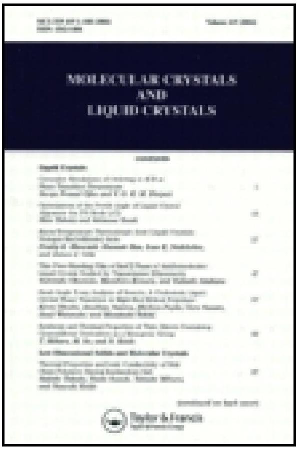

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Transitions in Mixtures of a Nematic Polymer and Chiral Nematic Liquid Crystals which form Blue Phases

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To cite this article: Upindranath Singh, Fredric Davis & Helen Gleeson (2001): Phase Transitions in Mixtures of a Nematic Polymer and Chiral Nematic Liquid Crystals which form Blue Phases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 357:1, 239-247

To link to this article: http://dx.doi.org/10.1080/10587250108028257

Mol. Cryst. Liq. Cryst., Vol. 357, pp. 239-247
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Phase Transitions in Mixtures of a Nematic Polymer and Chiral Nematic Liquid Crystals which form Blue Phases

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(Received September 16, 1999; In final form June 12, 2000)

Phase diagrams of mixtures of an acrylate-based nematic side-chain polymer and chiral nematics, which form blue phases, were deduced from polarized light microscopy. The blue phase can be used as a probe of miscibility since it is sensitive to small amounts of impurities. Miscibility appears to be enhanced by the flexibility of the parent compounds and dipole-dipole interaction; it is characterized by decreased transition temperatures and stabilized phases.

Keywords: chiral liquid crystals; polymeric liquid crystal; phase transitions; light microscopy

INTRODUCTION

Blends of polymers and conventional liquid crystals are attracting considerable scientific and technological interests. The phase behaviour and miscibility of polymer-liquid crystal blends have been found to depend on the chemical structure, mesophase properties and concentration of the components[1]. These systems, depending on the miscibility of the components may be tailored for specific applications over a broad temperature range with many advantages over the single components. For example, liquid crystals can act as plasticizers for polymers thereby reducing the glass transition temperature and enhancing its processability[2]. On the other hand, polymer-dispersed liquid crystals (PDLC)

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and polymer-stabilized liquid crystals (PSLC) have shown considerable promise for liquid crystal display applications[3–5], Hence, in order to exploit the potential of these blends, a thorough understanding of their phase behaviour is essential.

Theoretical phase diagrams for binary mixtures of polymeric liquid crystals and low molecular mass liquid crystals have been developed for nonchiral[6,7] systems. The theory is based on a combined Flory-Huggins (FH) free energy of mixing and the Maier-Saupe (MS) free energy for nematic ordering. Experimental results[8,9] are consistent with theoretical predictions. Phase diagrams for binary mixtures of biaxial nematogens have also been published[10]. On the other hand, corresponding phase diagrams for systems in which one or both components are chiral are virtually non-existent.

The combined FH/MS theory assumes that the total free energy density (g) of mixing for a binary nematic mixture of a polymer and a liquid crystal can be expressed as the sum of two terms. These are the free energy of mixing of isotropic liquids (g_i) and the free energy of anisotropic ordering of liquid crystals (g_a). The isotropic component of the free energy density is usually expressed in terms of the Flory-Huggins theory[11].

$$g_i = \frac{G_i}{nkT} = \frac{\Phi_1}{r_1}\ln\Phi_1 + \frac{\Phi_2}{r_2}\ln\Phi_2 + \chi\Phi_1\Phi_2 \tag{1}$$

r_l is the number of sites occupied by one liquid crystal molecule and r_2 represents the number of sites occupied by a single liquid crystalline polymer chain; $\phi_{1,2}$ represent the volume fractions of each component; $n = n_l r_l + n_2 r_2$ where n_l and n_2 are the numbers of liquid crystal and liquid crystalline polymer molecules and $\chi = A + B/T$ is the Flory-Huggins interaction parameter (A and B are constants).

