established using POM and DSC. The data are analyzed with a theoretical formalism based on a combination of the Flory–Huggins lattice theory for isotropic mixing [15] and the Maier–Saupe theory of nematic ordering [16,17].

2. Experimental

2.1. Materials

PPEA has been prepared by a radically induced polymerization technique using 2,2'-Azobisisobutyronitrile as the initiating species [18]. The polymer was purified and characterized by gel permeation chromatography (GPC) and DSC. The molecular weight and the molecular weight

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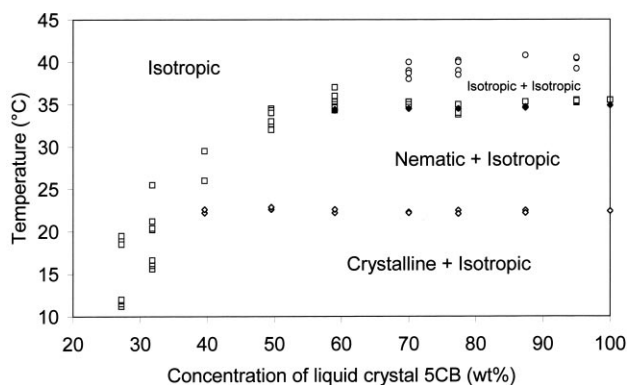


Fig. 1. Equilibrium phase diagram of poly(2-phenoxyethylacrylate) ($M_w = 181\,000$ g/mol)/5CB. The symbols in this diagram represent experimental data obtained by POM and DSC. The open squares (\square) represent microscopy data for the two series of samples of the same composition and indicate the transition from (N + I) to a region of coexisting isotropic phases, or from (N + I) to a single isotropic phase. The open circles (\circ) represent optical microscopy data for the same series of samples showing the transition from a region of two coexisting isotropic phases to a single isotropic phase. The open (\diamond) and filled (\blacklozenge) diamonds represent DSC data for the two series of samples.

distribution (M_w/M_n) were obtained by GPC calibrated with standard poly(styrene) samples. These measurements were performed in toluene at room temperature and led to an average $M_w = 181\,000$ g/mol and $M_w/M_n = 2.3$. The glass transition temperature of the pure polymer was obtained by DSC as $T_g = 10^\circ\text{C}$.

The LC 5CB was purchased from Merck Ltd (Poole, GB), showing crystalline, nematic and isotropic phases. 5CB presents in the pure state the following transition temperatures provided by the manufacturer: crystalline–nematic transition temperature $T_{CN} = 23^\circ\text{C}$, and nematic–isotropic transition temperature: $T_{NI} = 35.3^\circ\text{C}$ (values given by Merck Ltd, Merck House, Poole, Great Britain).

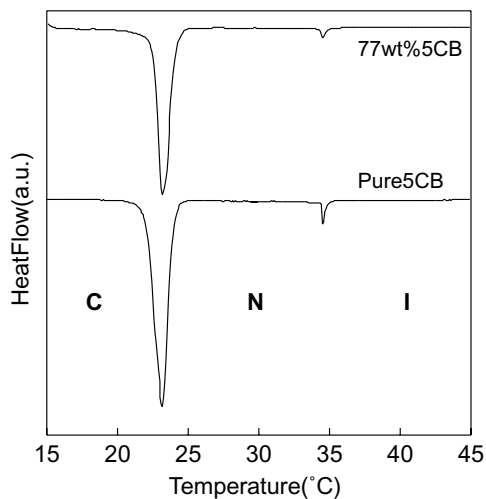


Fig. 2. Typical thermograms for the pure 5CB and a LC/polymer blend including 77 wt% 5CB as obtained by DSC. C, crystalline; N, nematic; and I, isotropic.

2.2. Sample preparation

The polymer and 5CB with different LC compositions were dissolved in a common organic solvent (tetrahydrofuran, THF) at a concentration of 50 wt%, at room temperature. The resulting mixture was stirred mechanically for 12 h. A small quantity of the mixture was cast on a clean glass slide, and the sample was dried at room temperature for two days. After complete evaporation of the THF, another glass slide was put on top of the first one. The same procedure was repeated to have two or more samples of the same composition, prepared independently, to check for reproducibility of the results.

