

Thermal Properties of Liquid Crystalline Aromatic Random Copolyesters Containing Two Different Mesogenic Modifications within a Polymer Backbone

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Synopsis

Two types of semiflexible mesogenic random copolyesters which contained both nematic and smectic type repeating units within the main chain were prepared and the thermal properties as well as the mesomorphic structures were characterized by differential scanning calorimetry and by polarizing microscope. The first type of copolymer (copolymer I) contained two repeating units which differed in the rigid mesogenic groups and the second (copolymer II) contained repeating units which differed in the length of flexible segment. Copolymerization disrupted the structural regularity of the crystal, lowered the crystal-mesophase transition temperature, and destabilized the molecular order of the smectic phase. These effects were more pronounced for copolymer II. However, the isotropization temperature was changed only slightly with the incorporation of the other mesogenic component. The crystal melting temperatures of both copolymers exhibited a eutectic behavior. A smectic to nematic transition, which was not observed for the homopolymers, occurred in the range of 0.4-0.6 mole fractions of the smectic units for copolymer I and 0.5-0.85 for copolymer II. The molecular order of the nematic phase was slightly increased as the smectic units were incorporated, while those of the smectic phase became more disordered upon addition of the nematic units.

INTRODUCTION

Numerous investigations have been made on binary mixtures of low molecular weight mesogens. As an example, Demus and Sackmann¹ developed the so-called rule of miscibility which has been used to identify the mesogenic polymorphs. These mixtures have played an important role in display technology because of their improved properties compared to the single components, including a broader temperature range of the mesophase and a better orientational behavior in an electric field.² Contrary to such low molecular weight mesogens, very few research results were published on the polymeric binary systems containing two different mesogenic repeating units, which can be prepared by mechanical blending of the two mesogenic homopolymers and by random or block copolymerization of the two repeating units. There are a few articles³⁻⁵ which described only the mixtures of liquid crystalline polymers with low molecular weight mesogens.

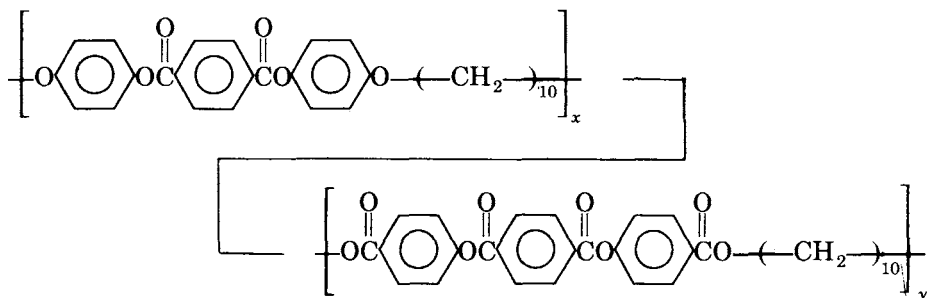
Investigation of the polymeric binary systems is of considerable importance because of both the possible exploitation of modified mesogenic materials with

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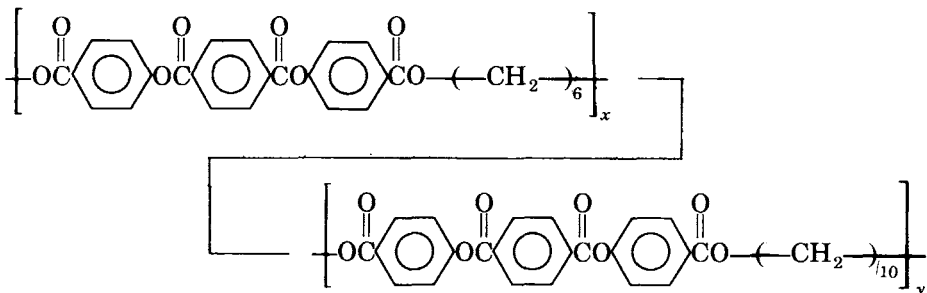
unique properties and profound understanding on the nature of polymeric mesophases. Watanabe and Krigbaum⁶ investigated the thermal properties of mesogenic binary homopolymer mixtures and random copolymers based on the 4,4'-dihydroxybiphenyl rigid unit with pairs of dibasic acid having different numbers of methylene units. Jin et al.⁷ also studied those of semiflexible mesogenic homopolymer mixtures. These investigations were mainly concerned with the binary systems having two different components of the same mesogenic type such as smectic-smectic, nematic-nematic, or nematic-cholesteric. However, very little information has been reported in the literature on the binary systems containing two components which exhibit different mesogenic modification.