The anisotropic component is given by the Maier-Saupe Mean-Field expression[12,13].

$$g_a = \frac{G_a}{nkT} = -\sum_1 \Phi_1 - \sum \Phi_2 - \frac{1}{2}\nu_{11}s_1^2\Phi_1^2 - \frac{1}{2}\nu_{22}s_2^2\Phi_2^2 - \nu_{12}s_1s_2\Phi_1\Phi_2 \tag{2}$$

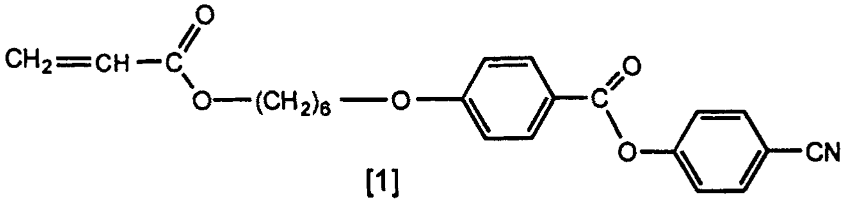
$\Sigma\phi$ represents the decrease of entropy due to alignment of individual LC molecules and mesogenic group of the polymer respectively while s_1 and $s_2$are orientational order parameters. The geometric mean assumption[14] relates the interaction parameters of pure components v_{11} and v_{22} to the cross-interaction term v_{12}. This relation is $v_{12} = c\ (v_{11}\ v_{22})^{0.5}$. The proportionality constant, c, characterizes the strength of the cross interaction between dissimilar mesogens as compared to that in the same species. If $v_{12} > v_{11}, v_{22}$ then mixing leads to enhanced order. The interaction parameters are all inverse functions of temperature.

The temperature and composition dependence of the free energy can be determined from the minimization of the anistropic component of the free energy with respect to s_1 and s_2. The co-existence curves are then determined by equating the chemical potential of each component in the two equilibrium phases. The phase diagrams may then be determined by a double tangent method.

The minimization of the free energy of a chiral nematic is a highly non-trivial problem, which has not been solved exactly. The source of the difficulty is that the bulk and gradient free energies are separately minimized by different forms of the order parameter[15]. The gradient free energy favours a strongly biaxial form of the order parameter while the nongradient free energy favours a uniaxial order parameter. Also, for our mixture, equation 2 will contain a term reflecting the chiral order induced in the polymer by the chiral liquid crystal. Owing to these difficulties, it is not surprising that theoretical phase diagrams for chiral polymer/liquid crystal blends do not exist.

EXPERIMENT

The polymer (CBZ6/HEA) used in this study is an acrylate-based side-chain nematic liquid crystal polymer[16]. It was prepared by the free radical polymerization of the mesogenic cyanophenyl benzoate monomer (I) with 10% hydroxy ethyl acrylate (II), using AIBN at 55° C as the initiating system. Under such conditions, a number average degree of polymerization of ~ 200 units and a polydispersity of ~ 2 were obtained.



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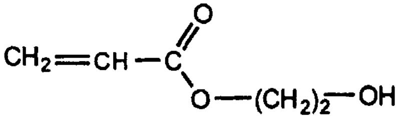
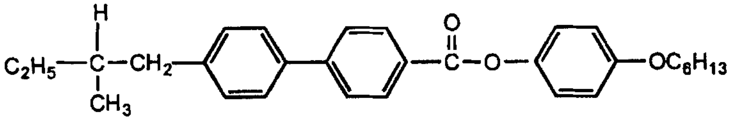


[11]

The liquid crystalline materials are 4′(-2-methylbutyl)-biphenyl-4-carboxylic acid 4-hexyloxy phenylester (CE3: III) and (+)-2-methyl butyl p-[(p-methoxy benzylidene) amino]-cinnimate (MBMBAC: IV). Both liquid crystalline materials form blue phases but the isotropic-blue phase transition for CE3 (forms BPI) is higher than that of the polymer while that of MBMBAC (forms BPIII, BPII and BPI) is lower. The aim of this study is to investigate how chemical structure and differences in transition temperatures of the parent componds influence the miscibility of the blends.



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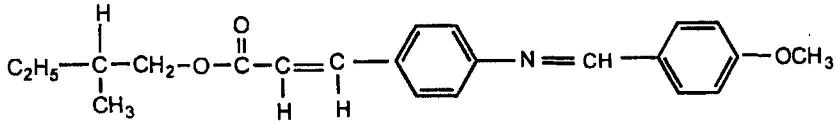


[M]

The blends were prepared by dissolving the polymer and the liquid crystal in a minimum amount of dry dichloromethane. The solution was then cast on a cover slip and the solvent was allowed to evaporate at room temperature. CBZ6 and MBMBAC may be partially miscible since these blends retained the characteristic yellow colour of the liquid crystal even at high polymer concentrations (CBZ6 and CE3 are both white). The blue phases could not be identified from DSC scans hence the exclusive use of light microscopy.

The samples were heated into the isotropic phase and left to equilibrate overnight. They were cooled slowly at a rate of 1 degree every ten minutes up to 5°C above the transition. Subsequent cooling was at a rate of 0.05 °C/min. All transitions were observed while the samples cooled. Temperature control to ± 0.005°C was achieved by using an Instec MK1 temperature controller.