Samples with pure components have been prepared in a similar way as the polymer/LC blends. The phase behavior was the same compared to the case of samples prepared without THF.

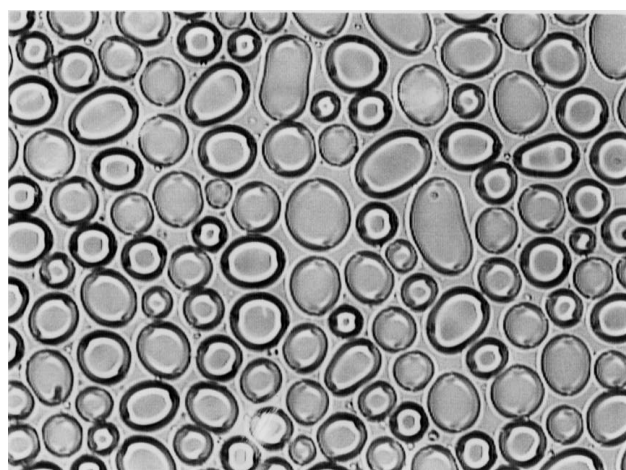
For the DSC measurements, the samples were prepared by introducing approximately 3 mg of the initial mixture into the aluminum pans, prior to solvent evaporation.

2.3. DSC measurements

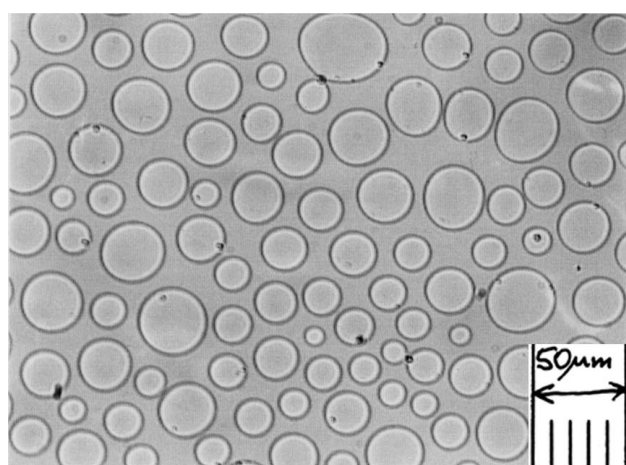
DSC measurements were performed on an apparatus of the type SEIKO DSC 220 C equipped with a liquid nitrogen system. The apparatus cell was purged with nitrogen at a rate of 50 ml/min. The same heating–cooling ramps were used as for the microscopy measurements in the temperature range spanning $-100/+100^\circ\text{C}$. Data were recorded systematically on the second heating ramp.

2.4. POM measurements

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. All samples underwent the same treatment. They were heated at three different rates of 2, 1, and $0.5^\circ\text{C}/\text{min}$ from room temperature, to 15 degrees above the transition temperature leading to the isotropic phase. Samples were kept for approximately 5 min in the isotropic state. Then, the samples corresponding to 50 wt% 5CB or higher were cooled to room temperature, at the rates indicated previously. For samples with a low concentration of LC, the same ramps were applied but cooling was performed at $T = 10^\circ\text{C}$ to allow the phase separation and the formation of ordered regions if a LC phase exists. This procedure is followed after 5 min by a heating ramp, at different rates. Transition temperatures were recorded during the heating ramp. Micrographs were taken by means of a videocamera (JVC TK-1070E) and printed on high-density paper to record the textures, choosing several regions of the sample (border and centre).



(a)



(b)

Fig. 3. Micrographs taken by POM from poly(2-phenoxyethylacrylate) ($M_w = 181\,000\text{ g/mol}$)/ 5CB at 70 wt% of LC and a temperature of: (a) $T = 32^\circ\text{C}$ corresponding to the (N + I) biphasic region. This micrograph shows clearly the nematic region in the form of droplets; (b) $T = 37^\circ\text{C}$ showing a typical texture of the (I + I) miscibility gap.

