Induction of the Smectic Phase in Blends of Side-Chain Liquid-Crystalline Polymers by Electron Donor–Acceptor Interactions

Yozo Kosaka

Central Research Institute, Dai Nippon Printing Company, Ltd., Ichigaya-Kagamachi, Shinjuku-ku, Tokyo 162-01, Japan

Toshiyuki Uryu*

Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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ABSTRACT: Miscible polymer blends were prepared from poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] and poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)-aniline]. These polymer blends exhibited homogeneous smectic phases when the proportion of the mesogenic carbazolyl unit was in the range of 0.3–0.6, though the smectic phase did not appear in both homopolymers. The 1:1 (mole ratio) polymer blend showed a smectic phase from 69 to 190 °C. A similar tendency on the thermal behavior was observed for the binary mixtures of both low-molecular-weight compounds containing the same electron donor and acceptor mesogens. On the other hand, the polymer blend composed of both electron-donating side-chain liquid-crystalline polymers containing carbazolyl and methoxyphenyl groups showed a phase separation. In addition, the thermal behaviors were examined on a blend of an electron-donating polymer with an electron-accepting compound. The miscibility in the polymer blends was caused by intermolecular electron donor–acceptor interactions which made the blends orient to organize a smectic phase.

Introduction

With the progress of research on side-chain liquid-crystalline polymers in which mesogenic units are attached to the polymer backbones as pendant groups through flexible spacers,[1,2] new types of side-chain liquid-crytalline polymers were recently synthesized. Their liquid crystallinities are caused or induced by such interactions as intermolecular hydrogen bonds,[3–5] ionic interactions,[6–8] and electron donor–acceptor interactions.[9–12]

Side-chain liquid-crystalline polymers containing electron donor and acceptor groups are considered to have great potentials in various fields such as information storage, nonlinear optics, and electro-optic devices.[1,2] Previously, it was reported that copolystyrenes containing both electron-donating 4-methoxyazobenzene and electron-withdrawing 4-nitroazobenzene groups exhibited smectic phases in wide temperature ranges.[11,12] The formation of charge transfer complexes between non-liquid-crystalline discoid polymers and 2,4,7-trinitrofluorenone induced enantiotropic mesophases.[13] Similar behaviors were observed for the binary mixtures of both monomeric electron donor and acceptor compounds.[14–17]

In our previous paper, liquid-crystalline side-chain copolymers containing both a mesogenic carbazolyl group with electron-donating character and a nitrophenyl or cyanophenyl group with electron-accepting character were prepared.[18] In the copolymers, the induction of the smectic phase and the enhancement in the thermal stability occurred by the intra- and intermolecular donor–acceptor interactions.

In this paper, we report that liquid-crystalline polymer blends showing a similar smectic-phase induction can be prepared by mixing a polymer containing a (2-carbazolylmethylene)aniline group and one containing a (4-nitrobenzylidene)aniline group through intermolecular donor–acceptor interactions. For mixtures of polymethacrylate having mesogenic electron-donating a (carbazolylmethylene)aniline group with low-molecular-weight electron-withdrawing benzylideneaniline derivatives, their liquid-crystalline behaviors were also observed as well as for mixtures of a (carbazolylmethylene)aniline derivative with benzylideneaniline derivatives. These binary mixtures were characterized by optical polarizing microscopy, differential scanning calorimetry, and X-ray diffractometry.

Results and Discussion

Thermal Properties of Binary Mixtures Composed of Low-Molecular-Weight Electron Donor and Acceptor Compounds. 4-(Hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA) was synthesized as a model compound with an electron-donating group, i.e., a (carbazolylmethylene)aniline group. 4-(Hexyloxy)-*N*-(4′-X-substituted benzylidene)anilines (HBA-X; X = NO_2, CN, OMe, H) were electron-acceptor model compounds. Their molecular structures are shown in Chart 1.

Thermal properties of HCMA, HBA-Xs, and the 1:1 (mole ratio) binary mixtures of HCMA with HBA-X, which were prepared by evaporation of the mixture solution in THF, are given in Table 1. HCMA and 4-(hexyloxy)-*N*-(4′-cyanobenzylidene)aniline (HBA-CN) exhibited enantiotropic nematic phases. A monotropic nematic phase was seen from 97 to 90 °C for 4-(hexyloxy)-*N*-(4′-methoxybenzylidene)aniline (HBA-OMe). On the other hand, both 4-(hexyloxy)-*N*-(4′-nitrobenzylidene)aniline (HBA-NO_2) and 4-(hexyloxy)-*N*-benzylideneaniline (HBA-H) were not mesomorphic.

Although HBA-NO_2 is not liquid-crystalline, its 1:1 mixture with HCMA showed an enantiotropic smectic phase from 81 to 87 °C followed by a nematic phase from 87 to 116 °C. The smectic phase was characterized by a focal-conic fan texture with the polarized microscope observation (Figure 1A). Since HBA-NO_2 is of strong

