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Thermal behavior of the smectic/nematic thermotropic liquid crystalline polyester blends

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SUMMARY

Crystalline and liquid crystalline behavior of the mesogenic binary blends consisting of smectic and nematic liquid crystal polyesters were investigated by differential scanning calorimetry and by polarizing microscope. The blends did not form eutectic mixture and the homopolymers were partially miscible in the solid state. The liquid crystalline phase of the blend showed coexisting nematic and smectic phases at a certain composition.

INTRODUCTION

Numerous investigations have been made on binary mixtures of low molecular weight mesogens. Demus and Sackmann[1] developed the rule of miscibility which was used to identify the smectic polymorphs. These mixtures have played an important role in display technology because of their improved properties compared to the single component.[2] Contrary to such low molecular weight mesogens, very few research results were published on the blends of two different liquid crystalline polymers. There are a few articles[3-5] which described only the mixtures of liquid crystalline polymers with low molecular weight mesogens.

The investigation of the mesogenic binary blends is of considerable importance because of both the possible exploitation of the modified mesogenic materials with unique properties and also for the understanding on the nature of polymeric mesophases. Watanabe and Krigbaum[6] investigated the thermal properties of mesogenic binary homopolymer mixtures based on the 4,4'-dihydroxybiphenyl rigid unit with pairs of dibasic acid having different numbers of methylene units. Jin et al.[7] also studied those of semi-flexible mesogenic homopolyester mixtures. But these investigations were mainly concerned with the binary mixtures having two different components of the same mesogenic type. Very little information has been reported in the literature on the blends containing two components which exhibit different mesogenic modification.

The objective of this study is to investigate the thermal properties of mesogenic binary blends consisting of smectic and nematic type mesogenic polymers. The structural effect of both rigid mesogenic group and the flexible spacer on the crystalline and liquid crystalline phase of the blend was also studied.

EXPERIMENTAL

Two different nematic polyesters, NP6 and NP10, and one smectic polyester(smectic A), SP10, were selected for the present study. The preparation method and properties of the homopolymers were reported earlier by Lenz et al.[8-11]

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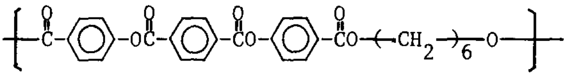
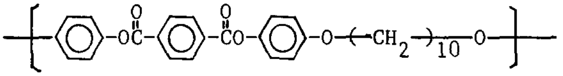
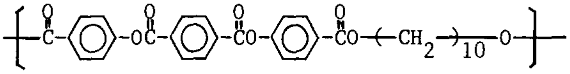


NP6



NP10



SP10

Two types of blends were prepared from the polymers, NP6-SP10 and NP10-SP10. The former contained two components which differed in the length of flexible segment, while the latter contained those with differing in the rigid mesogenic group. The thermal properties of the blends were studied by DSC(du Pont 910) and on a cross-polarizing microscope(Leitz, Ortholux) equipped with a hot stage(Mettler FP-2). All the DSC runs were made under a nitrogen atmosphere with a heating or cooling rate of 10 ^oC/min. The DSC curves obtained on the second heating cycle were used to obtain all of the experimental data. The peak temperature was taken as the transition temperature. DSC data agreed very well with the microscopic observations.

The blends were prepared from the mixtures of the homopolymers using solution/precipitation method. Blends of different composition were prepared by dissolving in the desired weight ratio in p-chlorophenol at 60 ^oC. The total concentration was in the vicinity of 10% in weight. These solution were stirred for 30 min and then added dropwise to a large excess of cold acetone, causing rapid coprecipitation. The precipitate was filtered off and washed with acetone in order to remove p-chlorophenol completely. The final precipitate was dried in vacuum at 90 ^oC for 48 hrs.

RESULTS AND DISCUSSION

The DSC thermograms of the NP6-SP10 blend are illustrated in Fig.1. The phase diagrams of the two blends determined by the DSC curves and from the polarizing microscopic observations are shown in Figures 2 and 3. The peak temperatures of the endothermic transition were used to construct the phase diagrams. As shown in Figures 2 and 3 the phase diagrams are divided into eight regions, A to H. From these phase diagrams, it is found that the two homopolymer blends do not form eutectic mixture and the melting point of each polymer upon mixing is depressed, indicating that the homopolymers are partially miscible in the solid state. For the NP6-SP10 Blend(Fig. 2), the melting point of NP6 crystals shows very slight decrease at concentrations of SP10 component up to 80%. At higher SP10 concentrations, no crystal melting transition of NP6 could be observed. This suggests that at lower concentration of NP6 the crystallization of the polymer is greatly inhibited by the large amount of SP10 (possibly due to the kinetic reasons). The melting temperature of SP10 also exhibits similar behavior as the NP6 concentration is increased. Below 30% of SP10 component concentration, no melting transition is observed for the SP10 crystals and this is related to the disappearance of the smectic mesophase in the liquid crystalline state. The NP6 and SP10 polymers form a single nematic phase in the liquid crystalline state and the crystallization of the SP10 polymer may be restricted because of the difficulties of forming crystals from the nematic state. Mixed crystal phase is observed for the mixtures having concentration of SP10 in the range 30 - 80% (region A). At higher temperature, this mixed phase changes into a mixture of NP6 crystal and smectic liquid crystalline phase of SP10 (region D).