The objective of this study therefore is to investigate the mesomorphic properties of binary systems formed by random copolymers, which contained both nematic and smectic type repeating units within a polymer backbone. In order to investigate the structural effects of both rigid mesogenic group and the flexible spacer on the crystalline and liquid crystalline phases of the copolymers, two types of such random copolymers were prepared with the following structures:

(1) Copolymer I contained two repeating units which differed in the rigid mesogenic groups.



(2) Copolymer II contained those with differing in the length of the flexible spacer.

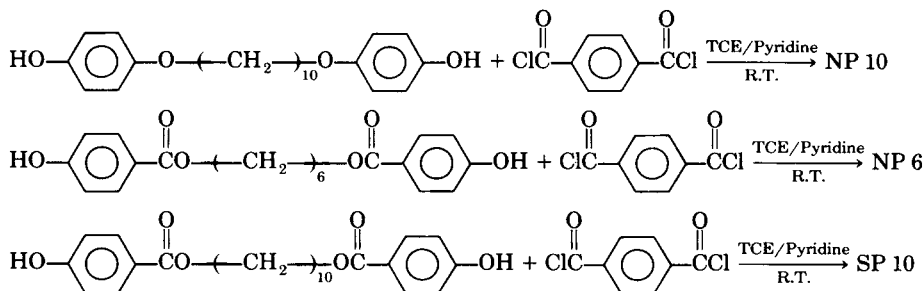


The investigation of these copolymers has the advantage that the crystalline and liquid crystalline behavior of the homopolymers has been well characterized in several studies.⁸⁻¹¹ Thermal behavior of the copolymers was determined by differential scanning calorimetry (DSC) and by the polarizing microscopy.

EXPERIMENTAL

Preparation of Materials

The preparative methods for three biphenol monomers were described in earlier reports.^{12,13} The homopolymers were prepared by reacting the monomers with terephthaloyl dichloride at room temperature^{13,14} as shown below.



1,1,2,2-tetrachloroethane (TCE) was used as the reaction medium and pyridine as an HCl acceptor. The homopolymers prepared from 4,4'-dihydroxy-1,10-diphenoxydecane (NP10) and 1,6-bis(4-hydroxybenzoyloxy)hexane (NP6) formed nematic mesophases, whereas the homopolymer from 1,10-bis(4-hydroxybenzoyloxy)-decane (SP10) formed smectic A in liquid crystalline state. The synthetic methods of random copolymers were very similar to those of homopolymers. Copolymer I was prepared by reacting the mixtures of NP10 and SP10 monomers with terephthaloyl dichloride, and copolymer II was prepared from the mixtures of NP6 and SP10 monomers and terephthaloyl dichloride.

Measurements

Structural analysis. The structures of the monomers and polymers were confirmed by infrared (IR) spectra obtained on a JASCO A-102 IR spectrophotometer. The structures of the monomers were further confirmed by their proton nuclear magnetic resonance (NMR) spectra obtained on Varian T60A (60 MHz) NMR instrument.

Solution Viscosity. Inherent viscosities of the polymers were determined at 45°C using 0.5 g/dL solutions in a *p*-chlorophenol. Ubbelohde type viscometer was used.