3. Results and discussions

3.1. Transition temperature data

Fig. 1 shows the phase diagram of the analyzed PPEA/5CB system. The symbols represent the transition temperatures versus LC concentration as obtained by POM and DSC for the two series of samples, of equal composition. Four distinct regions are clearly identified in this diagram. In the upper region, a single phase is obtained, where the polymer and LC form an isotropic solution. The phase diagram shows three biphasic regions below the coexisting curve: crystalline + isotropic (C + I), nematic + isotropic (N + I), and isotropic + isotropic (I + I). It is clear that on the axis corresponding to a LC concentration of 100 wt%, below $T_{CN} \approx 23^\circ\text{C}$ one has a pure LC in the crystalline state; between $T = 23^\circ\text{C}$ and approximately $T = 35^\circ\text{C}$ there is pure LC in the nematic order. The

(C + I) to (N + I) and (C + I) to (I) transitions were observed by DSC, while the (N + I) to (I + I) and (N + I) to (I) transitions were detected by DSC and optical microscopy. Typical thermograms are given in Fig. 2 for the pure 5CB and one polymer/LC blend with 77 wt% 5CB. The thermograms of the two samples show distinctly the transitions from crystalline to nematic and from nematic to isotropic regions. The (I + I) to (I) transition was revealed only by POM. We shall consider the three main transitions separately.

3.2. Crystalline–nematic transition

The open diamonds in Fig. 1 represent DSC data for two series of samples of the same composition, and indicate the transition from the crystalline phase below about $T = 23^\circ\text{C}$ to a nematic phase above this temperature. One can see a complete agreement between the two series of samples from separate experiments. In the range of LC compositions above 40 wt% the (C + I) to (N + I) transition temperature is almost constant at about $T = 23^\circ\text{C}$, which corresponds approximately to the crystalline–nematic transition of 5CB. This observation indicates that the nematic phase is a pure LC phase.

3.3. Nematic–isotropic transition

The open squares in Fig. 1 represent microscopy data for the two series of samples of the same composition and indicate the transition from (N + I) to an (I + I) or an (I) phase. The filled diamonds represent DSC data for the same series of samples. Here again, a good agreement exists between the two techniques. Typical DSC thermograms are shown in Fig. 2. The optical micrographs in Figs. 3a and b were taken at 70 wt% of 5CB exhibiting different textures. In Fig. 3a, the texture corresponding to a temperature of $T = 32^\circ\text{C}$ clearly shows nematic domains in the form of droplets having a relatively narrow distribution with an approximate mean diameter of $30\ \mu\text{m}$. Fig. 3b, which corresponds to the same composition and the temperature of 37°C , exhibits two isotropic phases in equilibrium.

The above mentioned two transition lines ((C + I)–(N + I) and (N + I)–(I + I)) seem to be parallel to each other and follow the same trends below and above 60 wt% of 5CB.

3.4. Isotropic–isotropic transition

The open circles in Fig. 1 represent optical microscopy data for the same series of samples showing the transition from a region of two coexisting isotropic phases to a single isotropic phase. For some duplicate samples one observes a slight difference, which is due to the difficulty to capture exactly the temperature at which the two phases merge together to form a single isotropic phase. This figure shows a typical UCST (Upper Critical Solution

