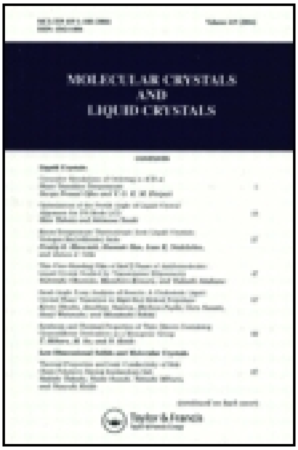

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Phase Behaviour of Polymer-Liquid Crystal and Polymer-Polymer Blends

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Phase Behaviour of Polymer-Liquid Crystal and Polymer-Polymer Blends

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DSC and optical microscopy were used to study the phase behaviour of blends of two members of a group of side-chain cholesteric liquid crystalline silicones. One of these siloxane-based polymers forms a single blue phase. The experimental phase diagram is constructed and then compared to the case in which one of the polymers is replaced by a chiral nematic liquid crystal, which also forms a blue phase.

Keywords: blue phase; phase diagram; side-chain polymer; chirality

INTRODUCTION

The idea of mixing two or more polymers to form new substances having a combination of all the attributes of the parent compounds is quite attractive. However, in practice this is rarely accomplished and in only a few cases have polymer blends achieved industrial importance. The main reason is that most common polymers do not mix with one another to form homogeneous blends. Polymers of different chemical composition rarely show miscibility, even over a limited composition range due mainly to the low entropy of mixing. This constant search for new materials with improved performance has led to the study of blends in which at least one component displays liquid crystalline order.

Studies of polymer-liquid crystal systems have attracted attention in recent years [1-5]; however, there are few reports on mixtures of liquid crystalline polymers[6]. The phase behaviour and miscibility of polymer-liquid crystal blends have been found to depend on the chemical structure, mesophase properties and concentrations of the components[7]. On the other hand, interactions among the basic structural units in polymer-polymer mixtures can lead to effects not seen in polymer-liquid crystal blends and such systems offer the greatest potential for synergisms in mechanical and thermal properties.

According to the rule of selective miscibility for low molar mass liquid crystals, identical phases are completely miscible [8]. Assuming this rule is applicable to liquid crystalline polymers, then polymers and liquid crystals with chemically similar mesogens are expected to be miscible over a broad composition range. This may also be true for blends of polymers derived from the same homologous series. In this study, we examine the miscibility of a cholesteric side-chain liquid crystal silicone with one of its homologues and with a low molar mass liquid crystal.

EXPERIMENT

The chemical structures of the materials used in this study are shown in figure 1. The polymeric liquid crystals are siloxane-based side-chain cyclic copolymers. These polymers differ only in the ratio of chiral (cholesterol derivative) to nonchiral mesogens (x:1-x). As this ratio increases, the pitch of the polymer decreases. The chiral and nonchiral mesogens are attached to the backbone of the polymer in an alternating sequence by flexible $(CH_2)_3$-O- spacers. Mixtures of polymers with ratios of 3:7 and 11:9 (respective codes 4768 and 4745) were studied in conjunction with blends of 4745 and the low molar mass liquid crystal, CE3. The polymers are available from Wacker and the liquid crystal (CE3) from BDH. All materials were used as obtained.

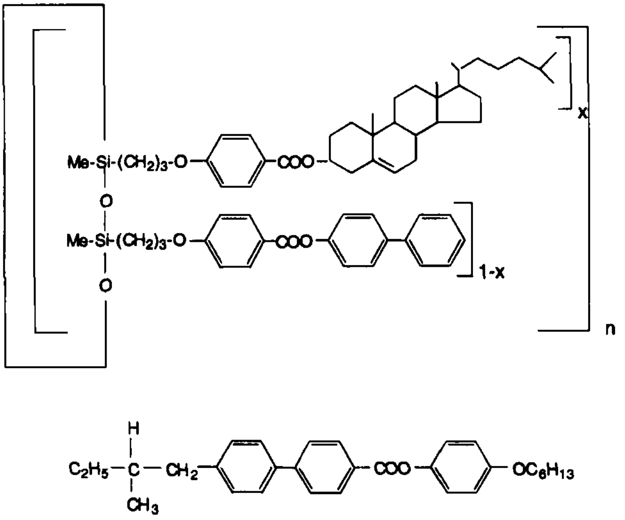

FIGURE 1 Chemical structures of the materials used. Top, Idealized structures of the cholesteric liquid crystal silicones ($0<x<1$ and $4 \leq n \leq 8$). Bottom, CE3.

The blends were prepared by dissolving the relevant mixtures in dry dichloromethane. The solution was then cast onto a polyamide sheet and allowed to evaporate at room temperature. The samples were then kept at 50 ° C for 24 h to remove all remaining solvent.

DSC and polarized light microscopy were used to examine the phase behaviour of the mixtures. The thermograms were obtained by using a Seiko SSC/5200 DSC, which is equipped with a heating unit and nitrogen circulation. The heating and cooling rates were 10° C/min. Observations were made with a Zeiss-Axiolab Pol polarizing microscope. An Instec HS1-I hot stage and temperature controller combination provided temperature control to ± 0.005 K. The blue phase was studied exclusively by light microscopy since it did not show up on DSC scans. The clearing temperatures deduced from light microscopy are constantly higher than those derived from DSC scans by about 3 K. However, DSC was more convenient than microscopy in determining melting transitions.

