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Induction of the Smectic Phase in the Polymer Complexes between Electron-Accepting Ionic Nitrostilbazoles and Electron-Donating Liquid-Crystalline Polymers

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ABSTRACT: A new type of miscible polymer complex was prepared from electron-accepting *trans-N*-alkyl-4-nitro-4′-stilbazolium bromides or iodides and electron-donating polymers containing a mesogenic (carbazolylmethylene)aniline. The 1:1 (mole ratio) polymer complexes showed smectic behavior. For example, the 1:1 polymer complex of *trans-N*-hexyl-4-nitro-4′-stilbazolium bromide and the electron-donating polyacrylate exhibited a smectic A phase from 75 to 140 °C, although the smectic phase did not appear in both individual components. The isotropic temperature of these polymer complexes increased with increasing carbon number of the alkyl chain in the nitrostilbazolium bromide. Similar tendencies on the thermal behavior were observed for the complexes of the ionic nitrostilbazoles and a low-molecular-weight nematic compound containing the same carbazolyl group. It was concluded that the miscibility and the induction of the smectic phases are caused by the complex formation between the ionic nitrostilbazole group and the nonionic mesogenic (carbazolylmethylene)aniline group by ionic and electron donor–acceptor interactions.

Introduction

The mixing of liquid crystals has been utilized for the control of mesogenic properties for low-molecular-weight compounds and the identification of mesophases.[1,2]

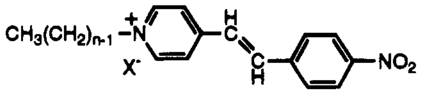
Recently, new classes of liquid-crystalline mixtures have been prepared through hydrogen bonds,[3–8] ionic interactions,[9–11] and electron donor–acceptor interactions.[12–21] These liquid-crystalline compounds exhibited the thermal stability and the induction of mesophases. The electron donor–acceptor interaction is one of the interactions which causes miscibility between two kinds of compounds. For example, this behavior appears when electron donor–acceptor interactions act between two kinds of compounds, i.e., one having such highly polar groups as nitro, cyano, and isothiocyanato as electron acceptors and the other having such nonpolar groups as alkyl and alkyloxy as electron donors. Liquid-crystalline polymers by electron donor–acceptor interactions were also reported on main-chain and side-chain polymers.[22–25]

Previously, we reported that the miscibility and the induction of smectic phases in the copolymers and the blends of polymers were caused by intermolecular electron donor–acceptor interactions.[20,21,26,27] Moreover, a new type of miscible liquid-crystalline complex was prepared from low-molecular-weight nonionic (carbazolylmethylene)anilines as the electron donor and ionic nitrostilbazoles as the electron acceptor.[12] These complexes showed stable smectic phases.

In this paper, we wish to report the thermal properties and the miscibility of the mixtures of electron-donating liquid-crystalline polymers with electron-accepting ionic low-molecular-weight compounds. The polymers contain a mesogenic (carbazolylmethylene)aniline group and the low-molecular-weight compounds have a nitrostilbazolium group (Chart 1). The liquid-crystalline properties of the mixtures of low-molecular-weight ionic compounds with mesogenic compounds were also examined. These mixtures were characterized by optical polarizing microscopy, differential scanning calorimetry, and X-ray diffractometry.

Chart 1. Molecular Structures of (A) Electron-Accepting *n*XSzNO$_2$ and (B) Electron-Donating HCMA, PA6Cz, and PM6Cz

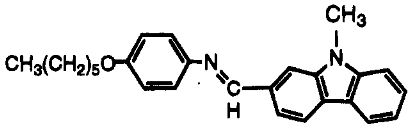
(A) Electron-accepting compounds



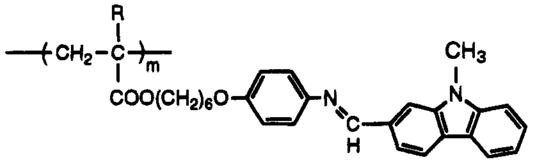
nXSzNO$_2$

n: 5-10; X: Cl, Br, or I
SzNO$_2$: nitrostilbazole group

(B) Electron-donating compounds



HCMA (K 91 N 122 I)



