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## BLUE PHASE FORMATION IN LIQUID CRYSTAL-POLYMER MIXTURES

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**Abstract** Polarized light microscopy was used to investigate blue phase formation in mixtures of the chiral nematic (+)-2-methylbutyl p-[(p-methoxybenzylidene)amino]-cinnamate (MBMBAC) and the nematic side chain polymer composed of cyanophenyl benzoate monomer (CBZ6) copolymerized with 10% of 2-hydroxy ethyl acrylate (HEA). The phase diagram and textures are compared to the case in which the polymer was replaced by the low molecular weight nematic p-azoxyanisole (PAA).

### INTRODUCTION

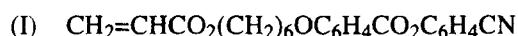
Conventional chiral nematics of sufficiently short pitch may form up to three distinct blue phases<sup>1-5</sup>: two cubic (BPI and BPII) and one amorphous (BPIII or fog phase). If such a chiral nematic is cooled, the transition sequence isotropic-BPIII-BPII-BPI is seen. In general, the number of blue phases formed and their corresponding temperature intervals generally increase with increasing chirality<sup>6</sup> (decreasing pitch). The blue phase has also been found in side chain oligomers<sup>7,8</sup>, side chain polymers<sup>9</sup>, crossed-linked polymers<sup>10</sup> and mixtures of a chiral nematic and a main chain nematic polymer<sup>11</sup>.

Blends of polymers and conventional liquid crystals are attracting great scientific and technological interest. These systems, depending on the miscibility of the components, may be tailored for specific applications<sup>12</sup> in a broad composition and temperature range with many advantages over the single components. On the other hand, liquid crystals dispersed as droplets in an immiscible polymer matrix have been investigated for electro-optic applications<sup>13</sup>. The phase behaviour and miscibility of polymer-liquid crystal blends has been found to depend on the chemical structure, mesophase properties, and concentrations of the components<sup>14</sup>. In this study we examined the modification to the blue phase in MBMBAC when varying amounts of CBZ6 were added. In order to carry out some comparisons, the experiment was repeated with CBZ6 replaced by PAA (transition temperature,  $T_c \sim 135^\circ\text{C}$ ) which has been extensively studied. The chiral

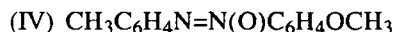
nematic MBMBAC forms three blue phases<sup>15,16</sup> ( $T_c \sim 99^\circ\text{C}$ ) despite a relatively long pitch; while the polymer CBZ6 forms a nematic phase ( $T_g \sim 35^\circ\text{C}$  and  $T_c \sim 123^\circ\text{C}$ )<sup>17</sup>. The transition temperatures of PAA and CBZ6 are about  $35^\circ\text{C}$  and  $25^\circ\text{C}$  respectively above that of MBMBAC and thus there is always the possibility of new phases existing in the mixtures which are not present in the parent systems provided that the two are miscible to some extent.

## EXPERIMENT

The polymer CBZ6/HEA was prepared by free radical polymerization of the mesogenic monomer (I) and hydroxyethyl acrylate (II) in appropriate proportions, using AIBN at  $55^\circ\text{C}$  as the initiating system. Under such conditions a number average degree of polymerization of  $\sim 200$  units and a polydispersity of  $\sim 2$  were obtained.



MBMBAC (III) and PAA(IV) were obtained from Eastman Kodak and Sigma, respectively, and were used without further purification.



The blends were prepared by dissolving the relevant mixtures in a minimum amount of dry dichloromethane. The solution was then cast on a polyamide sheet and the solvent allowed to evaporate at room temperature. The polymer-liquid crystal blends retained the characteristic yellow colour of MBMBAC even at high concentrations of the polymer (CBZ6 is white and PAA is yellow). The samples were heated into the isotropic phase and left overnight. They were then cooled slowly at a rate of  $1^\circ\text{C}$  every ten minutes up to about  $5^\circ\text{C}$  above  $T_c$ . Subsequent cooling was at a rate of  $2^\circ\text{C/h}$ . All transitions were observed while the samples cooled since the blue phase is much more easily observed on cooling<sup>18</sup>. Temperature control to  $\pm 0.01\text{ K}$  or better was achieved with a custom-designed proportional temperature controller.