RESULTS AND DISCUSSION

The phase diagram for the CBZ6/MBMBAC blends is shown in figure 1. Phase separation occurs in the isotropic phase (observed with uncrossed polarizers) as

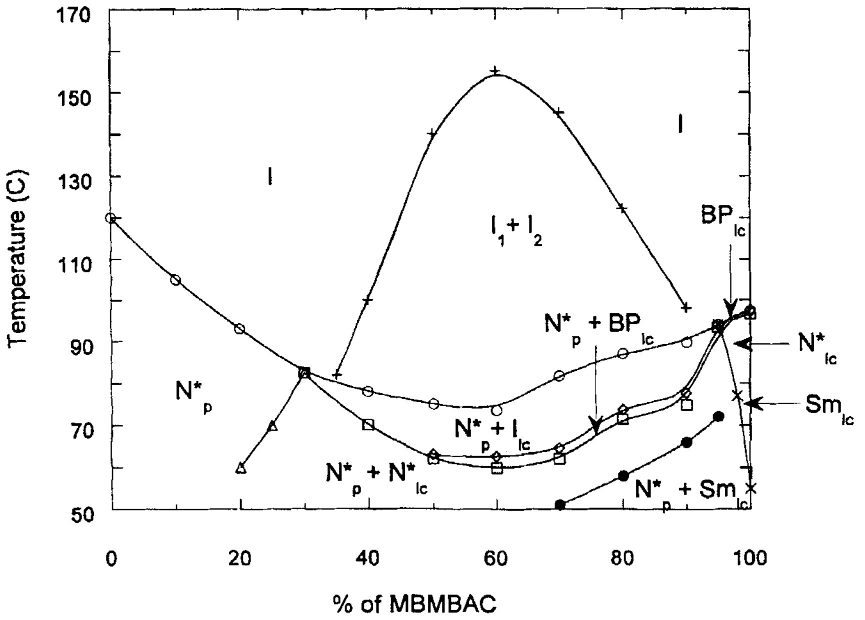


FIGURE 1 Phase diagram for the MBMBAC/CBZ6 blend. The subscripts (lc) and (p) refer to the liquid crystal and polymer respectively. The lines are meant to be a guide for the eye. MBMBAC has a lower transition temperature than CBZ6

well as in the liquid crystalline phases. Each component depresses the isotropic-liquid crystalline phase transition temperatures of the other. Hence, a eutectic point appears at a 60% MBMBAC concentration (T= 71.5 °C). The transition temperatures of the other liquid crystalline phases in MBMBAC are also depressed. In mixtures whose MBMBAC concentrations are ≤30% a single transition from the isotropic melt is observed. Both cholesteric fingerprint and planar textures are evident in these mixtures. For higher liquid crystalline concentrations, biphasic regions of the isotropic phase of the liquid crystal and the liquid crystalline phase of the polymer are observed. The blue phase (BPII and BPI) grew out of these isotropic regions. In general, the temperature range of the blue phase is greater in these mixtures than in the pure chiral material. Mixtures with MBMBAC concentrations ≥95% behaved essentially like the pure material.

Polymerization of the monomer with HEA provides cross-linking sites, which may be used, for preparing elastomers[16]. The MBMBAC molecules may combine chemically with the polymer by attaching themselves to these sites. The dispropionate yellow colour of the mixtures and the strong temperature dependence of concentrations are indications of some miscibility in the ordered phases. Also, if the materials were not miscible to some extent in the ordered phases, the blue phase would have formed as long as MBMBAC was present.

The phase diagram for the CE3/CBZ6 blend is shown in figure 2. The components are, at best, only slightly miscible in both the isotropic and ordered phases. This imiscibility is most evident from the blue phase which exist for CE3 concentrations ≥40%. The corresponding isotropic-blue phase transition temperatures and temperature intervals are essentially unchanged from that of the pure material. Unlike the previous blends, the transition temperatures from the isotropic melt all lie between those of the parent compounds. Also, the critical temperature at which the two observed isotropic phases merge is > 250 ° C (from extrapolation) and lies beyond the range of our apparatus.

