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Calorimetric studies of poly(2-phenoxyethylacrylate)/5CB mixtures

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The thermophysical properties of mixtures of poly(2-phenoxyethylacrylate) and 4-cyano-4′-pentyl-biphenyl, 5CB, are investigated using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The polymer has a molar mass $M_w = 181\,000\ \mathrm{g\ mol^{-1}}$; the low molecular mass liquid crystal exhibits a nematic to isotropic transition at 35.3°C and crystallizes below 23°C. The phase diagram exhibits miscibility gaps in certain regions of temperature and composition where coexisting nematic and isotropic phases are found. From a practical point of view when considering the electro-optical applications of these systems, it proves to be useful to know precisely the amount of small liquid crystal molecules dissolved in the polymer matrix and the concentration of polymer in the nematic phase. The former quantity has a mechanical impact due to a plasticizing effect, an optical impact since it changes the polymer refractive index, while the polymer in the nematic phase shifts the transition temperatures influencing the electro-optical response of the liquid crystal. The present work addresses these important aspects using POM and DSC.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) are heterogeneous mixtures generally consisting of micron-sized ordered domains dispersed in a solid polymer matrix. These composite materials can be switched electrically from an off-state (i.e. no electric field) highly scattering film to an on-state (i.e. by applying an external field) transparent film [1–5]. Investigation of the phase behaviour and thermophysical properties of these materials provided details of the important parameters influencing the electro-optical response and film performance under practical conditions. This was rightly pointed out by Russel *et al.* [6] who reported a detailed thermal characterization of PDLCs by differential scanning calorimetry (DSC). They used commercial polymers and 5CB to quantify the degree of phase separation using both the melting and clearing enthalpies of the liquid crystal. The present study is of a similar nature but instead of commercial polymers, for which the complete formulation is in principle not known, we use here a chemically well defined system involving poly(2-phenoxyethylacrylate), PPEA, of molecular mass $M_w = 181\,000\ \mathrm{g\ mol^{-1}}$ and 5CB. Furthermore, this investigation is part of a recent series of studies of the physical properties of systems involving a large variety of polymers and liquid crystals (LCs) [7–11].

The phase diagram established using polarizing optical microscopy (POM) and DSC exhibits two coexisting phases, one isotropic polymer-rich phase and another nematic liquid crystal-rich phase. From the practical point of view, it is important to know precisely the composition of the two phases in equilibrium. In particular, the amount of LC dissolved in the polymer-rich phase may lead to a drastic reduction of the glass transition temperature and hence reduce its mechanical strength. In addition, the polymer refractive index may change with unfavourable consequences for the optical and electro-optical responses of the material. The presence of polymer within the LC-rich phase can change the

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extent of order shown by the LC and shift its transition temperature. In view of the importance of these problems, an attempt is made here to address these issues using a model system consisting of linear polymers having a known chemical structure and molecular mass and a single component low molecular mass LC whose transition temperatures are accurately known.

2. Experimental

2.1. *Materials*

Poly(2-phenoxyethylacrylate) (PPEA) was prepared by radically induced polymerization using 2,2′-azo-bis-isobutyronitrile as the initiating species. The polymer was purified and characterized by gel permeation chromatography (GPC) and DSC. The molecular masses, M_w and M_n, and polydispersity (M_w/M_n) were obtained by GPC calibrated with standard poly(styrene) samples. These measurements were performed in toluene at room temperature, to give $M_w = 181\ 000\ \mathrm{g\ mol^{-1}}$ and $M_w/M_n = 2.3$. The low molecular mass LC, 5CB, was purchased from Merck Eurolab GmbH (Darmstadt, Germany), and exhibits crystalline, nematic and isotropic phases. 5CB as provided by the manufacturer shows the transition temperatures: crystal–nematic $T_{CrN} = 23°C$, and nematic–isotropic $T_{NI} = 35.3°C$.

