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Phase behaviour and morphology of polymer/liquid crystal blends

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The phase behaviour of blends of poly(ethylene oxide) (PEO) with the liquid crystal *p*-azoxyanisole (PAA) has been studied by differential scanning calorimetry and optical microscopy. This system exhibits partial miscibility of the components in the molten state (at temperatures above 337 K). The melting temperature and enthalpy of the PAA phase has been found to depend on the blend composition, whereas the melting behaviour of the polymer phase remains quite unaltered. The occurrence of the PAA nematic phase, dispersed within an isotropic liquid phase, has been observed at high concentrations of liquid crystal. The morphology of the blends in the solid state changes largely with the PAA content, depending on the solubility of the components in the liquid phase.

1. Introduction

Blends of polymers with low molecular weight liquid crystals (LCs) constitute a class of materials whose properties are attracting great scientific and technological interest. These systems, depending on the miscibility of the components, may be tailored for a variety of uses in a broad composition and temperature range with many advantages with respect to the properties of the single components.

The addition of liquid crystals to thermoplastic polymers has been suggested to induce improvements in the mechanical properties of polymeric materials, due to the anisotropy of the LC mesophase under shear fields [1, 2]. The LC component can also act as a plasticizer for the polymer, reducing the glass transition temperature and the melt viscosity of the blend and, thus, enhancing its processability [2–4]. On the other hand, liquid crystals dispersed as microdroplets in a (non-interacting) polymer matrix, namely polymer dispersed liquid crystals (PDLCs), have been largely investigated in recent years as materials for electrooptic applications (optical displays, light valves, sensors, etc.) [5, 6].

In general, the phase behaviour and the miscibility of polymer blends containing LC components has been found to depend on chemical structure, mesophase behaviour and concentration of the components [7]. In some cases, the presence of biphasic regions consisting of a nematic phase and an isotropic phase has been observed at low polymer contents on cooling from the isotropic melt [8].

In this respect, we examined blends of comb-shaped polymers (having paraffinic or mesogenic side groups) with some smectic and nematic LCs in order to study the effect of composition and molecular structure on the morphology and phase transitions of the components [9, 10]. In the present paper, we report a calorimetric and microscopic study of the phase behaviour of blends of poly(ethylene oxide) (PEO) with the nematic LC, *p*-azoxyanisole (PAA).

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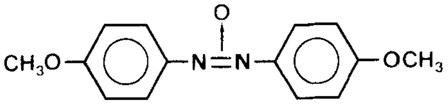
2. Experimental

Poly(ethylene oxide) is a commercial polymer (Fluka AG) having a nominal $M_w = 20000$; *p*-azoxyanisole



is a commercial product (Hoechst, Germany) with a nematic phase in the range 393–409 K. All materials were used as received.

PEO/PAA blends, with compositions from 0 to 100 wt% of PAA, were obtained by mechanical mixing of the finely powdered components followed by melting at 430 K. For comparison, blends were also prepared by dissolving weighted quantities of the pure components in chloroform and then evaporating the solvent under vacuum. Samples obtained by this procedure showed in some cases a non-homogeneous composition.

The thermal analysis of the blends was carried out with a Perkin–Elmer DSC-2C calorimeter equipped with Data Station 3600. The samples (4–6 mg) placed in DSC aluminium pans were first heated to 430 K (about 20 K above the nematic to isotropic transition of PAA) at a rate of $10\,\mathrm{K\,min^{-1}}$ under nitrogen flow, then cooled to 300 K using rates of 2·5, 5 and $10\,\mathrm{K\,min^{-1}}$ and reheated to 430 K at $10\,\mathrm{K\,min^{-1}}$ (second heating run). The melting behaviour of blends rapidly cooled (at a nominal rate of $320\,\mathrm{K\,min^{-1}}$) from the isotropic melt was also analysed. The phase transition temperatures were determined both at the onset and the maxima of the DSC peaks; the heats of transition were calculated from the area of the peaks by a standard software program (TADS).