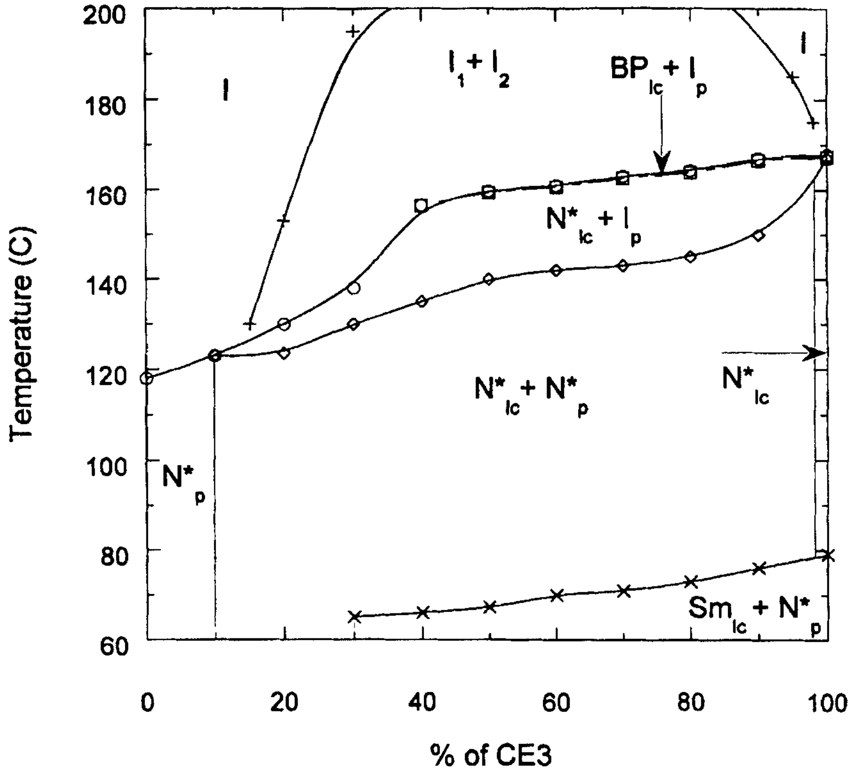
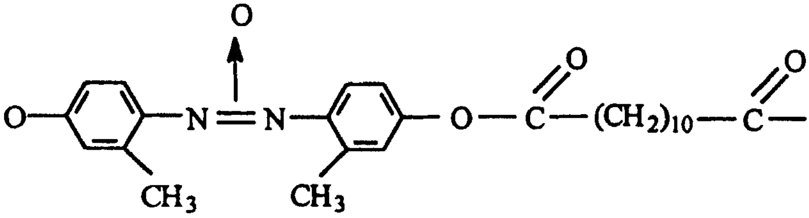


FIGURE 2 Phase diagram for the CE3/CBZ6 blend. The subscripts (lc) and (p) refer to the liquid crystal and polymer respectively. The lines are meant to be a guide for the eye. CE3 has a higher transition temperature than CBZ6

The influence of the polymer on the blue phase formed by CE3 is captured in the photographs of figure 3a. Since CE3 has a much higher transition temperature than CBZ6, isotropic polymer droplets act as nuclei for the growth of large BPI crystals. The BPI phase platelets in MBMBAC are much smaller but better-defined (figure 3b). In the MBMBAC blends both the cholesteric and smectic phases are also stabilized. In the CE3 blend these phases are not miscible with the polymer and hence not stabilized.

D'Allest, Gilli and Sioux[17] have studied phase transitions in mixtures of CE3 and the main chain nematic polymer DDA-9 (see monomer V; Tc ~ 122 C). One can intuitively infer from the phase diagram that these compounds are much more miscible than CE3 and CBZ6 since all three blue phases were observed (in CE3) at low concentrations of DDA-9. The miscibility with DDA-9 was enough to increase the pitch of CE3 from 230 nm (BDH data sheet) to one at which supported three blue phases. Studies on CB15 and CE2 have shown if the pitch of these highly chiral materials is increased by adding E9 and CE2R[18,19] respectively, additional blue phases are seen. It is quite likely that a eutectic point exist in CE3/DDA-9 blends since the I-BPIII phase transition is lowered as the polymer concentration was increased. Unfortunately, mixtures with polymer concentration > 30% were not studied.



[V]

Most experimental miscibility studies involving polymer liquid crystal blends involve those in which the polymer has the greater transition temperature greater than that of the liquid crystal[6–9,20,21]. However, there is one theoretical study based on the reverse situation, which predicts a eutectic point[22]. Hence, differences in transition temperatures of the constituents may not be as important as previously thought. This is also supported by the results of CE3 and DDA-9 (CE3 has the greater clearing temperature).