DSC Analysis. Thermal behavior of the polymers was determined by Du Pont 910 Thermal Analyzer. All the runs were made under a nitrogen atmosphere with a heating or cooling rate of 10°C/min. The DSC curves obtained on second heating cycles were used to obtain all of the experimental data. The peak temperature was taken as the transition temperature. The calculated values of ΔH_i and ΔS_i were from the endothermic peak area in the thermogram. Indium ($\Delta H_m = 6.8$ cal/g) was used as a standard.

Thermal Gravimetric Analysis (TGA). Thermal stability of the homopolymers was determined with Du Pont 1090 TGA instrument at a scanning rate of 20°C/min.

TABLE I
Inherent Viscosities and Thermal Properties of Homopolymers^a

Polymer	η_{inh}	T_m	T_i	T_{di} ^b	ΔT ^c	T_{de} ^d	ΔH_i	ΔS_i
NP10	0.54	238	267	265	29	385	0.6	1.1
NP6	0.32	226	288	285	62	390	0.5	0.9
SP10	0.43	216	264	255	48	380	1.9	3.5

^a T values are in °C. ΔH , ΔS values are in kcal/mol, cal/mol · K.

^bDeisotropization temperature.

^cTemperature range of the mesophase ($T_i - T_m$).

^dThermal degradation temperature (5 wt% loss).

Optical Analysis. The optical textures of the polymers in liquid crystalline state were observed on a hot stage (Mettler FP-2) attached to a polarizing microscope (Leitz, Ortholux).

RESULTS AND DISCUSSION

General

All the homopolymers and copolymers were soluble in *p*-chlorophenol and trifluoromethanesulfonic acid, and the molecular weights of the polymers were relatively low as reflected by their low inherent viscosity in *p*-chlorophenol solution (Table I). Most of the polymers exhibited the multiple melting endotherms on DSC analysis, as shown in Figures 1 and 2. Similar multiple transitions were reported for other thermotropic liquid crystal polymers with mesogenic units connected by flexible spacers in the main chain.^{15,16} This complex thermal behavior may be due to the factors such as solid-solid phase transitions, various polymorphic crystal forms, or reorganization of the pre-formed crystallite.^{17,18} All of the polymers exhibited a rather broad endothermic peak at the clearing temperature of the mesophase as shown in Figures 1 and 2. According to Antoun et al.,⁸ the polydispersity of the molecular weight as well as the kinetic effects that affect the transitions are the major factors that lead to the occurrence of the broad endotherm. We chose the peak maxima for simple interpretation. These clearing transitions and the smectic to nematic transitions which were observed only for some copolymers occurred reversibly, indicating that all the present polymers are enantiotropically thermotropic. The transition from the isotropic phase to the liquid crystal phase (deisotropization) in all cases showed smaller degree of supercooling compared to the recrystallization process.

Homopolymers

The thermal properties of the homopolymers synthesized and their inherent viscosities are listed in Table I. The transition temperatures and thermodynamic parameters are relatively in good agreement with those reported in earlier papers.^{8,13} An interesting aspect to be noted from the table is that the

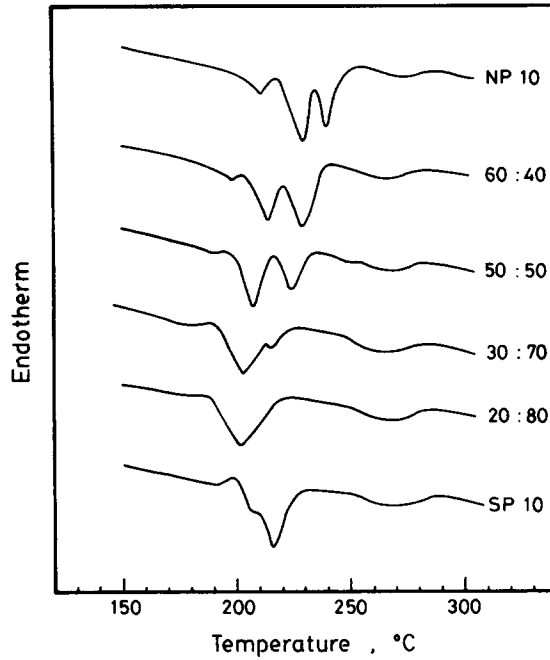


Fig. 1. Typical DSC thermograms of copolymer I taken at 10°C/min. A smectic to nematic transition is observed for the 50:50 copolymer.