The morphology of the blends was examined by a Leitz Ortholux polarizing optical microscope equipped with a Mettler FP52 hot stage and a Mettler FP5 control processor. To ensure the homogenization of the components, blend specimens obtained by cooling from the melt in the DSC were employed. The samples sandwiched between microscope slides were first melted in the hot stage to a temperature above 420 K, then cooled to room temperature at a controlled rate in the range 0·2–$10\,\mathrm{K\,min^{-1}}$ and again heated to the clearing temperature. The phase transition processes of the components were recorded by a JVC camera.

3. Results and discussion

3.1. *Differential scanning calorimetry*

The DSC thermograms of PEO/PAA blends and the pure components on the second heating run are presented in figure 1.

The PEO sample exibits a melting peak with a maximum at 337·4 K ($\Delta H_m = 166{\cdot}4\,\mathrm{J\,g^{-1}}$); pure PAA shows a sharp crystal (Form I) to nematic transition at 393 K ($\Delta H_m = 114{\cdot}1\,\mathrm{J\,g^{-1}}$) and a weak nematic to isotropic transition at 409 K ($\Delta H_i = 2{\cdot}9\,\mathrm{J\,g^{-1}}$). The measured LC phase transition parameters are in good agreement with those reported by Martire and others [11]. A further endothermic peak was observed at about 379 K for PAA samples rapidly cooled from the melt and it was referred to the melting of Form II crystals [11]. These are formed on cooling from the nematic phase and transform to Form I crystals at a temperature near 335 K. In the blends, as shown in figure 1, the melting behaviour of the polymer is almost unaffected by the composition, whereas the melting of PAA appears as a broad transition whose maximum decreases on increasing the PEO fraction. For PAA contents < 20 wt%, no

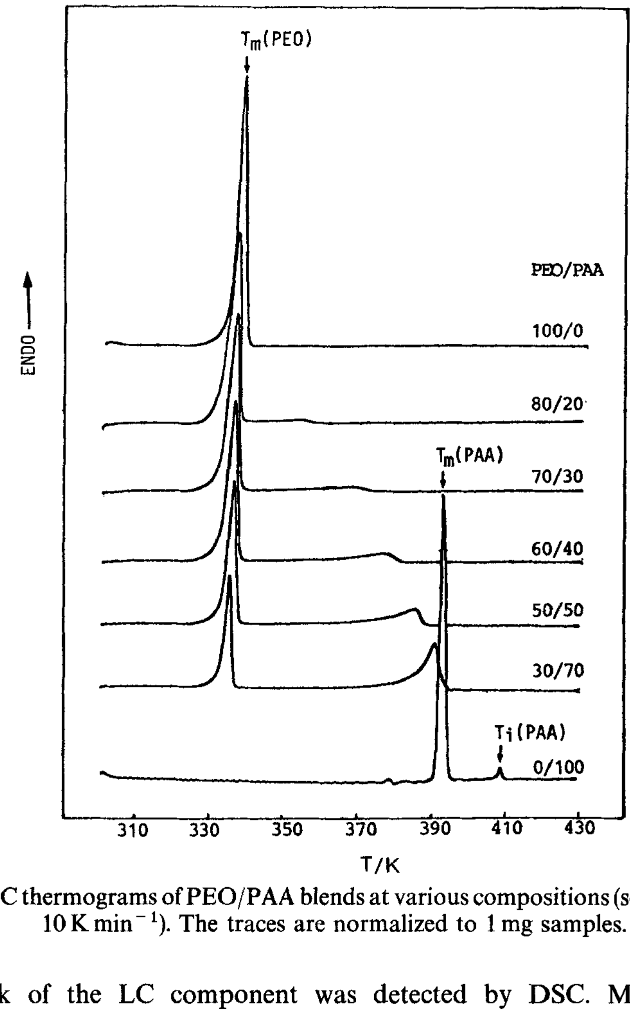


Figure 1. DSC thermograms of PEO/PAA blends at various compositions (second heating run, 10 K min^{-1}). The traces are normalized to 1 mg samples.

melting peak of the LC component was detected by DSC. Moroever, in the composition range 20–80 per cent of PAA, the DSC endotherms of the blends do not show any peak relevant to the nematic–isotropic transition of the LC phase. This behaviour has been confirmed by microscopic analysis, as discussed later. The values of the melting temperatures, determined both at the onset (T_{ons}) and the maxima (T_m) of the DSC peaks, and the nematic to isotropic transition temperatures T_i of the blend components are reported in figure 2 as a function of the LC content.