## RESULTS AND DISCUSSION

The phase diagram for the MBMBAC/CBZ6 mixtures is shown in Figure 1. The clearing temperature from the isotropic melt depends strongly on the concentrations of the constituents. However, the concentrations at different points of the sample are expected to differ slightly. In mixtures whose MBMBAC concentrations are  $< 50\%$  (by weight), a

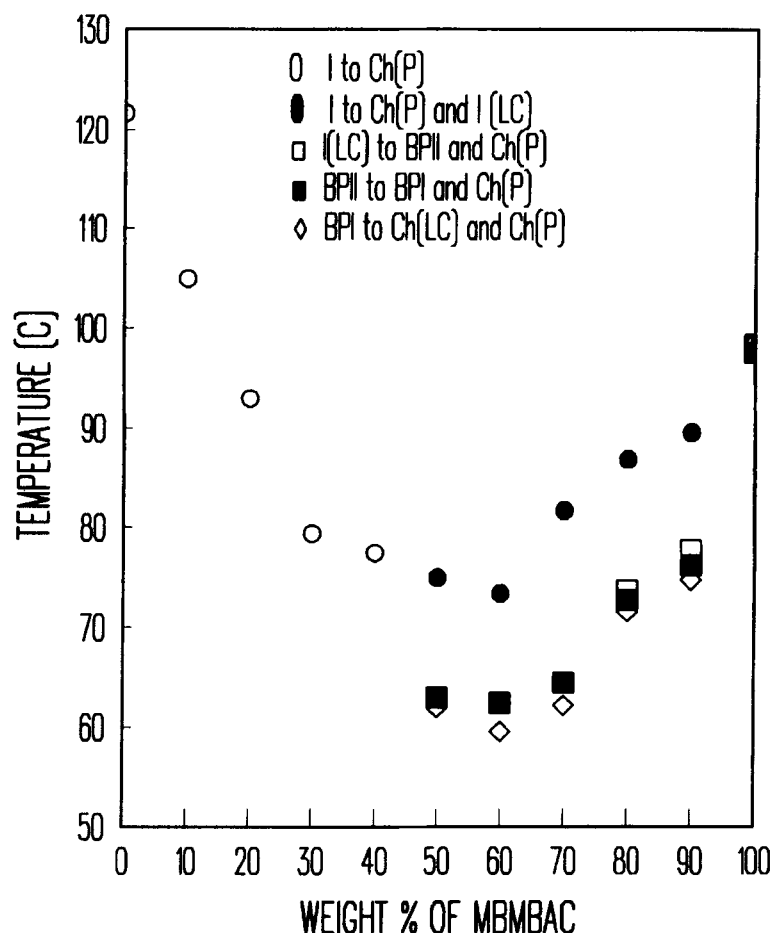


FIGURE 1 Phase diagram of CBZ6-MBMBAC mixtures.

single transition from the isotropic melt to the cholesteric phase of the polymer was seen. For higher concentrations of MBMBAC, we observed biphasic regions of the isotropic phase of the liquid crystal and the cholesteric phase of the polymer just below the clearing temperature. The blue phase (BPII and BPI) grew out these isotropic regions

The temperature range of the blue phases (see Table 1) is greater in the mixtures than in the pure chiral nematic. A similar behaviour seen in mixtures of a polysiloxane based main chain nematic polymer and the chiral nematic CE3<sup>11</sup> has been attributed to the polydispersity of the samples. The fog phase was seen in these CE3 mixtures (in polymer concentrations up to 20%) but not in our samples. In MBMBAC, the fog phase has been observed<sup>15</sup>, but only when the sample was agitated by small electric fields. Also, CE3 has

a much shorter pitch than MBMBAC and this would enhance the formation of the blue phase. Hence, in our results the fog phase is included in BP<sub>II</sub>. Observations of these mixtures in the presence of small electric fields are in progress.

Microscopic observations revealed that the isotropic phases of the polymer and the liquid crystal are completely miscible. The dispropionate yellow colour of the mixtures and the strong temperature dependence of concentration are indications of some miscibility in the ordered phases. Also, if the materials are not miscible to some extent in the ordered phase, the blue phase would have emerged as long as MBMBAC was present. Hence, one can use blue phase formation in other composite systems as an indication of the extent of miscibility.

Polymerization of CBZ6 with HEA provides cross-linking sites which may be used for preparing elastomers<sup>17</sup>. In these mixtures, MBMBAC molecules may combine chemically with the polymer by attaching themselves to these sites. Phase separation and blue phase formation occur if these sites become exhausted as in the case of high liquid crystal concentrations. At lower MBMBAC concentrations, the MBMBAC molecules are absorbed into the polymer matrix and are not free to form blue phases. One possible explanation for the apparent miscibility of the constituents is dipole-dipole interactions of the C=O groups which are present in the polymer backbone, the side-chain mesogen and the liquid crystal. There is also the possibility of a small amount of hydrogen bonding involving the OH group on the polymer backbone and the C=O group of the liquid crystal.