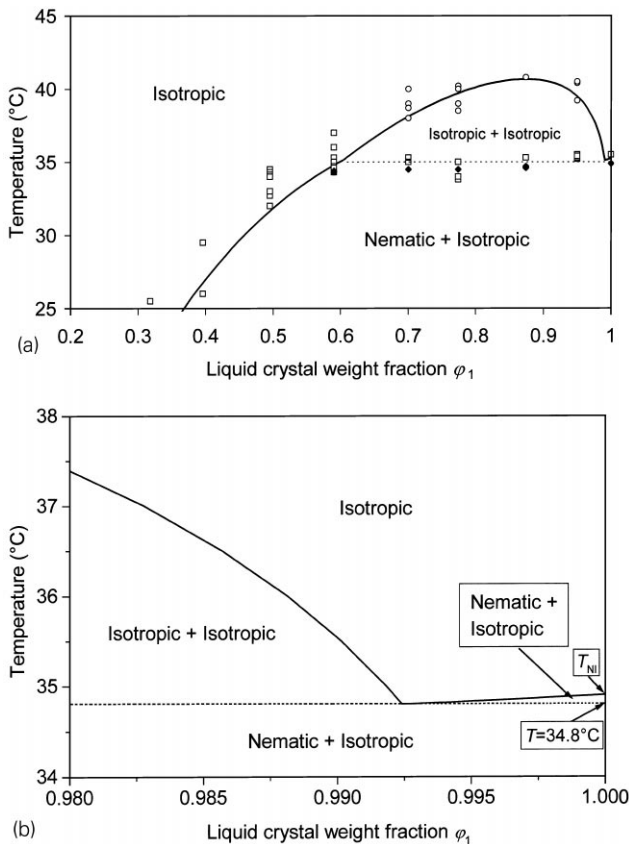


Fig. 4. (a) Theoretical (solid curve) and experimental (symbols) results representing the equilibrium phase diagram of poly(2-phenoxyethylacrylate)/5CB mixtures. The calculated curve corresponds to $N_1 = 1$, $N_2 = 48$, $\chi = -4.16 + 1511/T$ and $T_{NI} = 35^\circ\text{C}$. (b) An amplified view of the calculated curve in the vicinity of $\varphi = 1$.

Temperature) phase diagram. It is worth noting that the DSC thermograms did not exhibit the (I + I)/(I) transition.

3.5. Theoretical interpretation

A theoretical interpretation of these data is possible using models developed by various authors [11–14,19–23]. One of these models, which turns out to be very useful in describing the phase behavior of mixtures of linear polymers and LMWLC, is based on a combination of the Flory–Huggins [15] lattice model for isotropic mixing and the Maier–Saupe [16,17] theory of nematic order. In recent years, this theory has been used by many authors [11–14,19–23] to describe the phase properties of various systems. In particular, Kyu and coworkers [13] used it to describe successfully the phase diagrams of PMMA/E7, while some of the present authors reported a detailed experimental and theoretical investigation of PS/8CB [24,25] and other systems such as poly(*n*-butylacrylate) and E7 mixtures [26]. Therefore, it would be interesting to check whether this formalism can describe the present data involving blends of PPEA and 5CB. However, it should be pointed out that it is possible to calculate the miscibility limit only in the composition and

temperature range, where the system is isotropic or exhibits a nematic order either in two coexisting phases or in a single phase. The region below 23°C where the crystalline phase emerges is beyond the range of the modeling. This is the reason why we limit the theoretical binodal represented by the solid line of Fig. 4a to the range of temperature above 25°C and composition above 30 wt% 5CB. The detailed description of the formalism can be found in various references [11–14,19–26]. We limit ourselves to a brief outline of the method, which is based on a numerical resolution of the set of equations describing equalities of the chemical potentials of polymer and LC in coexisting phases. The starting point consists of writing the free energy as a sum of an isotropic and a nematic contribution indicated by the superscripts *i* and *n*, respectively

$$\frac{\Delta f^{(i)}}{k_B T} = \frac{\Delta F^{(i)}}{n_0 k_B T} = \frac{\varphi_1}{N_1} \ln \varphi_1 + \frac{\varphi_2}{N_2} \ln \varphi_2 + \chi \varphi_1 \varphi_2 \quad (1)$$

$$\frac{\Delta f^{(n)}}{k_B T} = \frac{\Delta F^{(n)}}{n_0 k_B T} = \frac{\varphi_1}{N_1} \left[-\ln Z + \frac{1}{2} \nu \varphi_1 S^2 \right] \quad (2)$$

where φ_1 and φ_2 are the volume fractions of LC and polymer, respectively. Assuming incompressibility and equality of molar volumes of species 1 and 2, one has $\varphi_1 = 1 - \varphi_2$. k_B represents the Boltzmann constant, T is the absolute temperature, and n_0 is the total number of molecules in the mixture. ΔF represents the change in free energy and Δf is the corresponding change in free energy density. The LMWLC has a single repeat unit $N_1 = 1$ while N_2 , the number of polymer repeat units is much larger than 1. The Flory–Huggins interaction parameter χ is function of temperature following $\chi = A + B/T$, A and B being numerical constants. Z is the nematic partition function, S is the order parameter and $\nu = 4.54 T_{NI}/T$ [2]. In a region where two phases (α) and (β) coexist, their compositions are calculated by solving numerically the set of equations