The melting temperature of the polymer in the blends changes slightly with the PAA content. This fact suggests that the liquid crystal is almost immiscible with the crystalline polymer phase below the melting point of PEO. By contrast, as the concentration of the LC component decreases to about 20 per cent, the melting temperature of PAA is depressed from 393 K (for the pure component) to *c*. 354 K, with a large broadening of the melting range. This trend does not depend on the thermal history of the samples; however, even if the melting behaviour of the blends is not affected to a large degree by the DSC heating rate, it must be noticed that kinetic effects determined by the sample morphology and/or by heat transfer limitations could influence the phase transition processes.

In figure 3, the values of the experimental melting enthalpy (ΔH_m) of PEO and PAA in the blends are plotted versus the PAA content.

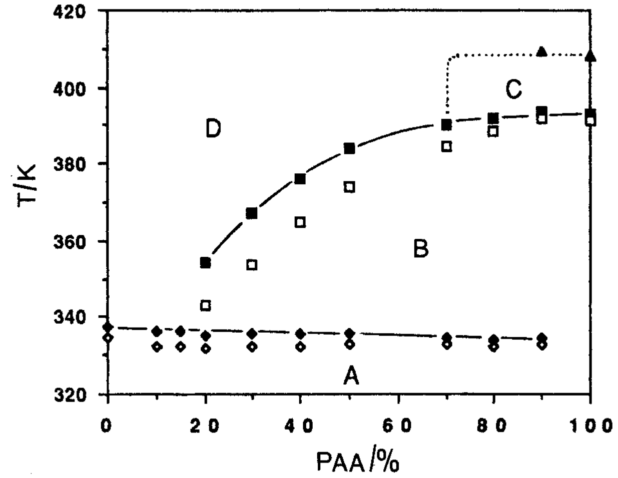


Figure 2. DSC transition temperatures of PEO/PAA blends as a function of PAA content. (◇): T_{ons} of PEO; (◆): T_m of PEO; (□): T_{ons} of PAA; (■): T_m of PAA; (▲): T_i of PAA. The dotted line indicates the nematic to isotropic transition temperature of the LC phase, as determined by optical microscopy.

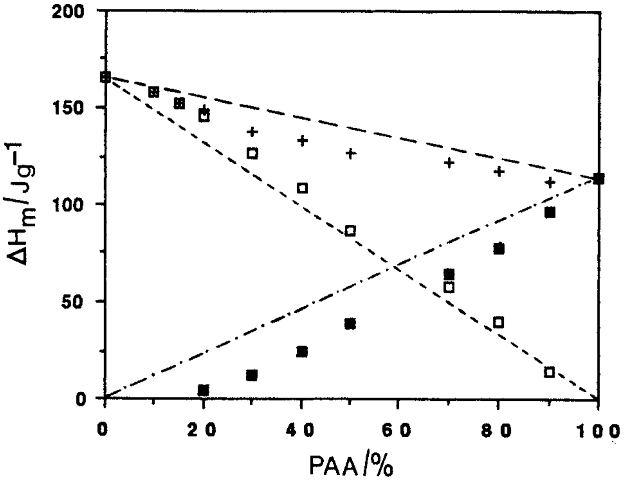


Figure 3. Melting enthalpy, ΔH_m (per gram of blend), of (□) PEO and (■) PAA in PEO/PAA blends as a function of PAA content. (+): $\Delta H_{m_{tot}}$ (PEO + PAA). The broken lines represent the melting enthalpies calculated by assuming a linear dependence of ΔH_m of the pure components on the concentration.

At each composition, the observed ΔH_m of PAA is lower than that calculated from the weighted ΔH_m of the pure component ($\Delta H_m = 114{\cdot}1 \pm 4\ J\ g^{-1}$) and increases almost linearly with PAA content for concentrations higher than 20 per cent. This behaviour may be explained assuming that, at the melting point of PEO (337 K), the LC dissolves in the polymer phase up to a saturation concentration of about 20 wt% as indicated by the temperature/composition plot in figure 2. Thus, the lowering of ΔH_m at a given composition corresponds to the fraction of PAA which is solubilized in the molten polymer.