TABLE 1 Blue phase transition temperatures in CBZ6-MBMBAC mixtures.  $T_c$  is the clearing temperature of the isotropic melt.

% CBZ	$T_c$ $\pm 0.01$ K	I - BP <sub>II</sub> $\pm 0.01$ K	BP <sub>II</sub> - BP <sub>I</sub> $\pm 0.01$ K	BP <sub>I</sub> - N* (Ch.) $\pm 0.01$ K
50	75.01	—	63.01	61.98
40	73.54	—	62.51	59.85
30	81.75	—	64.53	62.01
20	87.05	73.71	72.80	71.44
10	89.67	77.60	76.25	74.80
0	—	98.46	98.09	97.66

Two other factors which may affect the blue phase formation are the molecular weight of the polymer and the and the percent of HEA used in copolymerization. A higher molecular

weight polymer would be less miscible and a lower concentration of HEA would provide fewer cross-linking sites. Consequently, the blue phase would be expected to form at even lower MBMBAC concentrations for these two cases.

PAA and MBMBAC appear to be completely miscible and as expected, the mixtures behave as typical chiral nematics. In particular, the blue phase temperature range decreases with increasing PAA concentration (decreasing pitch). These ranges are shown in Table 2. The addition of >30% of the nematic is required to remove the blue phase.

TABLE 2 Blue phase temperature ranges ( $\pm 0.01$ K) in PAA-MBMBAC mixtures.

% PAA	BPII $\pm 0.01$ K	BPI $\pm 0.01$ K
0	0.37	0.43
10	0.33	0.45
20	0.18	0.35
30	—	0.21

In general, for the same composition by weight, the PAA-MBMBAC platelets (Figure 3a) were slightly bigger but less defined than those of the CBZ6-MBMBAC mixtures (Figure 3b). This may be attributed to slower crystallization rates in the higher molecular weight polymer. Also, we were able to grow large BPI platelets in a 70% MBMBAC-30% CBZ6 polymer mixture in a relatively short time (Figure 3c). Attempts to grow blue phase crystals in the PAA mixtures proved to be unsuccessful.

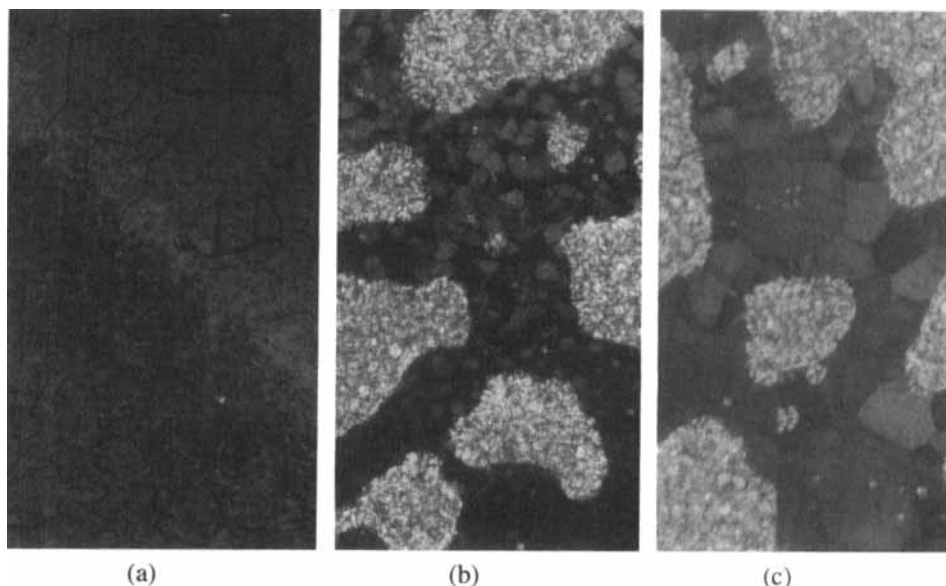


FIGURE 3 (a) Blue phase (BPII and BPI) textures in a 80% MBMBAC-20% PAA mixture. There is a clearly defined region separating BPII (top) and BPI (bottom).  
 (b) BPI emerging from the isotropic phase of the liquid crystal which is in equilibrium with the N\* phase of the polymer in a 70% MBMBAC-30% CBZ6 mixture .  
 (c) BPI in a 70% MBMBAC-30% CBZ6 mixture after it was allowed to grow for about two hours. Magnification is 200 X. (See Color Plate I).

### CONCLUSION

The results show that MBMBAC and CBZ6 form blue phases in high concentrations of the chiral nematic. The formation of the blue phase can indicate the extent of miscibility which may be due to dipole-dipole interactions and hence enthalpy driven.

### ACKNOWLEDGEMENTS

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