R = H: PA6Cz (g 69 N 169 I)
CH$_3$: PM6Cz (g 79 N 172 I)

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Table 1. Thermal Properties of *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium Halides (nXSzNO$_2$s)[a]

n	X	phase transition temp[b] (°C)	ΔH_i[c] (kJ/mol)
5	Br	K 146 I	
6	Cl	K 129 $\mathrm{S_A}$ 190 I	4.8
6	Br	K 149 I	
6	I	K 193 I[d]	
7	Br	K 146 $\mathrm{S_A}$ 168 I	6.7
8	Br	K 170 $\mathrm{S_A}$ 175 I	5.8
9	Br	K 154 $\mathrm{S_A}$ 175 I	5.1
10	Cl	K 167 $\mathrm{S_A}$ 227 I[d]	6.2[d]
10	Br	K 175 $\mathrm{S_A}$ 186 I	4.7
10	I	K 147 I	

[a] Reference 12. [b] Transition temperature (°C) determined by DSC at 10 deg/min on the first (6ISzNO$_2$ and 10ClSzNO$_2$) and the second heating rungs and by microscopic observation. K: crystalline. $\mathrm{S_A}$: smectic A. I: isotropic. [c] Measured by DSC. ΔH_i: enthalpy change in the clearing. [d] Partial decomposition observed.

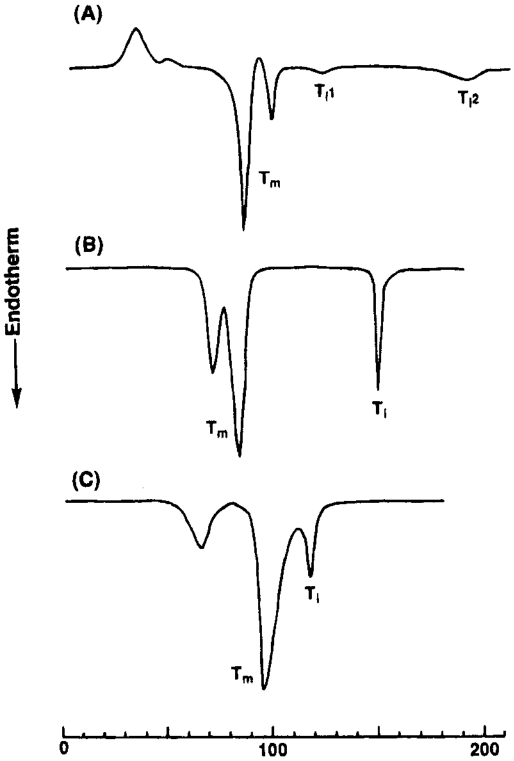


Figure 1. DSC thermograms of the 1:1 binary mixtures of (A) 6ClSzNO$_2$ with HCMA, (B) 6BrSzNO$_2$ with HCMA, and (C) 6ISzNO$_2$ with HCMA on the second heating run at 10 deg/min.

Results and Discussion

Thermal Properties of Binary Mixtures of Low-Molecular-Weight Compounds, nXSzNO$_2$ and HCMA. *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium halides (nXSzNO$_2$, n = 5–10; X = Cl, Br, I; SzNO$_2$, nitrostilbazole group)[12] and 4-(hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA)[20] were chosen as ionic electron-accepting and as nonionic electron-donating compounds, respectively. The molecular structures and the thermal properties of these compounds are shown in Chart 1 and Table 1.