On the other hand, the ΔH_m values recorded for the polymer component at the various compositions are slightly higher than those calculated taking $\Delta H_m = 166{\cdot}4$

$\pm 6\,\mathrm{J\,g^{-1}}$ for pure PEO. However, the melting enthalpy of PEO in the blends decreases almost linearly with the LC concentration. The difference between the observed and calculated values of ΔH_m could be accounted for by an additive (positive) enthalpic contribution due to the PAA fraction which dissolves to saturation in the polymer melt. Other factors which may affect the melting enthalpy of the PEO phase, such as reorganization phenomena of the crystals during the heating run or morphological effects depending on the composition [12], should be excluded as the melting temperature of PEO is essentially independent of blend composition and thermal history.

The observed total melting enthalpy of the two components ($\Delta H_{m_{tot}}$) for each blend is also reported in figure 3 as a function of PAA content. These values are found to be lower than those calculated from the sum of the weighted melting enthalpies of the pure components. The area between the two curves should indicate a negative value of the total mixing enthalpy of the system. It is noteworthy that Cser *et al.* [13] found for various mixtures of liquid crystal polymers, with smectic and nematic LCs, that the melting enthalpies of the polymers at the clearing points were proportional to the polymer content of the mixtures, while the enthalpy changes of the solid–LC transitions were proportional to the saturation concentration of the LC in the polymer.

The DSC thermograms of PEO/PAA blends on cooling from the isotropic melt display distinct crystallization peaks for PEO and PAA. The crystallization temperatures (T_c) of the components show a composition dependence similar to that reported in figure 2 for the melting behaviour. The T_c of PEO is near 310 K, whereas the T_c of PAA decreases from 352 K (nematic to crystal Form II transition) for the pure LC to about 327 K for a PAA concentration of 30 wt%.

In figure 4, the measured and calculated crystallization enthalpies (ΔH_c) of PEO and PAA in the blends and the total crystallization enthalpies ($\Delta H_{c_{tot}}$) are plotted versus PAA content. For pure PAA a ΔH_c of $84{\cdot}4\,\mathrm{J\,g^{-1}}$ has been found, which corresponds to the formation of the Form II crystals. For the blends, at concentrations $\geqslant 30$ per cent of PAA, the observed ΔH_c values follow a linear dependence on

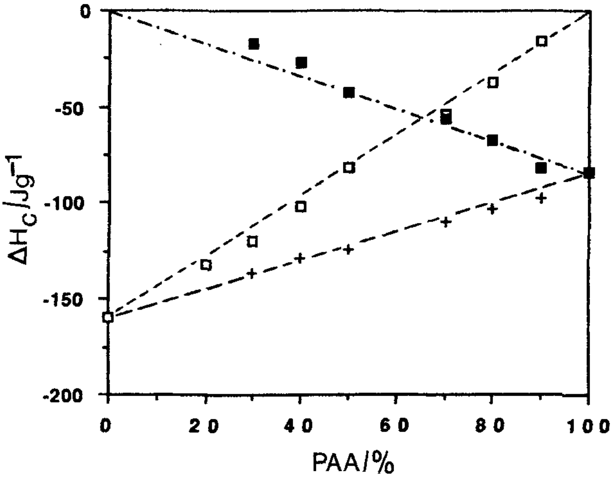


Figure 4. Crystallization enthalpy, ΔH_c (per gram of blend), of (□) PEO and (■) PAA in PEO/PAA blends as a function of PAA content. (+): $\Delta H_{c_{tot}}$ (PEO + PAA). The broken lines indicate the enthalpy values calculated from the weighted ΔH_c of the pure components.