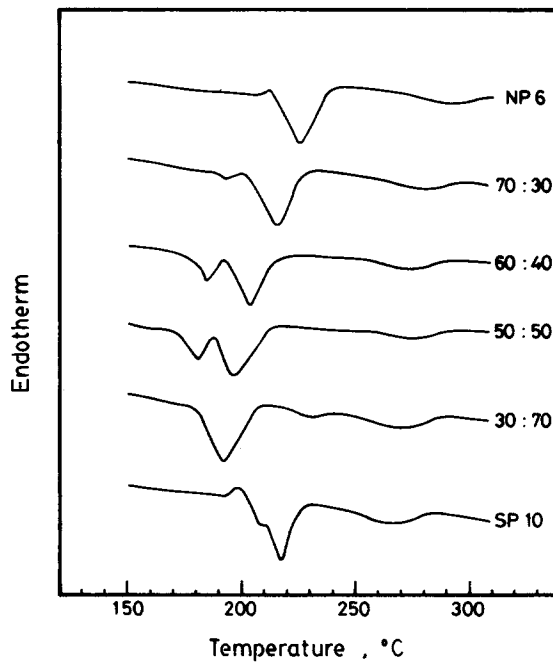


Fig. 2. Typical DSC thermograms of copolymer II taken at 10°C/min. S → N transition is observed for the 30:70 copolymer.

deisotropization of SP10 homopolymer showed a relatively higher degree of supercooling compared to those of NP10 and NP6, as indicated by ($T_i - T_{di}$). It is now commonly agreed that the deisotropization shows very low supercooling,¹⁹ but much higher supercooling has been observed for more highly organized smectic mesophase such as smectic H mesomorph.²⁰ This suggests that the formation of the highly ordered smectic layer from the isotropic state is more difficult and slower than that of the lower ordered nematic phase. This higher degree of supercooling of the smectic mesophase is of considerable interest because of the opportunity which it offers to expand our knowledge to the kinetics of the deisotropization, but no information has been reported in the literature on the deisotropization kinetics.

Another interesting fact is that NP10 and NP6 homopolymers showed approximately the same value of the entropy change in isotropization (ΔS_i), while SP10 showed much higher value of ΔS_i than those of NP10 and NP6. As discussed in an earlier report,¹⁰ this shows indirectly that the NP10 and NP6 have identical nematic phase structures and SP10 forms higher ordered smectic phase. Values of ΔS_i should give some indication of the order present in the mesophase, but the absolute values for ΔS_i are not an exact indication of the degree of order of the mesophase. It should be also noted that NP6 homopolymer showed broader temperature range of the mesophase (ΔT) and higher thermal degradation temperature (T_{de}) than those of either polymer NP10 and SP10, indicating that NP6 is thermally most stable among the homopolymers.

Copolymers

Crystalline Melting Behavior. The transition temperatures and thermodynamic data of copolymers I and II, as determined by the DSC heating thermograms and the observation on the polarizing microscope, are summarized in Tables II and III. Typical DSC thermograms for the copolymers are illustrated in Figures 1 and 2, respectively. For copolymer I, the multiple melting endotherms of both homopolymers become more simplified as other

TABLE II
Transition Temperatures and Thermodynamic Data for Copolymer I^a

Polymer	T_m	T_{n-i}	T_{s-n}	T_{s-i}	ΔH_{n-i}	ΔH_{s-n}	ΔH_{s-i}	ΔS_{n-i}	ΔS_{s-n}	ΔS_{s-i}
NP10	238	267			0.6			1.1		
90 : 10	237	265			0.7			1.2		
80 : 20	236	264			0.6			1.1		
60 : 40	229	263	232 ^b		0.8	— ^c	—	1.5	—	—
50 : 50	224	262	249		0.8	0.3	1.1	1.5	0.6	2.1
40 : 60	220	260	256 ^b		—	—	1.0	—	—	2.0
30 : 70	216			260			1.2			2.2
20 : 80	201			262			1.1			2.1
10 : 90	206			260			1.5			2.8
SP10	216			264			1.9			3.5

^a T values are in °C. ΔH , ΔS values are in kcal/mol, cal/mol · K.

