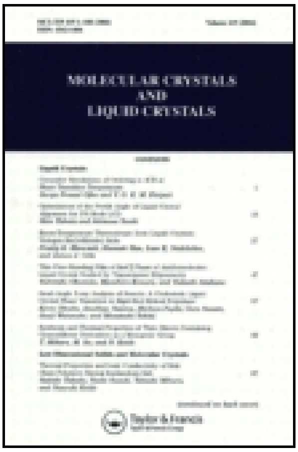

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Miscibility and Liquid Crystal Behaviour of P-Azoxy Anisole in Polymer Blends

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MISCIBILITY AND LIQUID CRYSTAL BEHAVIOUR OF P-AZOXY ANISOLE IN POLYMER BLENDS

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Abstract The phase behaviour of two polymer/liquid crystal blends has been investigated by DSC and optical microscopy. In one case, blends of poly(octadecylethylene) (POE) and p-azoxyanisole (PAA) are found almost immiscible below the isotropization temperature of the liquid crystal. The crystallization process of PAA in the blends takes place with a sporadic growth of dendritic structures determined by the dispersion of the nematic phase in the molten polymer. In the other case, blends of poly(biphenylyloxyexylacrylate) (PBHA) and PAA display a different phase behaviour indicating partial miscibility of the two components at temperatures above the melting point of the polymer. At high concentrations of PAA a nematic phase dispersed in a isotropic liquid mixture of polymer and liquid crystal is observed. These results are accounted for by the different side-chain structure of the polymer components.

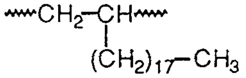
INTRODUCTION

Blends of polymers with low molar mass liquid crystals have gained growing interest in the recent years due to their potential applications for advanced technology materials. The anisotropic properties of the liquid crystal component may in fact be exploited for enhancing the processability and some performances of thermoplastic polymers[1], or for developing systems for electro-optic applications, as polymer dispersed liquid crystal devices.[2] The phase behaviour and the properties of polymer/liquid crystal blends have been investigated by several authors.[3] In general, it has been reported that the miscibility of these systems depends on the chemical structure and molar mass of the polymer, as well as the mesophase behaviour of the components.[4-7]

In this respect, we examined some blends of flexible or mesogenic polymers with nematic and smectic liquid crystals mainly with the aim to study the thermodynamics and kinetics of the phase transitions and the relevant morphological characteristics of the components, and their interactions phenomena.[8] In a previous paper the phase behaviour and the miscibility of blends of poly(ethylene oxide) (PEO) with the nematic liquid crystal p-azoxyanisole (PAA) were analysed.[9] Here, we report on a thermal and morphological study of blends of PAA with two comb-shaped polymers, poly(octadecylethylene) (POE) and poly(biphenylyloxyexylacrylate) (PBHA), characterized only by the different structure of their side chains, focusing the effect of the polymer structure and composition on the miscibility behaviour of the components.

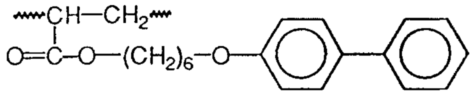
EXPERIMENTAL

POE is an isotactic poly(α-olefin) obtained by stereospecific catalysis as described in ref.[10]:



$$\sim CH_2-\underset{(CH_2)_{17}-CH_3}{\underset{|}{C}H}\sim$$

The Mw of this polymer is about 1.7×10^5 and the melting point *T*m is in the range 331-356 K. PBHA (poly[1-(4-biphenylyloxycarbonyl)ethylene]) was synthetized by radical polymerization according to ref.[11]:



The side-chains of this polyacrylate, containing the biphenylyl group, are able to crystallize owing to the presence of a long aliphatic spacer (*T*m= 330 K).The liquid crystal PAA was a commercial product (Hoechst, Germany) with a nematic mesophase between 393 K and 409 K.[12] Binary blends POE/PAA and PBHA/PAA, with composition range from 0 to 100 wt% of PAA, were prepared by mechanical mixing of the finely powdered components followed by melting at 430 K, about 20 degrees above the isotropization temperature of PAA. Blend films were also obtained by casting from methylene chloride solutions.