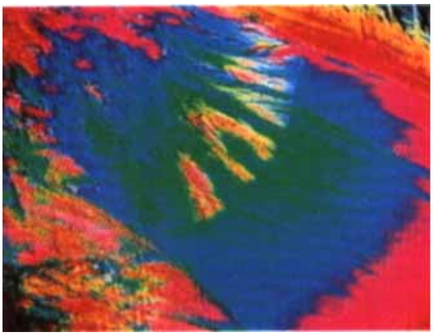
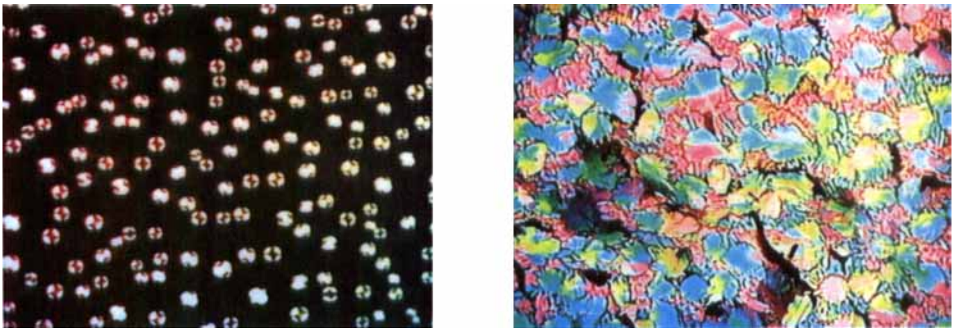


Figure 5. Optical micrograph of the PEO/PAA 80/20 blend on cooling to 303 K, showing the radial growth of PEO spherulites on PAA crystals (crossed Nicols, × 119).

Figure 6. Optical micrograph of the PEO/PAA 70/30 blend at 303 K, showing dendritic textures of PAA formed on cooling from the isotropic melt (crossed Nicols, × 100).



(*a*) (*b*)

Figure 7. (*a*) Optical micrograph of the PEO/PAA 20/80 blend at 384 K, showing the formation of nematic droplets of PAA on cooling from the isotropic phase (crossed Nicols, × 100). (*b*) Optical micrograph of the PEO/PAA 20/80 blend after cooling to 303 K (crossed Nicols, × 100).

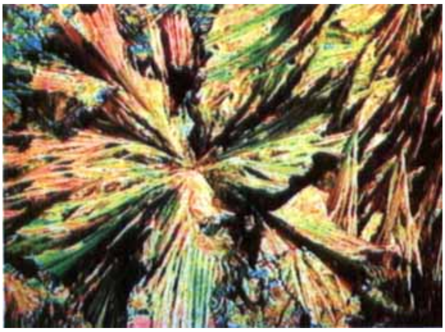


Figure 8. Optical micrograph of the PEO/PAA 5/95 blend at 303 K, showing PAA crystals grown on cooling from the nematic phase (crossed Nicols, × 100).

composition that agrees with the expected one. This is evidence that at the liquid–solid transition the polymer and the LC component give rise to separated crystal phases.

3.2. *Optical microscopy*

In order to get further information about phase structures and their transition processes, the crystallization and melting behaviour of the PEO/PAA blends were examined by optical polarizing microscopy.

In figures 5–8 are shown the optical micrographs of blend samples at various compositions, on cooling from the isotropic melt. For PAA contents <20 per cent, the morphology of the blends in the solid state (below the crystallization temperature of PEO) is characterized by the presence of birefringent PEO spherulites grown from an isotropic liquid phase (PEO + PAA). Similar textures were observed for pure PEO crystallized under the same conditions. This suggests that the solubility of PAA in the solid PEO is very limited.

For blends with a PAA content of 20 per cent (see figure 5), or higher, the crystallization of both PAA and PEO phases was observed on cooling from the

isotropic liquid phase (PEO + PAA). Similar textures were observed for pure PEO crystallized under the same conditions. This suggests that the solubility of PAA in the

The micrograph in figure 6 shows PAA textures of dendritic type obtained from a 70/30 blend. These structures develop from the whole mass of the molten blend below 330 K and display a solid state transition at lower temperature (*c.* 303 K) accompanied by a change of morphology. No evidence of such structures was found for undiluted PAA on cooling from the liquid phase under the same conditions. However, the formation of dendritic textures was also observed in the case of blends of PAA with a branched polyolefin, poly(octadecylethylene) [9] on cooling from the isotropic phase, and it was suggested to depend on a diffusion limited growth mechanism [14]. On the heating run, the dendritic aggregates melt over a broad temperature range and give rise to a homogeneous liquid phase.