^bEstimated from visual observations on the polarizing microscope.

^cCannot be measured.

TABLE III
 Transition Temperatures and Thermodynamic Data for Copolymer II^a

Polymer	T_m	T_{n-i}	T_{s-n}	T_{s-i}	ΔH_{n-i}	ΔH_{s-n}	ΔH_{s-i}	ΔS_{n-i}	ΔS_{s-n}	ΔS_{s-i}
NP6	226	288			0.5			0.9		
85:15	223	282			0.6			1.1		
70:30	216	276			0.6			1.1		
60:40	203	272			0.7			1.3		
50:50	195	272	201 ^b		0.9	— ^c	—	1.6	—	—
40:60	184	269	210		0.8	0.2	1.0	1.5	0.4	1.9
30:70	192	264	226		0.9	0.2	1.1	1.7	0.4	2.1
15:85	210	262	258 ^b		—	—	1.3	—	—	2.5
SP10	216			264			1.9			3.5

^a T values are in °C. ΔH , ΔS values are in kcal/mol, cal/mol · K.

^bEstimated from visual observations on the polarizing microscope.

^cCannot be measured.

repeating units are incorporated, leading to a single, broad melting peak such as shown in copolymer with 0.8 mole fraction SP10 units. This indicates that copolymerization, as expected, disrupts the structural regularity of the crystal, decreases the degree of crystallinity, and simplifies the crystallite structure. In contrast to the copolymer I, the crystal melting transition of copolymer II exhibit an unexpected behavior. As shown in Figure 2, an additional endothermic peak appears in the DSC curves for the copolymers having mole fraction of SP10 units in the range of 0.3–0.5. All other copolymers exhibit only a single melting endotherm as shown for 30:70 copolymer. This transition is illustrated in the phase diagram shown in Figure 4. The appearance of the additional peak is possibly due to the formation of new crystal form. The occurrence of a new crystal structure has been observed for other mesogenic copolymer systems⁶ containing two components with differing in the flexible spacer length. As shown in the phase diagrams (Figs. 3 and 4), the crystal

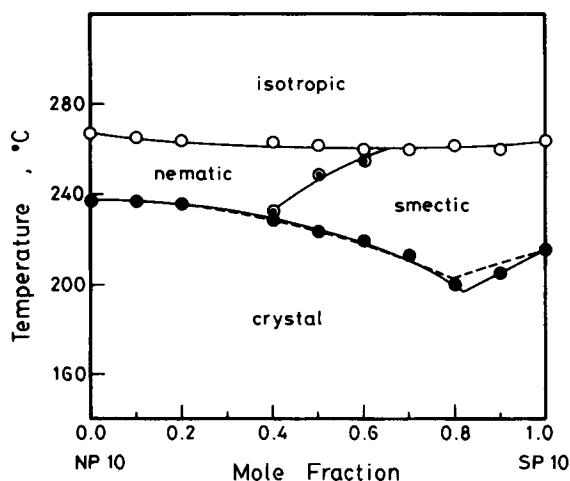


Fig. 3. Phase diagram based on the DSC heating curves and polarizing microscope for copolymer I having different composition.