2.2. *Sample preparation*

Mixtures of polymer and 5CB with different LC concentrations 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 and a small quantity was either cast on a clean glass slide or introduced into aluminum DSC pans (3 mg) prior to solvent evaporation. The samples were dried at room temperature for two days. After complete evaporation of THF, POM samples were prepared by placing another glass slide on top of the first one; DSC samples were sealed to avoid LC evaporation during the experiment. A combination of solvent induced phase separation (SIPS) and thermally induced phase separation (TIPS) processes was used in the elaboration of the films prepared for DSC and POM measurements. The same procedure was repeated at least twice to produce samples notionally having the same composition, to check the reproducibility of the results. Samples containing just the pure components were prepared in a similar way and the phase behaviour was not sensitive to the presence of THF.

2.3. *Polarizing optical microscopy measurements*

Thermo-optical data were obtained on a Jenapol microscope equipped with a Linkam THMS 600 heating/cooling stage and a Linkam TMS 92 temperature control unit. The same procedure was applied to all samples. Three different heating rates were selected: 2, 1 and 0.5°C min^{-1}. The samples were heated from room temperature to 15 degrees above the clearing temperature and held for approximately 5 min. For systems containing 50 wt % 5CB or greater, a cooling step was used to bring them to room temperature at the same rate. For systems with a lower concentration of LC, cooling to $T = 10°C$ was applied to allow phase separation and the emergence of ordered regions. This procedure was followed after 5 min by a heating ramp at different rates. Transition temperatures were recorded during this heating ramp.

2.4. *DSC measurements*

DSC measurements were performed on a Seiko DSC 220C instrument equipped with a liquid nitrogen system. The cell was purged with nitrogen at a rate of 50 ml min^{-1}. The same heating–cooling ramp was used for DSC and POM measurements in the temperature range −100 to 100°C. Data were recorded systematically on the second heating ramp. The polymer glass transition temperature was determined from the midpoint of the transition range. Enthalpy changes associated with the crystalline–nematic (ΔH_{CrN}) and nematic–isotropic (ΔH_{NI}) transitions are expressed as J g^{-1}, with an uncertainty of about 5% [12].

3. Results and discussion

The phase diagram of the PPEA/5CB system is given in figure 1 with data obtained by DSC and POM [7]. Transitions to the single isotropic phase have small

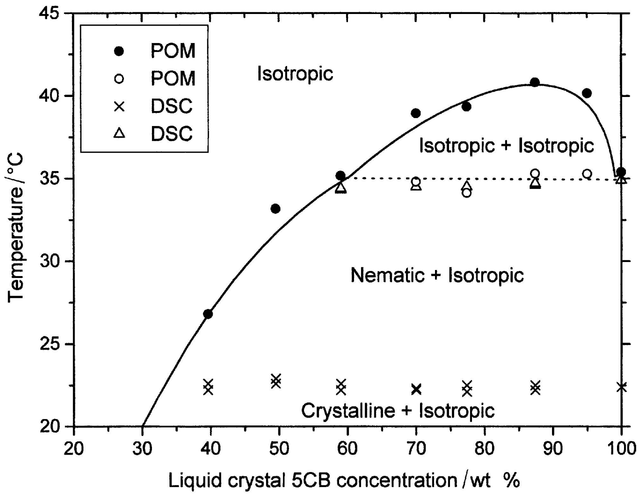

Figure 1. The phase diagram for poly(2-phenoxyethylacrylate) ($M_w = 181\ 000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 2.3$)/4-cyano-4′-*n*-pentylbiphenyl (5CB). The symbols represent experimental data while the solid line is the curve calculated using the procedure described elsewhere [7].

associated enthalpy changes which could not be detected by DSC. In such a situation, POM proves to be a valuable complementary tool with which to complete the phase diagram. The PPEA/5CB phase diagram contains two miscibility gaps. In the lower part, there is a nematic + isotropic (N + I) region in which a polymer-rich phase coexists with an almost pure LC phase. The polymer matrix dissolves a quantity of isotropic LC ranging from almost 40 to 60 wt % over the range of temperatures considered (25 to 35°C). The polymer solution coexists with a pure LC nematic phase. In the upper part of the diagram, one finds an isotropic + isotropic (I + I) miscibility gap indicating the strong interactions between the like molecular species even at temperatures exceeding the nematic–isotropic transition of the pure LC. The solid line is the binodal and has been calculated using the usual procedure of equal chemical potentials in coexisting phases [7]. This calculation is based on a free energy model given by the sum of the Flory–Huggins [13] free energy for isotropic mixing and the Maier–Saupe [14, 15] free energy of nematic order. More details on the computational procedure are given elsewhere [7–11].