The thermal analysis of the blends was carried out with a Perkin-Elmer DSC-2C differential scanning calorimeter equipped with Data Station 3600. The samples after heating to 430 K at a rate of 10 K/min under nitrogen flow, were cooled from the isotropic melt using cooling rates of 2.5 or 10 K/min and then reheated to 430 K at 10 K/min (second heating run). Molten samples were also crystallized in isothermal conditions at various temperatures in the range 340-360 K in order to analyse the kinetics of phase transition of PAA in the blends. The transition temperatures of the components were determined both at the onset and the maxima of the DSC peaks and the relevant enthalpies of transition calculated from the peak areas.

The morphology of the blends was examined by a Leitz Ortholux polarizing optical microscope equipped with a Mettler FP52 hot stage and by a Jeol scanning electron microscope (SEM). Blend specimens, obtained by cooling from the melt in DSC, were heated in the hot stage up to the isotropization temperature and then cooled to room temperature at rates of 0.2, 3 and 10 K/min.

RESULTS

POE/PAA blends

The DSC analysis of these blends shows that the melting behaviour of the components is practically unaffected by the composition and thermal history. The melting peak of POE is observed at about 353 K (ΔHm= 24.5 cal/g); PAA shows a sharp crystal (Form I) to nematic transition at about 393 K (ΔHm=27.5 cal/g) and a weak nematic to isotropic transition at about 409 K (ΔHi=0.7 cal/g). The values of the phase transition temperatures of the blends, recorded on the second heating run, are reported in Figure 1 as a function of the PAA content. The phase diagram indicates, at least for contents of PAA≥ 10%, the existence of biphasic regions with a liquid polymer phase and a solid PAA phase above 353 K, and with a liquid polymer phase and a nematic phase above 393 K. At temperatures higher than 409 K it exists a single phase consisting of the two components in the isotropic liquid state.

As shown in Figure 2, the melting enthalpies ΔHm of POE and PAA in the blends change proportionally to the concentration of the components, as expected for an immiscible system. On the contrary, the enthalpy changes observed for the nematic-isotropic transition of PAA in the blends are lower than those calculated from the weighted ΔHi of pure PAA .

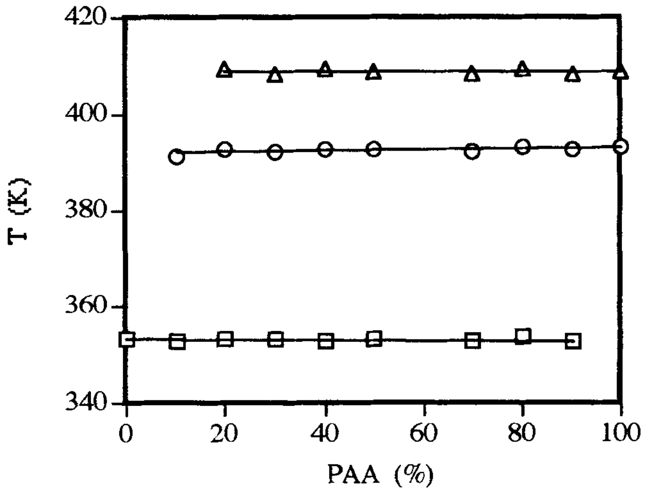


FIGURE 1 Phase transition temperatures of PEO/PAA blends as a function of PAA content. (□): melting temperature of POE; (○): melting temperature of PAA ; (△): isotropization temperature of PAA.