Table 2. Thermal Properties of the 1:1 Binary Mixtures of *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium Halides with 4-(Hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (nXSzNO$_2$–HCMA)

1:1 mixture	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)
6ClSzNO$_2$–HCMA	phase separation	
6BrSzNO$_2$–HCMA	K 83 $\mathrm{S_A}$ 149 I	2.9
6ISzNO$_2$–HCMA	K 96 $\mathrm{S_A}$ 118 I	2.2
10ClSzNO$_2$–HMA	phase separation	
10BrSzNO$_2$–HCMA	K 88 $\mathrm{S_A}$ 168 I	3.5
10ISzNO$_2$–HCMA	K 107 $\mathrm{S_A}$ 150 I	3.3

[a] Transition temperature (°C) determined by DSC at 10 deg/min on the second heating run and by microscopic observation. K: crystalline. $\mathrm{S_A}$: smectic A. I: isotropic. [b] Measured by DSC. ΔH_i: enthalpy change in the clearing.

The binary mixture of nXSzNO$_2$ with HCMA were prepared by evaporation of chloroform solutions of these mixtures. The DSC thermograms of the 1:1 (mole ratio) binary mixtures of HCMA with 6XSzNO$_2$ having chloride, bromide, or iodide as a halide are given in Figure 1. For the binary mixture of 6ClSzNO$_2$ with HCMA, crystallization did not occur on the first cooling. On the second heating, an exotherm peak corresponding to the crystallization of HCMA and endotherm peaks due to the meltings and the isotropizations were observed for the mixture (Figure 1A). The endotherm peaks at 122 (T_{i1}) and 188 °C (T_{i2}) may correspond to the isotropic transitions of individual components, taking into account the microscope observation. These results suggest that the mixture caused phase separation. On the other hand, for the 1:1 binary mixtures of HCMA with 6BrSzNO$_2$ or 6ISzNO$_2$, crystalline–crystalline, crystalline–mesomorphic, and mesomorphic–isotropic transition peaks appeared, with no endothermic peaks originating from the individual components. These binary mixtures showed focal-conic fan and homeotropic textures on the microscopic observation, indicating that they have smectic A phases. The smectic A phases were observed from 83 to 149 °C and from 96 to 118 °C, respectively, though the smectic phase did not appear in both individual components (Table 2).

A similar tendency was observed for other mixtures having different alkyl groups. For instance, the 1:1 binary mixture of HCMA with 10ClSzNO$_2$ which has a decyl chain at the terminal showed phase separation. On the contrary, the mixtures having the bromide or the iodide exhibited smectic phases from 88 to 168 °C and from 107 to 150 °C, respectively. It is presumed that since a contact ion pair is formed between chloride and pyridinium groups by a stronger ionic interaction, the nClSzNO$_2$ acts as a weak electron acceptor which eventually holds a localized cationic charge. On the other hand, the bromide and iodide compounds containing a pyridinium group work as a stronger electron acceptor, probably because in both bromides and iodides a cationic charge is delocalized through the stilbazolium. The nBrSzNO$_2$–HCMA complex has a wider mesophase temperature range than the iodide homologue, exhibiting the formation of a more stable smectic phase. The enthalpy changes in the clearing for these complexes ranged from 2.2 to 3.5 kJ/mol.

The thermal properties of the 1:1 nBrSzNO$_2$–HCMA complexes are listed in Table 3. For the nBrSzNO$_2$–HCMA complexes, the transition temperatures are plotted as a function of carbon number of the alkyl chain in nBrSzNO$_2$ (Figure 2). All complexes exhibited stable smectic phases. For example, the 5BrSzNO$_2$–HCMA complex showed a smectic phase from 98 to 135 °C, although both individual components, i.e., 5BrSzNO$_2$ and HCMA, exhibited no smectic phase. The smectic phase was observed from 88 to 168 °C for the 10BrSzNO$_2$–HCMA complex. The isotropic temperature of these complexes increased with increasing carbon number of the alkyl chain in nBrSzNO$_2$. These isotropic temperatures were approximately 15 deg higher than the calculated value based on the proportion of the individual components. The odd–even effect was