The small LC molecules dissolved in the polymer matrix act as a plasticizer and substantially reduce its mechanical moduli. They also cause a shift away from the polymer's refractive index and the ordinary component of the LC refractive index being matched. This matching represents an important condition for a good quality electro-optical response of the material. This information can be deduced from DSC thermograms. Figure 2(*a*) shows DSC thermograms of 5CB (upper curve) and PPEA (lower curve) quenched at a rate of -30°C/min. The polymer shows single transition (glass transition T_{gP}) at 10°C whereas the low molecular weight LC exhibits 4 transitions: A glass transition at $T_{gLC} = -62$°C followed by a cold crystallization process at around -30°C, a melting transition at 23°C, and a nematic–isotropic transition at 35°C. Above this temperature, 5CB behaves as a simple isotropic liquid. Figure 2(*b*) shows thermograms of the PPEA/5CB blends having several compositions spanning the range from 39.6 wt % 5CB to pure LC. Interestingly, the transitions characteristic of the polymer and the LC do not overlap. T_{gLC} and the clearing temperature of the LC phase remain essentially the same as those of the bulk LC, confirming the phase diagram in which the phase separated LC does not contain polymer impurities.

Figure 3 shows the dependence of the glass transition temperatures on composition. The upper part shows that T_{gP} drops from 10°C (pure PPEA) to -15°C upon adding 20 wt % 5CB. Above this LC concentration, T_{gP} remains essentially constant due to the limit of the solubility of 5CB in the polymer. The drop of T_{gP} is a direct consequence of the plasticizing effect due to the small molecules dissolved in the polymer.

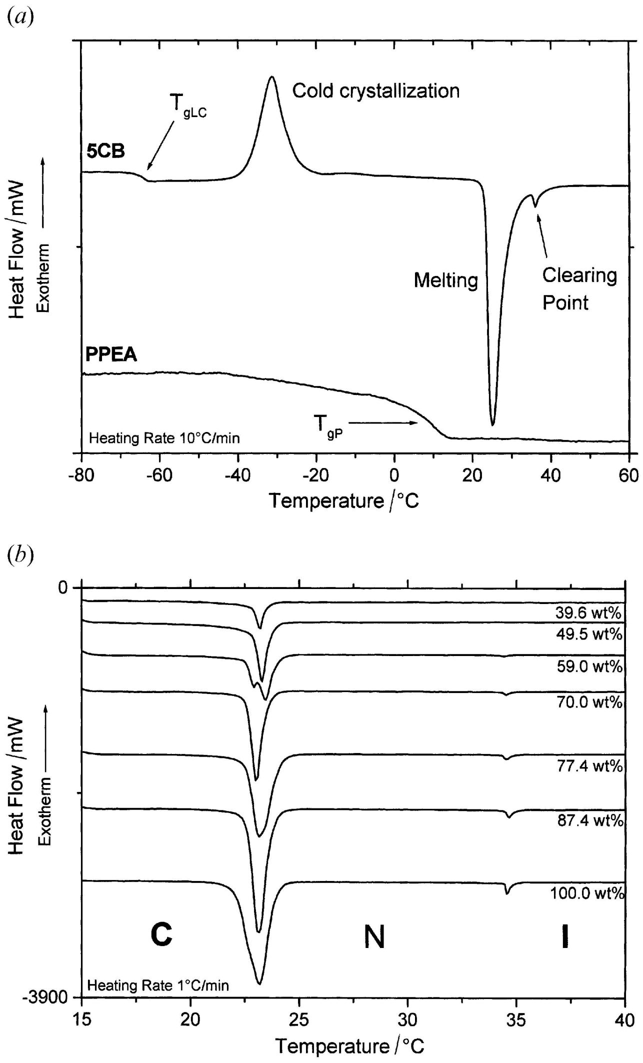

Figure 2. (*a*) DSC thermograms of 5CB (upper curve) and bulk PPEA (lower curve); (*b*) DSC thermograms of the PPEA/5CB system at LC concentrations varying from 39.6 to 100 wt %.