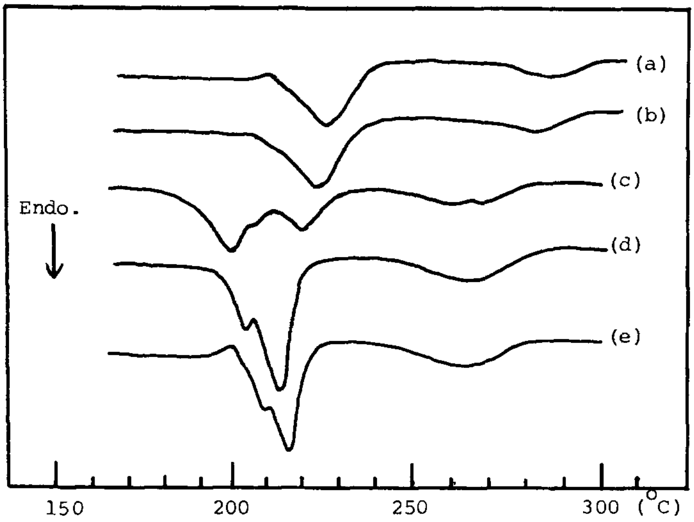


Fig. 1. DSC thermograms of the NP6-SP10 blend; (a) NP6 homopolymer, (b) 15 wt% SP10 component, (c) 50 wt% SP10, (d) 90 wt% SP10, (e) SP10 homopolymer.

For the NP10-SP10 homopolymer blend(Fig.3), similar behavior is also observed. The melting temperatures of both homopolymers are depressed upon the addition of the other polymeric component in the same way as those of NP6-SP10 blend. But at intermediate concentrations of SP10(40-70%), there is a significant depression of the melting point of SP10 crystal which suggests that the NP10 crystals may act as a nucleating agent for the SP10 crystallization. Since the crystallization of both homopolymers at the two extremes of blend composition is suppressed by the predominant component in the mixtures (region B and C), the mixed crystal phase is observed only in the range of 40 - 70% SP10 component concentration. The mixed crystal region of the NP10-SP10 blend is observed in a narrower composition range than that of the NP6-SP10 blend. This is possibly due to the similar chemical structure of the two components of the NP10-SP10 blend.

As shown in the phase diagrams, the isotropic transition temperatures of the homopolymers are depressed smoothly upon addition of the second component, and there are two clearing (isotropization)temperatures (Fig. 1(c))for the mixtures having weight fractions of SP10 in the range of 0.4 - 0.7 for the NP6-SP10 blend and 0.5 - 0.6 for the NP10-SP10 blend. Above the clearing point, isotropic liquid mixtures exist (Region H). It should be noted that a coexistence region of liquid crystalline and isotropic phase exists at this phase boundary line (according to the Gibbs phase rule), which was not given in the diagram. Microscopical examination of these mixtures revealed a wide two phase region for the liquid crystal to isotropic transition, and the DSC data showed rather broad peak for this transition as shown in Fig. 1. The endothermic maxima was chosen for the simplicity of presentation. The liquid crystalline phase of both blend systems is divided into three regions of E,F,and G shown in the diagrams. It shows the existence of a heterogeneous region(region F) in which the nematic and smectic phases are coexisting.

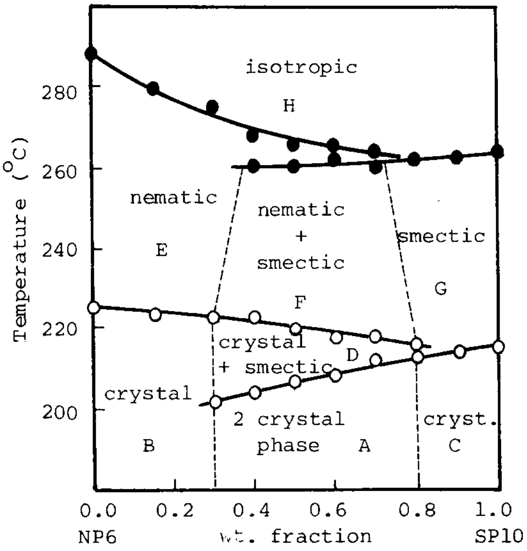


Fig. 2. Phase diagram of the NP6-SP10 blend determined from DSC and polarizing microscope; (●) liquid crystal to isotropic transition, (○) crystal to liquid crystal transition.