Table 3. Thermal Properties of the 1:1 Complexes of *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium Bromides with 4-(Hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (*n*BrSzNO$_2$−HCMA)

1:1 complex	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)
5BrSzNO$_2$−HCMA	K 98 S$_A$ 135 I	3.3
6BrSzNO$_2$−HCMA	K 83 S$_A$ 149 I	2.9
7BrSzNO$_2$−HCMA	K 112 S$_A$ 160 I	3.7
8BrSzNO$_2$−HCMA	K 90 S$_A$ 162 I	2.7
9BrSzNO$_2$−HCMA	K 92 S$_A$ 166 I	3.7
10BrSzNO$_2$−HCMA	K 88 S$_A$ 168 I	3.5

[a] Transition temperature (°C) determined by DSC at 10 deg/min on the second heating run and by microscopic observation. K: crystalline. S$_A$: smectic A. I: isotropic. [b] Measured by DSC. ΔH_i: enthalpy change in the clearing.

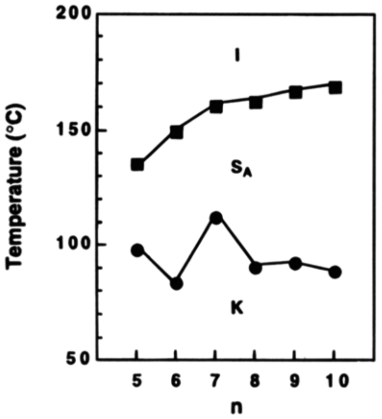


Figure 2. Dependence of the transition temperatures on the carbon number of the alkyl chain in *n*BrSzNO$_2$ for the 1:1 *n*BrSzNO$_2$−HCMA complexes.

Table 4. Thermal Properties of the 1:1 Polymer Mixtures of *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium Halides with Poly[(4-[[6-(acryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (*n*XSzNO$_3$−PA6Cz)

1:1 mixture	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)
6ClSzNO$_2$−PA6Cz	phase separation	
6BrSzNO$_2$−PA6Cz	g 75 S$_A$ 140 I	2.0
6ISzNO$_2$−PA6Cz	g 52 N 123 I	0.5
10ClSzNO$_2$−PA6Cz	phase separation	
10BrSzNO$_2$−PA6Cz	g 69 S$_A$ 168 I	2.0
10ISzNO$_2$−PA6Cz	g 65 S$_A$ 140 I	2.0

[a] Transition temperature (°C) determined by DSC at 10 deg/min on the second heating run and by microscopic observation. g: glassy. S$_A$: smectic A. N: nematic. I: isotropic. [b] Measured by DSC. ΔH_i: enthalpy change in the clearing.

seen for the crystalline−smectic transition temperature for the 1:1 *n*BrSzNO$_2$−HCMA complexes. The enthalpy changes in the clearing for these complexes were between 2.7 and 3.7 kJ/mol and showed an alternation tendency.

Liquid-Crystalline Properties of Polymeric Complexes of *n*BrSzNO$_2$ with PA6Cz. Poly[4-[[6-(acryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (PA6Cz)[28] and a polymethacrylate homologue (PM6Cz)[26] as electron-donating polymers showed nematic phases from 69 to 169 °C and from 79 to 172 °C, respectively (Chart 1). Thermal properties of 1:1 mixtures of the polyacrylate with *n*XSzNO$_2$ are given in Table 4. The 1:1 *n*XSzNO$_2$−PA6Cz mixtures had thermal behaviors similar to those of the 1:1 binary mixtures of *n*XSzNO$_2$ with monomeric HCMA.

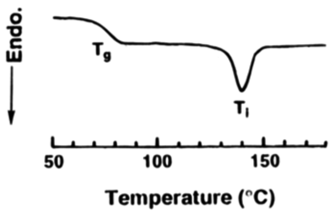


Figure 3. DSC thermogram of the 1:1 6BrSzNO$_2$−PA6Cz complex on the second heating run at 10 deg/min.