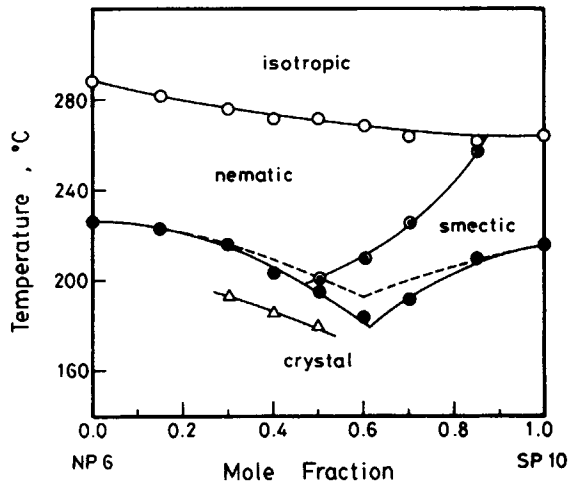


Fig. 4. Phase diagram for copolymer II as constructed from DSC heating curves and polarizing microscope.

melting temperatures of both components for copolymer I are depressed by a relatively modest amount since both units have similar chemical structure, leading to a eutectic composition at 0.8 mole fraction of SP10. Hence, each component of the copolymer crystallizes separately and independently. Copolymer II also exhibits a eutectic behavior at a composition of approximately 0.6 mole fraction, but the melting temperatures are more strongly depressed upon the addition of the second comonomer than those of copolymer I due to the large difference in the length of flexible spacer. From these observations, we find that the structure of the crystalline phase is more seriously perturbed by the presence of two repeating units which differ in the flexible spacer length.

The dashed line in the phase diagrams represents the calculated melting temperatures of the copolymers according to the following equation, well established by Flory.²¹

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_f} \ln N_A$$

where ΔH_f is the heat of fusion per mole of A repeating unit and N_A is their mole fraction in the random copolymer. The values of ΔH_f for NP10, NP6, and SP10 homopolymers are 23.9, 17.4, and 21.1 kcal/mole, respectively, which are estimated from group contributions.²² The eutectic composition and the melting temperatures calculated from the equation are in relatively good agreement with those obtained experimentally as can be seen in the phase diagrams (Figs. 3 and 4). The small deviation between the calculated and the observed values is possibly due to the polydisperse nature of the polymers and the estimated values of ΔH_f .

Liquid Crystalline Behavior. As shown in the phase diagrams, the isotropization temperature curves are nearly linear, in contrast to the melting temperatures, exhibiting the absence of a depression of the clearing temperature upon the addition of the other mesogenic repeating unit. This suggests that the second unit of the different mesogenic type can be accommodated in the mesophases without serious structural disruption to the extent of lowering the transition temperatures. Such slight change of the clearing transition has been generally observed in the binary systems composed of the same mesogenic type components.³⁻⁷ We conclude from this observation that copolymerization disrupts the structure of the crystalline phase much more than that of the liquid crystalline phase. Copolymerization lowers the crystal-mesophase transition temperature but does not affect the isotropization temperature as discussed above, so that the temperature range of the mesophase is increased. For example, the temperature span of the mesophase is broadened to almost 80°C for the equimolar composition of copolymer II. In view of technological application, this broad temperature range of the mesophase is of importance as is well known for the mixture of low molecular weight mesogens.

The thermotropic melts of both copolymers showed a smectic to nematic transition, which was not observed for the homopolymers, in the range of 0.4-0.6 mole fraction of SP10 for copolymer I and 0.5-0.85 for copolymer II as shown in the phase diagrams. This transition occurred reversibly. The DSC thermogram appearing in this transition is illustrated in Figures 1 and 2. In this region, the phases change from solid crystal to smectic, nematic, and isotropic phase with increasing temperature. The smectic structure for this region is relatively unstable because of the higher content of nematic-type repeating units (NP10, NP6), so that, when the smectic phase is heated, the layer structure of the mesophase is changed to one-dimensional nematic structure. Figure 5 illustrates a typical optical texture of this transition observed for the equimolar composition of copolymer I. Figure 5(a) shows the smectic texture of the copolymer observed at 235°C. When this smectic phase was heated, it was observed to transform to the nematic phase [Fig. 5(b)]. Further heating produced the nematic schlieren texture [Fig. 5(c)]. On cooling the sample to 220°C, a typical smectic fan-shaped texture was observed again [Fig. 5(d)]. Of considerable interest in the phase diagrams is the observation that the nematic phase of copolymer II is observed for the higher composition range of SP10 units than that of copolymer I. This indicates that the formation of smectic layer is more strongly inhibited by the presence of two repeating units differing in the spacer length compared to those with different rigid units. From these observations, we find that the difference of the flexible unit has a more significant effect on the crystalline structure and the formation of smectic layer than that of the rigid mesogenic group.