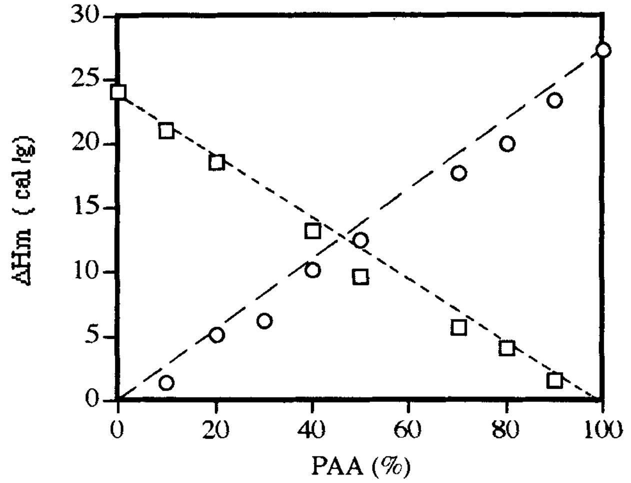


FIGURE 2 Melting enthalpy (per gram of blend) of PEO (□) and PAA (○) in their blends as a function of PAA content. The broken lines represent the weighted melting enthalpies calculated from the Δ*H*m of the pure components.

On cooling from the isotropic melt, a different behaviour of the liquid crystal phase is observed for blends with high polymer content. In Figure 3 are shown the DSC thermograms of POE/PAA blends and those of the pure components recorded on cooling run. It is seen that the isotropic to nematic transition of PAA occurs at about 407 K independently of the blend composition, whereas the crystallization from the nematic phase gives rise to multiple endothermic peaks spread on a wide temperature range (340-360 K), followed by the crystallization of the polymer at around 330 K. Pure PAA shows a sharp crystallization peak at about 356 K, corresponding to the formation of Form II crystals, which at lower temperature (335 K) transform to Form I crystals.[12] The crystallization enthalpies measured from the overall peak areas of PAA and from the peak of POE respectively vary proportionally to the concentration of the components in the blends, according to that found for the

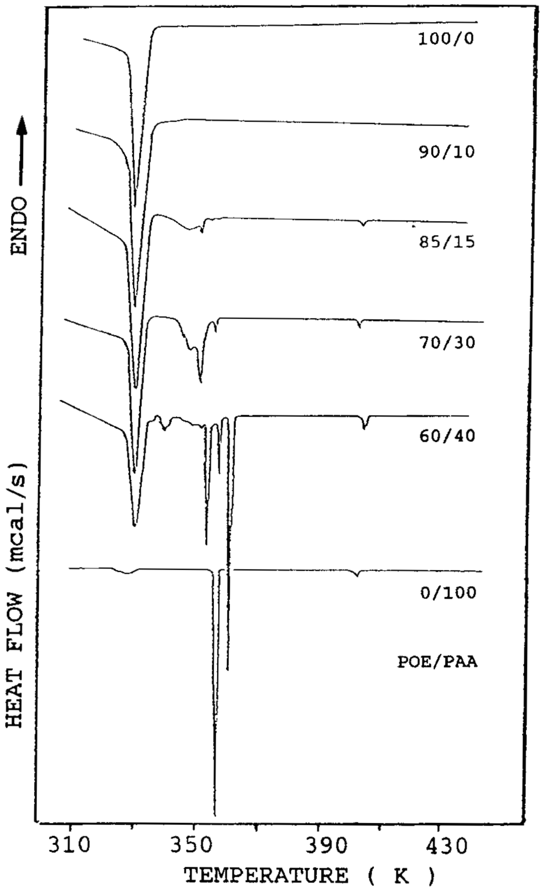


FIGURE 3 DSC thermograms of POE/PAA blends at various compositions on cooling from the isotropic melt (10 K/min).

melting enthalpy. This fact suggests that the unusual crystallization behaviour of PAA in the polymer rich blends is mainly determined by kinetic effects.