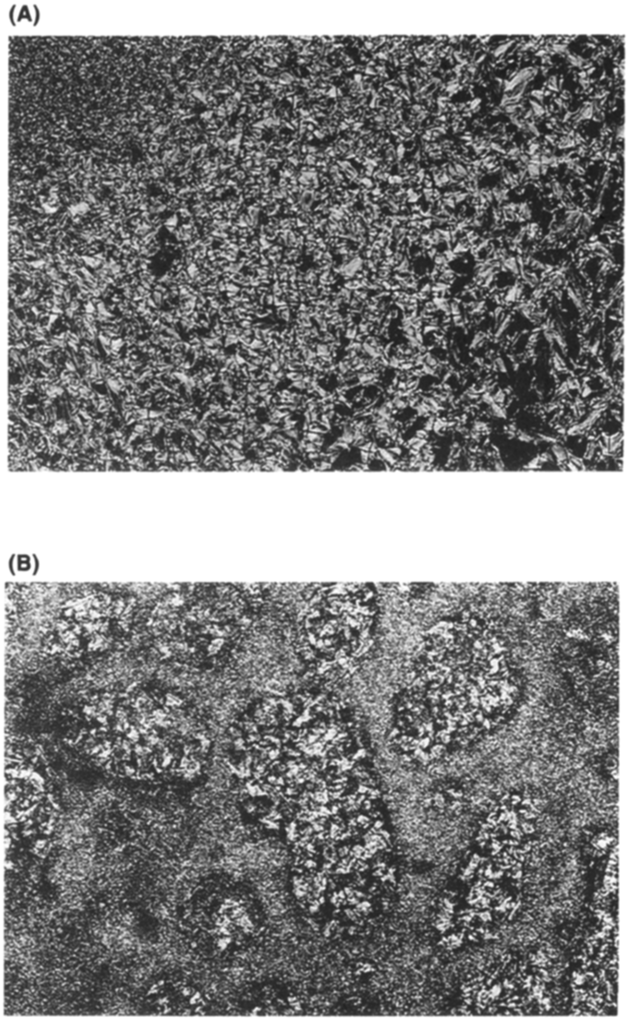


Figure 4. Optical polarized microphotographs of the 1:1 polymer mixtures of (A) 6BrSzNO$_2$ with PA6Cz at 130 °C and (B) 6BrSzNO$_2$ with PM6OMe at 120 °C on cooling.

Although the *n*ClSzNO$_2$−PA6Cz mixtures showed phase separation, the miscible polymer mixtures were obtained when X in *n*XSzNO$_2$ was Br or I. In addition, in the polymer mixtures of PA6Cz with 6BrSzNO$_2$ or 10ISzNO$_2$, the induction of the smectic phase was observed. For example, the 10ISzNO$_2$−PA6Cz mixture exhibited a smectic phase from 65 to 140 °C. A typical DSC thermogram of the 1:1 6BrSzNO$_2$−PA6Cz mixture showed the existence of the glass transition at 75 °C and the smectic−isotropic transition at 140 °C (Figure 3). Both microscopic and DSC studies revealed that the mixture had the miscible smectic phase (Figure 4A). No change in UV spectra of the mixture solution in chloroform was detected. However, miscible red mixtures were obtained from PA6Cz with *n*BrSzNO$_2$ or *n*ISzNO$_2$. The induction of the smectic phase and the miscibility revealed that the electron donor−acceptor interaction acted in the complex. On the other hand, for the 1:1 polymer mixture of 6BrSzNO$_2$ with a liquid-crystalline polymethacrylate containing an electron-donating (4-methoxybenzylidene)aniline group (PM6OMe) (Chart 2),[26] phase separation was observed, as shown in Figure 4B.