The lower part of figure 3 shows that T_{gLC} decreases by only a few degrees in the presence of polymer and is essentially T_{gLC} of the phase separated LC within the droplets. Below 40 wt % 5CB it was not possible to observe this glass transition due to the absence of phase separated LC domains. Above 40 wt % 5CB, a slight increase in T_{gLC} is found. A plateau is reached at 70 wt % corresponding to T_{gLC} of pure LC. This confirms that the LC phase in the (N + I) domain contains no trace of polymer and exhibits similar properties as the bulk LC. A broadening of the glass transition and associated data scattering are probably due to polymer polydispersity.

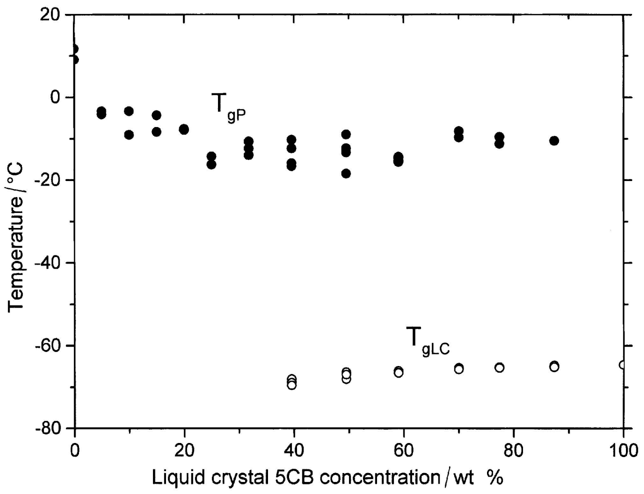

Figure 3. The glass transition temperatures T_{gP} of PPEA (closed circles) and T_{gLC} of 5CB (open circles) versus LC concentration.

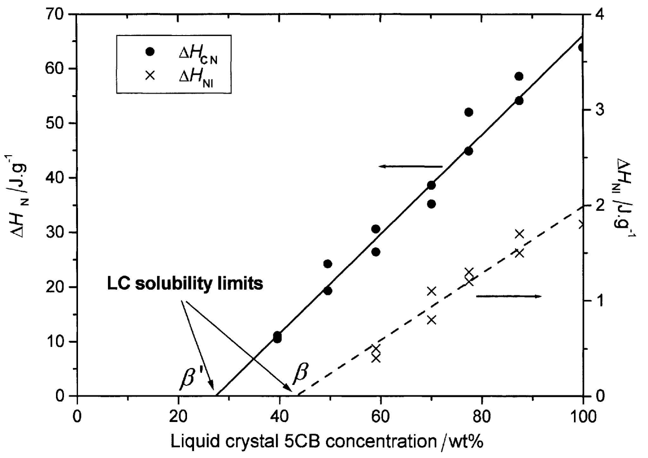

Figure 4. Variation of ΔH_{NI} (×, vertical axis on the right) and ΔH_{CrN} (●, vertical axis on the left) versus LC concentration for the PPEA/5CB system. The intercepts with the horizontal axis yield the solubility limits β and β'.

Other relevant parameters in the present analysis are the solubility limit of LC in the polymer denoted β and the amount of LC in the nematic droplets. In the crystalline state, the latter quantity is denoted α' and in the nematic state is called α. These parameters are deduced from the enthalpy changes ΔH_{CrN} and ΔH_{NI} at the crystalline–nematic and nematic–isotropic transition temperatures, respectively. δ is the ratio of enthalpy change at the nematic–isotropic transition for the polymer/LC mixture and that for the bulk LC (φ_{LC}=LC concentration):

$$\delta = \Delta H_{NI}(\varphi_{LC})/\Delta H_{NI}(\varphi_{LC}=1) \tag{1}$$

and δ' the corresponding ratio involving $\Delta H_{CrN}(\varphi_{LC})$

$$\delta' = \Delta H_{CrN}(\varphi_{LC})/\Delta H_{CrN}(\varphi_{LC}=1). \tag{2}$$