The investigations by polarizing optical microscopy show that, on cooling of these blends from the isotropic liquid at temperatures below *Ti*, the nematic phase segregates as small droplets dispersed in the polymer melt, and then, at temperatures lower than 360 K, the growth of dendritic-type PAA textures takes place sporadically in the whole mass of the sample, as shown in Figure 4. Such structures, which are not observed for plain PAA crystallized under the same conditions, at temperatures below 340 K show a marked morphological change corresponding to the Form II-Form I transition. The SEM micrographs of these samples evidence the presence of platelet-like PAA crystals (about 1μm thick) homogeneously dispersed in the polymer matrix. Similar dendritic textures were observed in the case of blends of poly(ethylene oxide) and PAA on cooling from the isotropic melt.[9] The growth process of these textures can be interpreted in terms of a diffusion limited aggregation model, as reported by Baehr *et al.* [13] for low molar mass discotic systems. Moreover, it was found by DSC that the kinetics of phase transition of PAA from the nematic to the solid state in POE/PAA blends were significantly affected by the polymer content.

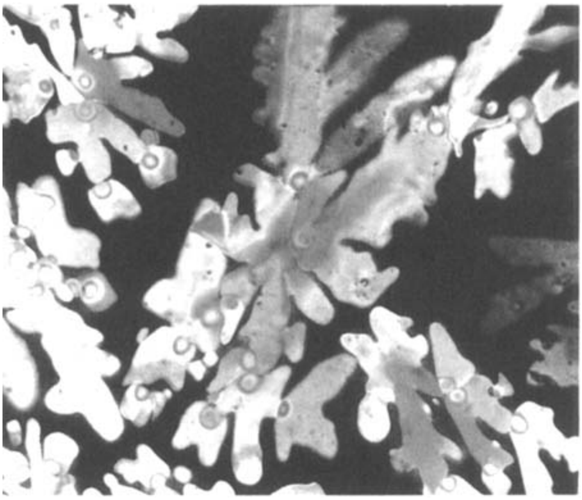


FIGURE 4 Optical micrograph of POE/PAA 80/20 blend showing dendritic textures of PAA formed at 357 K on cooling from the nematic phase (crossed Nicols, x 300). See Color Plate I.

PBHA/PAA blends

The DSC heating thermograms of PBHA/PAA blends at various compositions are shown in Figure 5. Contrary to what found for POE/PAA blends, the melting behaviour of the two components is markedly depending on the blend composition, as well as on the thermal history. For samples cooled from the isotropic melt, the melting peak of the polymer is shifted to lower temperature reaching a minimum for the blend with 20% of PAA, whereas the melting of PAA appears as a very broad transition whose onset temperature steadly decreases with increasing the polymer content. For blends with PAA content ≤ 20% no phase transition of the liquid crystal was detected by DSC; moreover, the nematic to isotropic transition was observed only for PAA concentrations ≥ 70%. This behaviour has been confirmed by optical microscopy. On cooling from the melt, a single PAA crystallization peak was observed in the blends, whose temperature decreases with decreasing the PAA content. The phase tran-

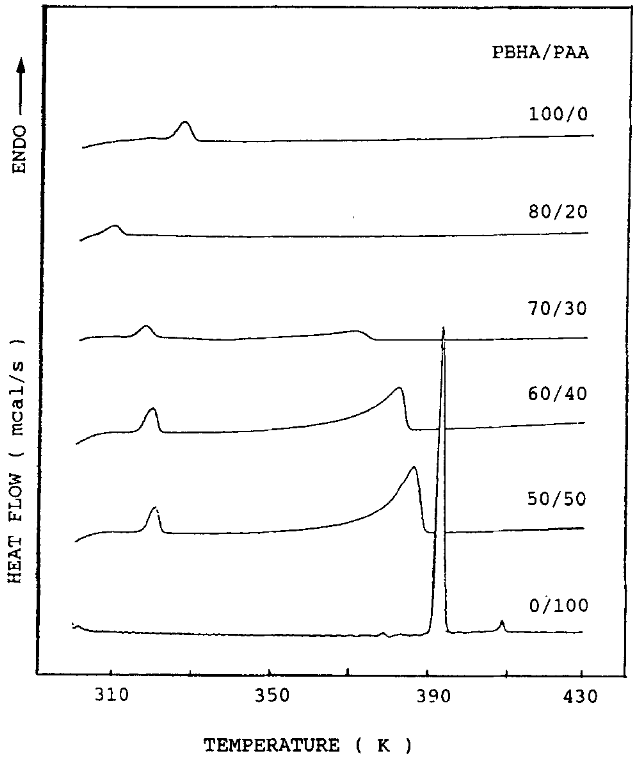


FIGURE 5 DSC thermograms of PBHA/PAA blends at various compositions (second heating run: 10 K/min).