The enthalpy and entropy changes for both copolymers are listed in Tables II and III. Figure 6 shows how the values of ΔS_i for copolymer I change with the incorporation of the other mesogenic repeating units. The thermodynamic parameters give further information on the mesophase structure. The entropy change from the mesophase to the isotropic state decreases with the addition of NP10 units. ΔS_{n-i} slightly increases with increasing mole fraction of SP10



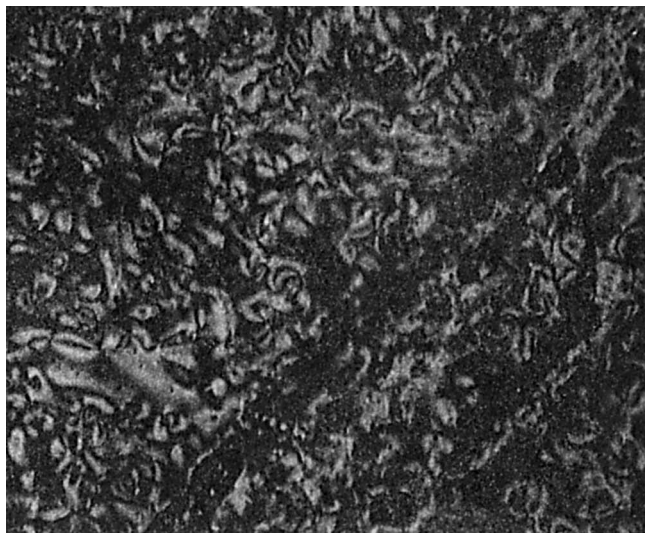
(a)



(b)

Fig. 5. (a) Fan-shaped texture observed for the smectic phase of the copolymer I having 0.5 mole fraction SP10 units upon heating to 235°C (magnification of 320X). (b) Texture of the S \rightarrow N transition found on heating the sample at 250°C. (c) Nematic Schlieren texture found at 260°C. (d) Fan-shaped smectic texture found on cooling the same sample at 220°C.

units, whereas $\Delta S_{s \rightarrow i}$ decreases with increasing NP10 units. This indicates that the incorporation of smectic mesogenic repeating units increases the order of the nematic mesophase and the smectic mesophase becomes more disordered as NP10 units are incorporated. The entropy changes for copolymer II exhibits the same trend as those for copolymer I.



(d)

Fig. 5. (Continued from the previous page.)

The structural effects discussed above apply only to the copolymer systems described in this paper, and different results might be anticipated for systems in which the spacer length and rigid unit are changed. Further investigations on the mechanical blends and block copolymers prepared from two different components of different mesogenic type is being carried out.

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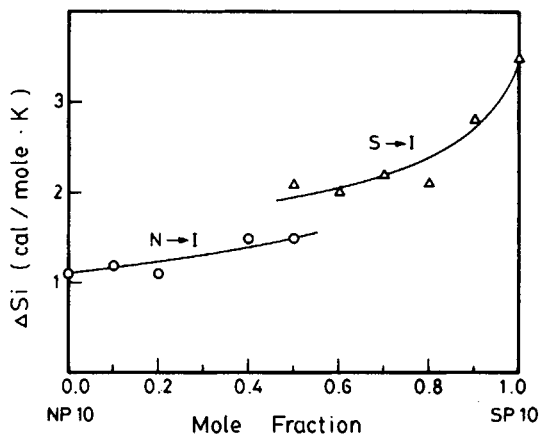


Fig. 6. Entropy changes for the mesophase-isotropic transitions of copolymer I; (○) nematic to isotropic, (Δ) smectic to isotropic transition.

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