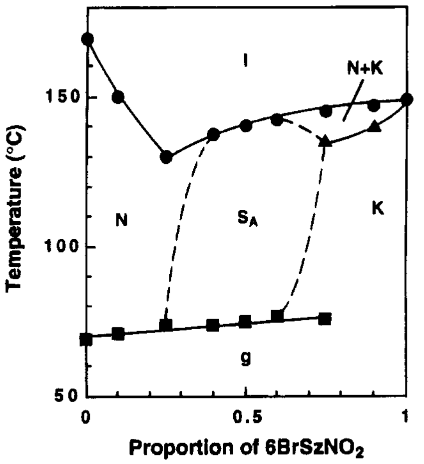
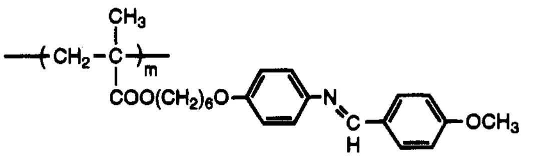


Figure 5. Phase diagram of the polymer mixtures of PA6Cz and 6BrSzNO$_2$ as a function of the proportion of 6BrSzNO$_2$.

Chart 2. Molecular Structure of PM6OMe



PM6OMe (g 56 N 123 I)

Table 5. Thermal Properties of the 1:1 Polymer Complexes of *trans*-*N*-Alkyl-4-nitro-4′-stilbazolium Bromides with Poly[4-[[6-(acryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (nBrSzNO$_2$–PA6Cz)

1:1 complex	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)
5BrSzNO$_2$–PA6Cz	g 67 S$_A$ 124 I	1.9
6BrSzNO$_2$–PA6Cz	g 75 S$_A$ 140 I	2.0
7BrSzNO$_2$–PA6Cz	g 75 S$_A$ 162 I	2.5
8BrSzNO$_2$–PA6Cz	g 74 S$_A$ 162 I	2.8
9BrSzNO$_2$–PA6Cz	g 69 S$_A$ 167 I	2.5
10BrSzNO$_2$–PA6Cz	g 69 S$_A$ 168 I	2.0

[a] Transition temperature (°C) determined by DSC at 10 deg/min on the second heating run and by microscopic observation. g: glassy. S$_A$: smectic A. I: isotropic. [b] Measured by DSC. ΔH_i: enthalpy change in the clearing.

The phase diagram of the 6BrSzNO$_2$–PA6Cz mixtures is presented in Figure 5. When the proportion of 6BrSzNO$_2$ was over 0.75, phase separation occurred. The smectic phase was induced at near equimolar compositions. However, in this system, the thermal stability of the smectic phase was not caused, unlike the mixture of HCMA with 6BrSzNO$_2$.[12]

For the 1:1 nBrSzNO$_2$–PA6Cz complexes, the clearing temperature increased with increasing carbon number of the alkyl chain, while the glass transition temperature did not depend on the alkyl length (Table 5 and Figure 6A). All polymer complexes exhibited smectic phases. For example, a smectic phase was observed from 74 to 162 °C for the 1:1 8BrSzNO$_2$–PA6Cz complex. The enthalpy changes in the clearing for these polymer complexes were from 1.9 to 2.8 kJ/mol. As shown in Figure 6B, similar thermal properties were seen for the 1:1 polymer complexes of nBrSzNO$_2$ with a polymethacrylate containing the same mesogenic carbazolyl group (PM6Cz).

It has been reported that the 1:1 polymer mixture of PM6Cz with a nonionic 4-(hexyloxy)-*N*-(4-nitrobenzylidene)aniline showed a nematic phase.[20] Therefore, the miscibility and the induction of the smectic phase for the polymer complexes of side-chain liquid-crystalline polymers containing the carbazolyl group with nBrSzNO$_2$ may be caused by a combination of electron donor–acceptor and ionic interactions.