In PEO/PAA blends with PAA content higher than 70 per cent the occurrence of the nematic phase was observed on cooling from the isotropic melt. In figure 7 (*a*), the formation of nematic droplets, dispersed within an isotropic liquid mixture, is shown for the 20/80 blend at about 384 K. This structure closely resembles those described for PDLC materials obtained by phase separation processes [5, 6]. Below the nematic to solid transition temperature (352 K), the crystallization of PAA occurs simultaneously from both the nematic and the isotropic liquid phase giving rise to a mosaic type texture (see figure 7 (*b*)). At temperatures $\leqslant 310$ K the crystallization of PEO is then observed. When the PAA concentration exceeds 90 per cent well-developed PAA crystals, with morphological characteristics similar to those of the pure PAA, were formed on cooling from the nematic phase (see figure 8).

4. Conclusion

On the basis of the results from calorimetric and microscopic analysis, it is possible to suggest an approximate equilibrium phase diagram for the PEO/PAA system. A synthetic description of the phase behaviour, as indicated in the temperature/composition plot of figure 2, is given as follows:

(i) Region A, at temperatures lower than the melting point of PEO, there is a two phase region consisting of a solid polymer and a solid LC phase.

(ii) Region B is a two phase region. One phase is the molten polymer containing a LC fraction proportional to the saturation concentration of PAA (about 20 wt%) at the PEO melting temperature. At temperatures above 337 K, an increasing amount of LC is dissolved in the liquid phase. The second phase is constituted by solid PAA, which can exist with different crystal textures depending on the blend composition and the temperature.

(iii) Region C, above the crystal–nematic transition of PAA, is a two phase region containing a homogeneous polymer/LC liquid mixture and a dispersed nematic PAA phase. This latter phase is observed by optical microscopy only for PAA concentrations ⩾ 70 per cent.

(iv) Region D represents a single phase consisting of a homogeneous mixture of the two components in the isotropic liquid state. This phase spans a temperature range from 337 K, for blends with high polymer concentration (up to about 20 per cent of PAA), to over 409 K for blends with high LC content.

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References

[1] Wissbrun, K. F., 1981, *J. Rheol.*, **25**, 619.

[2] Huh, W., Weiss, R. A., and Nicolais, L., 1983, *Polym. engng Sci.*, **23**, 779.

[3] Buckley, A., Conciatori, A. B., and Calundann, G. W., 1984, U.S. Patent, 4434262.

[4] Patwardian, A. A., and Belfiore, L. A., 1988, *Polym. engng Sci.*, **28**, 916.

[5] West, J. L., 1988, *Molec. Crystals liq. Crystals*, **157**, 427.

[6] Doane, J. W., Golemme, A., West, J. L., Whitehead, J. B., and Wu, B. G., 1988, *Molec. Crystals liq. Crystals*, **165**, 511.

[7] Dutta, D., Fruitwala, H., Kohli, A., and Weiss, R. A., 1990, *Polym. engng Sci.*, **30**, 1005 and references therein.

[8] Ballauf, M., 1986, *Molec. Crystals liq. Crystals*, **4**, 15.

[9] Pracella, M., Bresci, B., Lupinacci, D., and Magagnini, P. L., 1990, *3rd European Polymer Federation Symposium on Polymeric Materials*, Sorrento, Italy, Abstracts, p. 361.

[10] Pracella, M., Bresci, B., and Caldarelli, S., 1991, *European Conference on Liquid Crystals*, Courmayeur, Italy, Abstracts, p. 138.

[11] Chow, L. C., and Martire, D. E., 1969, *J. phys. Chem.*, **73**, 1127.

[12] Martuscelli, E., Pracella, M., and Ping Yue, W., 1984, *Polymer*, **25**, 1097.

[13] Cser, F., Nyitrai, K., Hardy, G., Menczel, J., and Varga, J., 1981, *J. Polym. Sci. Polym. Symp.*, **69**, 91.

[14] Baehr, C., Ebert, M., Frick, G., and Wendorff, J. H., 1990, *Liq. Crystals*, **7**, 601.