RESULTS AND DISCUSSION

The experimental phase diagram for CE3/4745 blends is shown in figure 2. Both materials display liquid crystalline behaviour over a broad range (~ 120 K for 4745 and ~ 100 K for CE3). The polymer and the liquid crystal appear to be miscible in the isotropic phase but phase separation occurs as soon as orientational order appears. The clearing temperatures of the mixtures all lie between those of the parent compounds. However, the concentration at different points within the sample may differ slightly. A eutectic point is seen at a 90%polymer concentration and two distinct melting points are observed in blends that contain 40 – 60 % of CE3.

The blue phase is formed by blends that have high concentrations of either CE3 or 4745. At intermediate concentrations, two-phase regions of isotropic and cholesteric phases were observed just below the clearing temperature. The addition of small amounts of polymer to CE3 destroys the smectic phase of the liquid crystal but enhances the blue phase of the material. Pure CE3 is a highly chiral nematic with a pitch of 230 nm (BDH data sheet) and forms a single blue phase (range of ~ 0.6 K). However, the blue phase is stable over a range of ~ 2 K when 10% polymer is added.

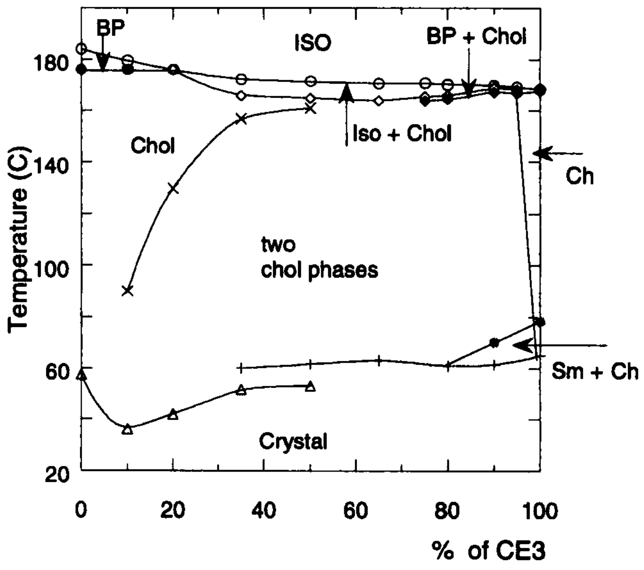

FIGURE 2 Phase diagram for 4745-CE3 blends. The clearing points were deduced from light microscopy and the melting points from DSC.

D' Allest, Gilli and Sioux [3] have observed three blue phases in blends of CE3 and the main-chain nematic polymer DAA-9. Studies of CB15 and CE2, have shown that if the pitch of these highly chiral nematics is increased by adding E9 and CE2R respectively [9,10] additional blue phases are seen. Hence, DAA-9 increases the pitch of CE3 to a much greater extent than 4745, suggesting greater miscibility between DAA-9 and CE3 than with CE3 and 4745. This difference in miscibility may be attributed to the structural differences between 4745 and DAA-9. The spacer unit in DAA-9 contains 10 carbon atoms and thus more flexible than that of 4745 which contains 3 carbon atoms. Also, DAA-9 contains the azo group, which provides a high electron concentration for dipole-dipole interaction.

The phase diagram for the polymer blends is shown in figure 3. The polymers are miscible in the isotropic phase and a single cholesteric phase exists over much of the phase diagram. There is no evidence either from DSC or direct observation for the existence of two cholesteric phases. The solid phases are only partially miscible since two distinct melting points appear on the DSC scans for 4745 compositions between 40-70 %.

A blue phase forms in mixtures that have concentrations of at least 40% of 4745. Also, if a blue-phase forming chiral nematic is mixed with its racemate or a

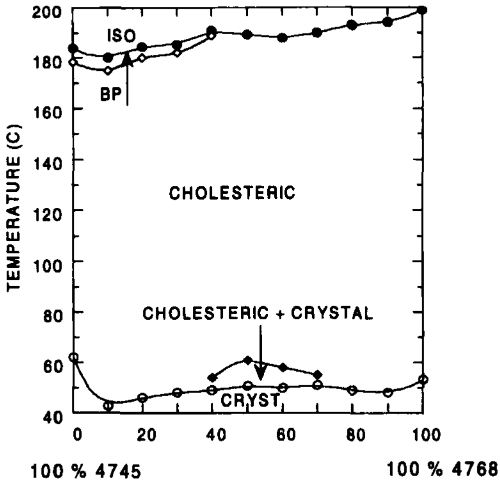

FIGURE 3 Phase diagram for the polymer blends (4745 and 4768). Narrow isotropic-blue phase and isotropic-cholesteric two-phase regions are omitted for clarity.

chiral nematic with a long pitch the blue phase disappears. Thus, with respect to blue phase formation the polymer blends and liquid crystal mixtures are similar.

The miscibility of the chiral polymers was not anticipated. Mitchell and Guo[6] have found that for mixtures of chemically similar acrylate based nematic side-chain polymers, almost complete separation occurs in the nematic phase. However, these polymers have a high degree of polymerization of ~ 200 units. By comparison, the backbone of 4745 or 4768 can have a maximum of 8 Si atoms. Thus, 4745 and 4768 may be miscible like ordinary liquid crystals.

In addition, the polymers each contain two flexible units, the spacer chain and the aliphatic group at the end of the chiral mesogen, which would favour miscibility. This study raises the question whether chiral polymers (chemically similar to 4745 and 4768) having backbones with much larger structural units (a greater number of silicon atoms) would be less miscible.

CONCLUSIONS

We have constructed phase diagrams for polymer liquid crystal blends using DSC and polarized light microscopy. The polymer-polymer blends are miscible over a large temperature and concentration range and they behave like ordinary liquid crystals with regard to blue phase formation and miscibility with each other. The polymer-liquid crystal blends are miscible only in the isotropic phase.

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