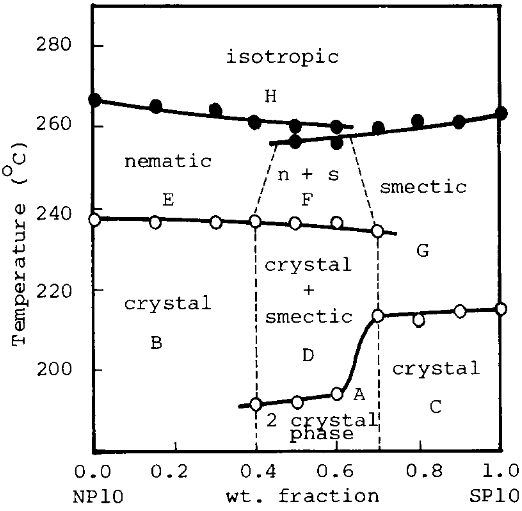


Fig. 3. Phase diagram of the NP10-SP10 blend determined from DSC and polarizing microscope; (●) liquid crystal to isotropic transition, (○) crystal to liquid crystal transition.

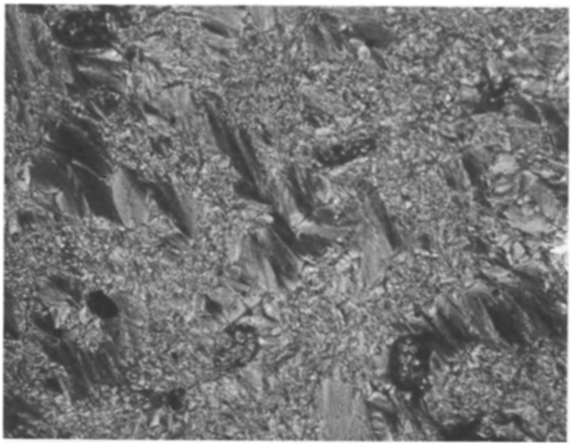


Fig. 4. Microphotography for the equimolar mixture of the NP6-SP10 blend(region F) taken at 240°C. Fan-shaped smectic domains and nematic domains are coexisting (Magnification of 320X).

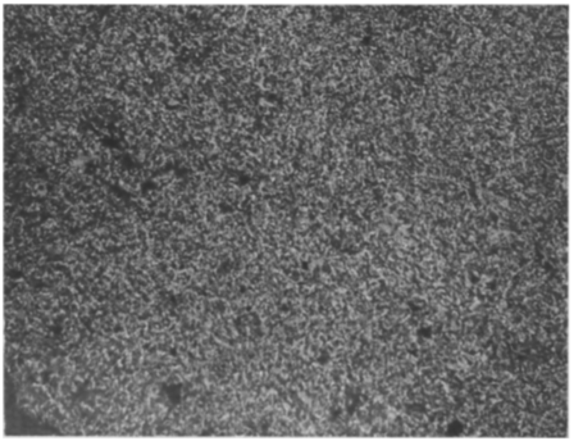


Fig. 5. Microphotography for the mixture of the NP6-SP10 blend having 15 wt% of SP10(region E) taken at 240°C. The homogeneous nematic texture is observed (Magnification of 320X).

In case of the random copolymer containing smectic and nematic repeating units,[12] a smectic to nematic transition was observed at these composition range. The phase separation into two mesogenic phases was confirmed by DSC (Fig. 1(c)) and microscopic observations of the sample as indicated in Fig. 4, which shows the optical texture observed for the NP6-SP10 blend containing 50 wt% of the SP10 components. When this heterogeneous phase is heated, the smectic domain is first transformed to isotropic phase, and the isotropization of the remaining nematic domain is observed. The textures of the NP10-SP10 blend in the two phase region (50 - 60 wt% of SP10) is very similar to those of the NP6-SP10 blend. It should be noted from the phase diagrams that the heterogeneous region of the NP6-SP10 blend can be observed in a wider composition range than that of the NP10-SP10 blend. This indicates that the mixtures consisting of components which differ in the length of flexible spacer show larger incompatibility compared to those which differ in the rigid mesogenic unit.

In contrast to the region F, homogeneous nematic and smectic textures are observed for region E and G respectively. For example,the optical texture of Fig. 5 clearly demonstrates the homogeneous nematic texture of the NP6-SP10 blend having 15 wt% of SP10 in the mesophase. The DSC curves for the mixtures in the region of E and G show only a single broad isotropization peak as shown in Fig. 1(b) & 1(d). Prolonged maintenance of the melts in their mesophases on a hot-stage did not result in any phase separation when observed through a polarizing microscope. These results, for the region E and G, indicate that molecules of a second polymeric mesogen can be accommodated in the other mesophase without disruption of its homogeneous structure.

Thermal behavior of the binary blends in the liquid crystalline state shows nearly the same trend as those known for the binary liquid crystalline low molar mass systems. Further investigations must be made to clarify the extent to which the results obtained can be generalized for other mesogenic polymer mixtures.

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