$$\Delta \mu_1^{(\alpha)} = \Delta \mu_1^{(\beta)} \quad (3)$$

$$\Delta \mu_2^{(\alpha)} = \Delta \mu_2^{(\beta)} \quad (4)$$

where $\Delta \mu_i^{(\alpha)}$ represents the chemical potential of constituent *i* in the phase (α). Using Eqs. 1 and 2 yields [11–14,19]

$$\frac{\Delta \mu_1}{k_B T} = \ln \varphi_1 + \left(1 - \frac{N_1}{N_2}\right) \varphi_2 + \chi N_1 \varphi_2^2 - \ln Z + \frac{\nu \varphi_1^2 S^2}{2} \quad (5)$$

$$\frac{\Delta \mu_2}{k_B T} = \ln \varphi_2 + \left(1 - \frac{N_2}{N_1}\right) \varphi_1 + \chi N_2 \varphi_1^2 + \frac{N_2}{N_1} \frac{\nu \varphi_1^2 S^2}{2} \quad (6)$$

The first three terms on the right-hand side of Eqs. (5) and (6) are isotropic contributions while the others are due to the nematic free energy. The first one estimates the number of repeat units N_2 from the experimental critical volume fraction $\varphi_c = 0.87$. Using the relationship $\varphi_c = (\sqrt{N_2}/(\sqrt{N_1} + \sqrt{N_2}))$ a value of $N_2 = 48$ was found. The true value of N_2 is

certainly higher than 48. This is probably due to an uncertainty in determining the critical volume fraction at the “zero approximation” assumption used in the Flory–Huggins model. Slightly higher φ_c values will immediately yield much higher N_2 values in this range of LC composition. The critical parameter χ_c can be related to N_1 and N_2 following

$$\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}} \right)^2$$

Recalling that $\chi_c = A + B/T_c$ and knowing $T_c = 40.7^\circ\text{C}$ yields $B = (\chi_c - A)T_c$. Within this procedure, one is left with a single unknown parameter A , which is determined via a best fit of data to the calculated curve. One obtains $A = -4.16$ or $\chi = -4.16 + 1511/T$, a result independent of blend composition. A similar procedure was used previously by Kyu et al. [11–14] and by us [24,25]. The results are illustrated in Fig. 4a, where the solid line represents the calculated curve while the symbols are experimental data. This figure is limited to the (T, φ_1) region where the calculation can be made within the present model. An amplified view in the vicinity of $\varphi_1 = 1$ is given in Fig. 4b to visualize the details of the phase diagram in this region. A numerical resolution of the set of Eqs. (3) and (4) using the full expression of chemical potentials in Eqs. (5) and (6) shows that below the temperature of the triple point (34.5°C), the volume fraction of 5CB in phase (β) is $\varphi_1^{(\beta)} = 1$, which means that (β) is a pure LC phase. Interestingly, the theoretical diagram does not exhibit a single nematic phase as shown by analogous systems with a low molecular weight polymer [11,19].

4. Conclusions

The equilibrium phase diagram of mixtures of PPEA and 5CB was established by POM and DSC measurements. The diagram exhibits an UCST and four distinct regions. Below $T = 23^\circ\text{C}$ for LC compositions above 30 wt%, a region where a pure crystalline 5CB phase coexists with an isotropic phase is observed. Between $T = 23^\circ\text{C}$ and $T = 35^\circ\text{C}$, at compositions roughly above 40 wt% LC two phases, one isotropic and the other nematic, are in equilibrium. Textures obtained under the microscope and the evolution of DSC thermograms give a clear evidence of these coexisting phases. Above this region, the phase diagram reveals a region where two liquid isotropic phases coexist. The glass transition temperature is below the range of temperatures shown in this diagram but seems to interfere only slightly at temperatures below 10°C .

The experimental results are analyzed using the theoretical framework based upon the Flory–Huggins and the Maier–Saupe theories. A very good agreement was found

between the theoretical predictions and the experimental data.

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