sition temperatures and the melting enthalpies of the blend components are plotted in Figures 6 and 7 respectively, as a function of percent of PAA.

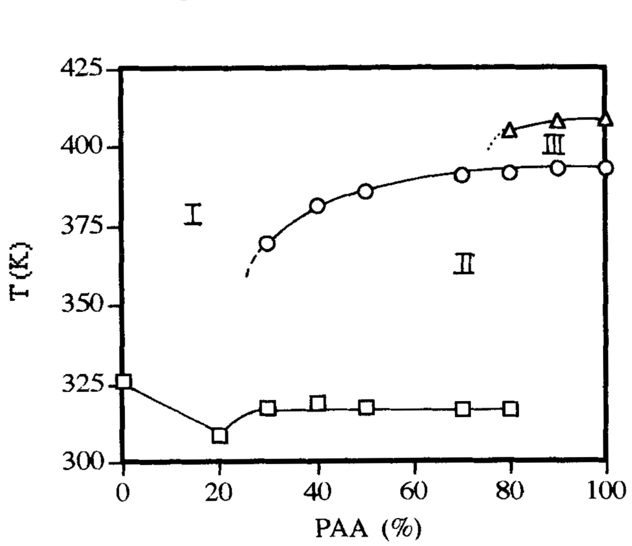


FIGURE 6 Phase transition temperatures of PBHA/PAA blends as a function of PAA content. (□): melting temperature of PBHA; (○): melting temperature of PAA; (△): isotropization temperature of PAA.

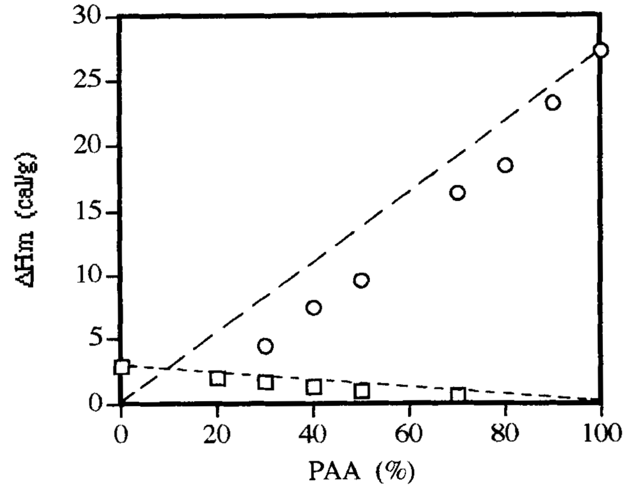


FIGURE 7 Melting enthalpy (per gram of blend) of PBHA (□) and PAA (○) in their blends as a function of PAA content. The broken lines represent the weighted melting enthalpies calculated from the Δ*H*m of the pure components.

The plot of Figure 7 shows that at each blend composition the observed melting enthalpy of the liquid crystal component is lower than that expected from the weighted Δ*H*m of pure PAA and changes almost linearly with the PAA content for concentrations ≥20%. This indicates that, at the melting point of PBHA, the liquid crystal is dissolved in the polymer phase up to a saturation concentration of about 20% by weight and the lowering of Δ*H*m at a given composition corresponds to the fraction of PAA which is solubilized in the polymer.[9] Similar findings were reported by Cser et al.[14] for some mixtures of mesomorphic polymers with low molar mass liquid crystals. On the other side, the melting enthalpy of PBHA (Δ*H*m=2.9 cal/g) in the blends is almost proportional to the polymer concentration, independently of the PAA content. For samples rapidly cooled from the isotropic melt, the DSC analysis evidenced that a fraction of PAA, which was solubilized in the molten polymer, recrystallized, on the subsequent heating run, at a temperature just above the melting point of the polymer.