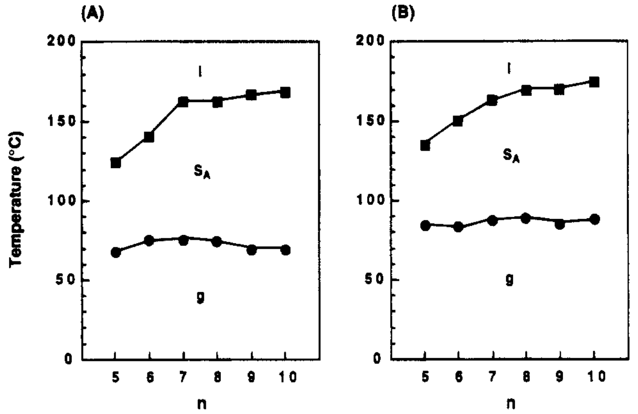


Figure 6. Dependence of the transition temperatures on the carbon number of the alkyl chain in nBrSzNO$_2$ for (A) the 1:1 nBrSzNO$_2$–PA6Cz complexes and (B) the 1:1 nBrSzNO$_2$–PM6Cz complexes.

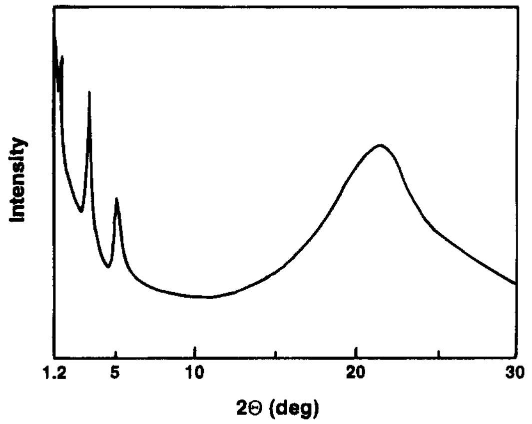


Figure 7. Wide-angle X-ray diffraction pattern of the 1:1 quenched 5BrSzNO$_2$–PA6Cz complex film.

The wide-angle X-ray diffraction pattern of the 1:1 5BrSzNO$_2$–PA6Cz complex film quenched from the liquid-crystalline state showed three sharp reflections at small angles and a broad reflection at wide angles (Figure 7). The broad peak centered at 2θ of 21.8° (d = 4.08 Å) is due to the distance between the planes on which the oriented mesogenic groups lies. The low-angle diffraction was measured by a small-angle X-ray diffractometer. Three sharp reflections were observed at 2θ of 1.75° (d = 50.4 Å), 3.50° (d = 25.2 Å), and 5.20° (d = 17.0 Å), respectively (Figure 8). The spacings of 25.2 and 17.0 Å are assumed to correspond nearly to the fully-stretched molecular lengths of A6Cz (26.5 Å) and 5BrSzNO$_2$ (19.5 Å), respectively. And, since the spacing of 50.4 Å is twice the spacing of the observed spacing of 25.2 Å, the polymer side chains might be oriented to form a doubly-layered conformation. Thus, both microscopic and X-ray diffraction studies suggest that the polymer complex had a smectic A phase. The smectic layer spacings measured by small-angle X-ray diffractions for these polymer complexes increased with increasing carbon number of the alkyl chain in nBrSzNO$_2$ (Figure 9). This widening of the spacing might originate from an increase in the whole length of the complex structure which was caused by the longer alkyl chain. The smectic phase of these complexes may have a mesophase close to a bilayer structure, in which the complex is formed between nBrSzNO$_2$ and PA6Cz, as illustrated in Figure 10.