It might be possible to deduce from an examination of the structures of CBZ6 and DDA-9 a possible explanation for the differences in miscibility. The spacer linking the mesogen unit to the polymer backbone is longer and thus more flexi-

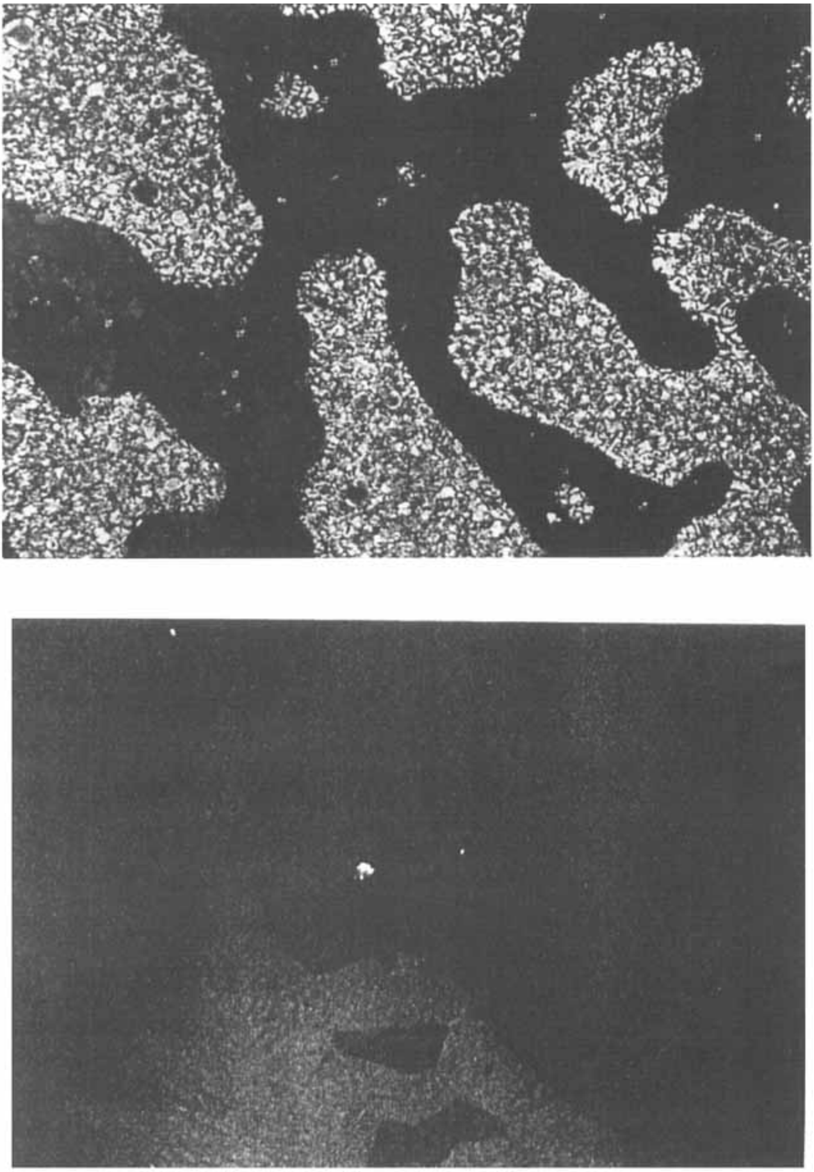


FIGURE 3 (top) A microphotograph showing the phase separation of MBMBAC and CBZ6. The blue phase (BPI) is seen emerging from the isotropic phase of the liquid crystal in a 70%MBMBAC/30% CBZ6 blend. The temperature is 64.50 ± 0.01 °C and the magnification is 200X. (bottom) A microphotograph showing the phase separation of CE3 and CBZ6. The blue phase (BPI) is seen growing around a globule of CBZ6 which is in its isotropic phase in a 90%CE3/10% CBZ6 blend. The temperature is 166.72 ± 0.01°C and the magnification is 200X ble in DAA-9 than in CBZ6 (10 and 6 carbon atoms respectively). Possibly, more crucial is the high electron density provided by the azo group, which is, absent in CBZ6. Hence, it is obvious that there is greater dipole-dipole interaction between CE3 and DAA-9 than between CE3 and CBZ6. Also, the CE3 molecule is probably more rigid than MBMBAC owing to the extra aromatic ring and hence less miscible than MBMBAC with CBZ6.

CONCLUSION

The generation of theoretical phase diagrams for chiral blends of polymers and low molecular mass liquid crystals represent quite a challenge for the theoretical scientist. However, based on our observations and those of D'Allest, Gilli and Sioux[17], one can conclude that the following factors can strongly influence the miscibility of polymer liquid crystal blends. Miscibility is improved by increasing the length of the spacer group which couples the mesogenic to the polymer backbone. Strong dipole-dipole interaction enhances the miscibility to a greater extent than the differences in transition temperatures. Also, the phase behaviour of the blue phase formed can indicate the extent of the miscibility.

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