By using the rule of inverse segments in the phase diagram, one finds the following relationship between δ and the solubility limit β [8, 11, 16]

$$\delta = (\varphi_{LC}-\beta)/(1-\beta). \tag{3}$$

This result assumes that the LC within the droplets and in the bulk have the same thermophysical properties and that the amount of LC dissolved in the polymer remains constant for $\varphi_{LC} \geqslant \beta$. In addition, it assumes that the nematic–isotropic transition temperature is unaffected by the presence of polymer. A similar expression can be written relating δ' and β' and replacing ΔH_{NI} by ΔH_{CrN}. In view of the particular importance of the variation of ΔH_{NI} and ΔH_{CrN} with φ_{LC} we consider these plots in figure 4. ΔH_{CrN} is the enthalpy change at the crystalline to nematic transition and is larger than ΔH_{NI} over the whole range of φ_{LC}. The solubility limit β is deduced from ΔH_{NI} by a linear regression of the data. At the intercept with the horizontal axis, one obtains $\beta = 0.44$ from ΔH_{NI} and $\beta' = 0.27$ from ΔH_{CrN}.

The parameters α and α' are obtained from [8, 11, 16]

$$\alpha = m^{D}_{LC}/m_{LC} = \delta/\varphi_{LC} \quad \alpha' = \delta'/\varphi_{LC} \tag{4}$$

where m^{D}_{LC} and m_{LC} represent the masses of LC in the droplets and in the whole sample, respectively.

Figure 5 shows the plots of α and α' versus φ_{LC}. At the miscibility limit, φ_{LC} is equal to β and both α and α' are zero. When φ_{LC} increases, the α' values also increase rapidly but tend to level off at φ_{LC} above 80 wt %, since the fraction of LC in the droplets approaches 100%. The continuous curve is calculated using $\beta' = 0.27$ whereas

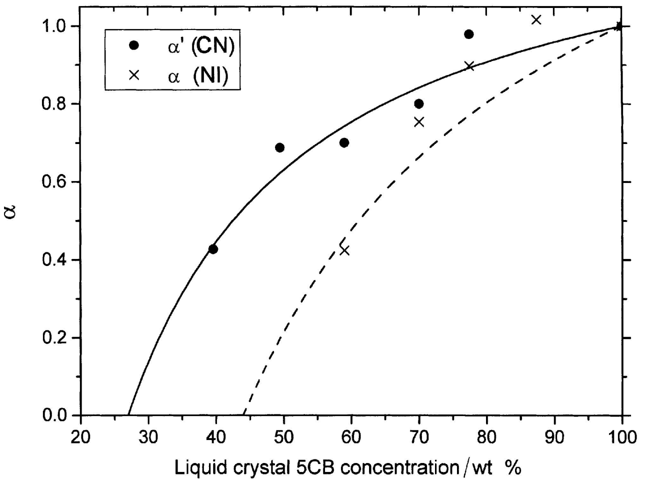

Figure 5. Variations of the amounts of LC dissolved in the polymer matrix, α and α', evaluated from ΔH_{CrN} (●) and ΔH_{NI} (×) versus LC composition. The solid and dashed lines represent the curves calculated from equation (4).

the dashed curve was obtained using $\beta = 0.44$. These calculations are in relatively good agreement with the experimental data.

4. Conclusion

Poly(2-phenoxyethylacrylate) of molecular mass $M_w = 181\,000\ \mathrm{g\,mol^{-1}}$ possesses a relatively high interaction parameter with 5CB. This is shown by DSC thermograms and complementary POM observations. Several results corroborate these findings. First the emergence of wide miscibility gaps, in particular the (I + I) region found above the nematic–isotropic transition temperature. The DSC thermograms reveal glass transition temperatures characteristic of two distinct phases, one polymer rich phase and the other, a practically pure LC phase. Furthermore, the amount of LC dissolved in the polymer, either in the crystalline phase (below 23°C) or in the molten stage (between 23 and 35.3°C), bears a strong impact on its thermophysical parameters. In the crystalline state, the solubility limit is lower than in the molten state. Similar observations were made by Russel *et al.* [6]. All these aspects have far-reaching consequences on the overall response of the polymer/LC composite material mainly in terms of its thermal stability, electro-optic applications, and mechanical resistance.

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