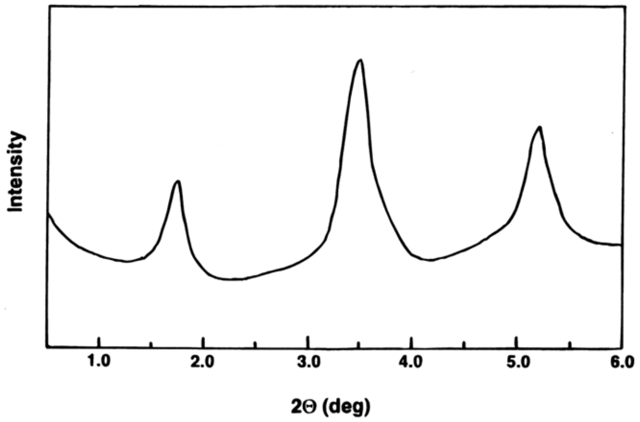


Figure 8. Small-angle X-ray diffraction pattern of the 1:1 quenched 5BrSzNO$_2$–PA6Cz complex film.

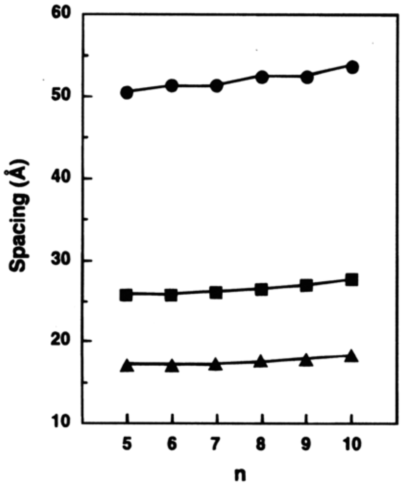


Figure 9. Dependence of the three spacings measured by small-angle X-ray diffractometry on the carbon number of the alkyl chain in nBrSzNO$_2$ for the 1:1 nBrSzNO$_2$–PA6Cz complexes. The widest spacing (●), the middle spacing (■), and the narrowest spacing (▲) corresponding to 2θ = around 1.7, 3.5, and 5.2°, respectively.

Experimental Section

Materials. *trans-N*-Alkyl-4-nitro-4′-stilbazolium halides (nXSzNO$_2$), 4-(hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA), poly[4-[[6-(acryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (PA6Cz), and poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (PM6Cz) were prepared according to the procedure previously described.[12,20,28]

Preparation of the Polymer Mixtures of nXSzNO$_2$ with PA6Cz. Polymer mixtures of nXSzNO$_2$ with PA6Cz were prepared by evaporation of the mixture solutions in chloroform, followed by drying under vacuum.

Characterization. A differential scanning calorimeter (Mettler DSC 30) was used to determine phase transition temperatures using heating and cooling rates of 10 deg/min. The peak temperature of endotherms was taken as the transition temperature. An optical polarizing microscope (Olympus BH-2) equipped with a Mettler FP-82 hot stage and a temperature programmer FP-80 was also used to observe phase transitions. X-ray diffraction data were collected using a Rigaku RINT 1500 X-ray diffractometer. Small-angle X-ray measurements were obtained with a Rigaku Rint 2500L X-ray diffractometer.

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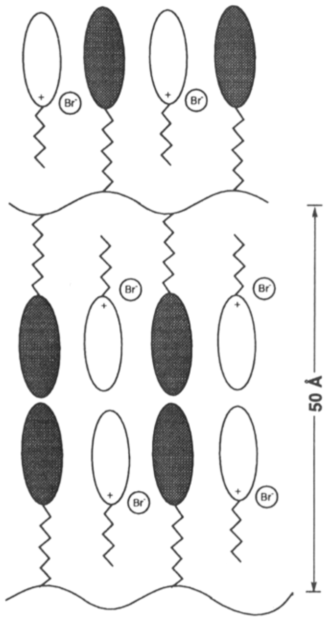

Figure 10. Schematic illustration of a proposed mesophase structure in the 5BrSzNO$_2$–PA6Cz complex: (shaded ellipses) electron-donating (carbazolylmethylene)aniline group; (open ellipses) electron-accepting nitrostilbazolium group.

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