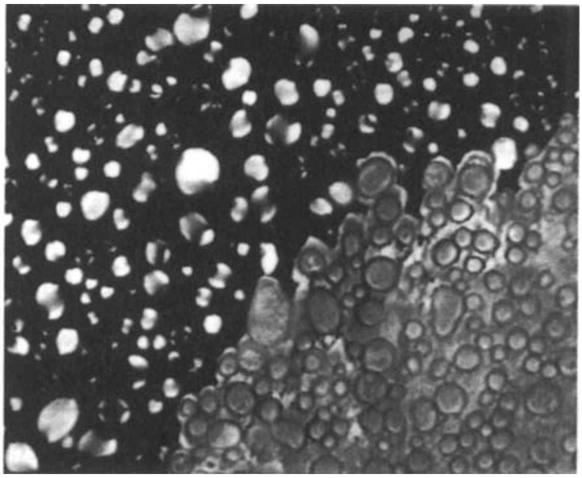


FIGURE 8 Optical micrograph of PBHA/PAA 30/70 blend on cooling from the nematic phase at 366 K (crossed Nicols, x 90).
See Color Plate II.

The microscopic analysis supports the existence of single isotropic liquid phase in the molten blends, for a PAA content ≤ 20%. With increasing the liquid crystal concentration, it is observed the coexistence of a liquid polymer phase and a solid PAA phase which, above the melting temperature of PAA, transform to an isotropic liquid mixture. In blends with PAA content ≥ 70%, the formation of nematic droplets dispersed within an isotropic liquid is found at temperatures below *Ti*. On cooling below the nematic to crystal transition, the crystallization of PAA occurs simoultaneously from both the nematic and the isotropic liquid phase giving rise to a grain-like texture, as shown in Figure 8 for the blend PBHA/PAA 30/70.

Thus the phase diagram of PBHA/PAA blends (Figure 6) may be explained assuming that above the melting point of the polymer, for a PAA content ≤ 20%, it exists a homogeneous liquid mixture of the two components (region I), whereas at higher PAA concentrations there is a two phase region (region II) consisting of a liquid PBHA/PAA mixture (with a PAA content proportional to the saturation concentration of liquid crystal in the molten polymer) and of a solid PAA phase. At temperatures above the melting point of PAA, for concentrations of liquid crystal higher than 70%, it is also present a two phase region (region III) with a molten polymer/liquid crystal mixture and a highly concentrated nematic PAA phase. Outside of this region, and over the isotropization temperature *Ti*, the molten components constitute a single isotropic liquid phase.

CONCLUSIONS

The results of the thermal and morphological analysis of blends of POE and PBHA with the nematic liquid crystal PAA indicate that phase behaviour of these systems is clearly affected by the chain structure of the polymer components. The composition dependence of the melting (and crystallization) thermodynamic parameters supports that POE/PAA blends are mostly immiscible in the solid and in the molten state below the isotropization temperature. On the contrary, a partial miscibility of the components in the PBHA/PAA blends above the melting temperature of the polymer is observed, with a saturation concentration of PAA of about 20%. This effect could be ascribed to the presence of molecular interactions of PAA with the polar and aromatic groups in the side chains of PBHA, as compared to the aliphatic structure of the side chains of POE. The phase behaviour of the PBHA/PAA blends is similar to that previously reported for blends of poly(ethylene oxide) with PAA.[9] However, it must be pointed out that owing to the low degree of crystallinity and the side chain structure of PBHA, a certain amount of liquid crystal can be solubilized in the solid polymer phase, decreasing its melting temperature.

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