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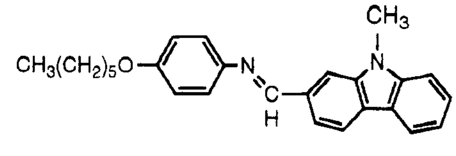
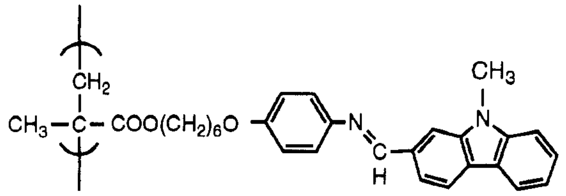
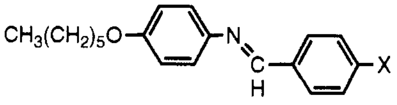
Chart 1. Molecular Structures of 4-(Hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA), 4-(Hexyloxy)-*N*-(4′-substituted benzylidene)anilines (HBA-Xs), Poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (PHCMA), and Poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-X-substituted benzylidene)aniline] (PHBA-X; X = NO_2, CN, OMe)



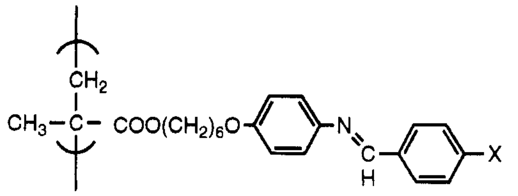
HCMA



PHCMA
(g 82 N 177 I)



X = NO_2: HBA-NO_2
CN: HBA-CN
OCH_3: HBA-OMe
H: HBA-H



X = NO_2: PHBA-NO_2
(g 56 N 120 I)
CN: PHBA-CN
(g 66 S 148 I)
OH_3: PHBA-OMe
(g 65 N 137 I)

4-(Hexyloxy)-N-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA) and 4-(Hexyloxy)-N-(4′-substituted benzylidene)aniline (HBA-X)

Homopolymers

Table 1. Thermal Properties of 4-(Hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA), 4-(Hexyloxy)-*N*-(4′-substituted benzylidene)aniline (HBA-X), and Their 1:1 Mixtures[a]

compd and 1:1 mixture	phase transition temp[b] (°C)	ΔH_i[c] (kJ/mol)	ΔT[d]
HCMA	K 91 N 122 I	0.34	
HBA-NO_2	K 84 I		
HBA-CN	K 68 N 101 I	0.39	
HBA-OMe	K 98 (N 97) I[e]	(0.53)[f]	
HBA-H	K 50 I		
HCMA/HBA-NO_2	K 81 S 87 N 116 I	0.38	13
HCMA/HBA-CN	K 67 (S 63) N 117 I[e]	0.37	5.5
HCMA/HBA-OMe	K 64 N 110 I	0.35	0
HCMA/HBA-H	phase separation		

[a] The 1:1 binary mixture of HCMA with HBA-X was prepared by evaporation of the mixture solution in THF. HBA-NO_2, 4-(hexyloxy)-*N*-(4′-nitrobenzylidene)aniline; HBA-CN, 4-(hexyloxy)-*N*-(4′-cyanobenzylidene)aniline; HBA-OMe, 4-(hexyloxy)-*N*-(4′-methoxybenzylidene)aniline; HBA-H, 4-(hexyloxy)-*N*-benzylideneaniline. [b] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the first cooling and second heating runs. The mesophase was determined by textures observed with the optical polarized microscope. K, crystalline; S, smectic; N, nematic; I, isotropic. [c] Measured by DSC. ΔH_i, enthalpy change in isotropization. [d] The increase in isotropic temperature over the average value based on the compositions. [e] Monotropic. [f] Enthalpy change from isotropic to nematic.

electron acceptability, it is assumed that in the mixture of HBA-NO_2 with an electron-donating HCMA, an electron donor–acceptor interaction between the mesogens induced the smectic phase having a highly-regulated molecular orientation.

As the phase diagram for the HBA-NO_2 and HCMA mixture is shown in Figure 2, the binary mixture formed the nematic phase over the entire composition and well produced the overlapping smectic phase in the HCMA proportion of 0.4–0.65. It is noted that the eutectic point was observed at the HCMA proportion of 0.25 and 0.75. The existence of the two eutectic points at the HCMA proportion of 0.25 and 0.75 suggests that the eutectic mixture is formed in the blend composed of both 50% of the 1:1 complex and 50% of either HCMA or HBA-NO_2 molecules, exhibiting the two minimum crystal-to-nematic transition temperatures. Moreover, it is presumed that the existences of the eutectic mixtures and of the smectic phase centered at the HCMA proportion of 0.5 indicate the formation of the 1:1 intermolecular interaction between the electron donor and acceptor molecules.

The 1:1 binary mixture of HCMA with HBA-CN also produced a miscible blend. In this blend, an enantiotropic nematic phase and a monotropic smectic phase were observed on optical polarized microscope observation and DSC measurement. On the other hand, for a 1:1 mixture of HCMA with HBA-H having weak or no electron acceptability, phase separation occurred. These phenomena indicate that the miscibility between the two kinds of compounds is caused by an electron donor–acceptor interaction. In the 1:1 mixture of HBA-OMe and HCMA, both of which are electron donors, the decrease in phase transition temperatures was seen.

Thermal Properties of the Blends of Polymethacrylates Containing an Electron Donor or Acceptor Mesogen. Poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (PHCMA), poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)aniline] (PHBA-NO_2), poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-cyanobenzylidene)aniline] (PHBA-CN), and poly[4-[[6-methacryloyloxy)hexyl]oxy]-*N*-(4′-methoxybenzylidene)aniline] (PHBA-OMe) were prepared by polymerization of the respective methacrylate monomers. The pendant groups containing mesogens were the same as those of the low-molecular-weight model compounds described in the previous section.

Both electron-donating PHCMA and electron-accepting PHBA-NO_2 showed nematic phases from 82 to 177 °C

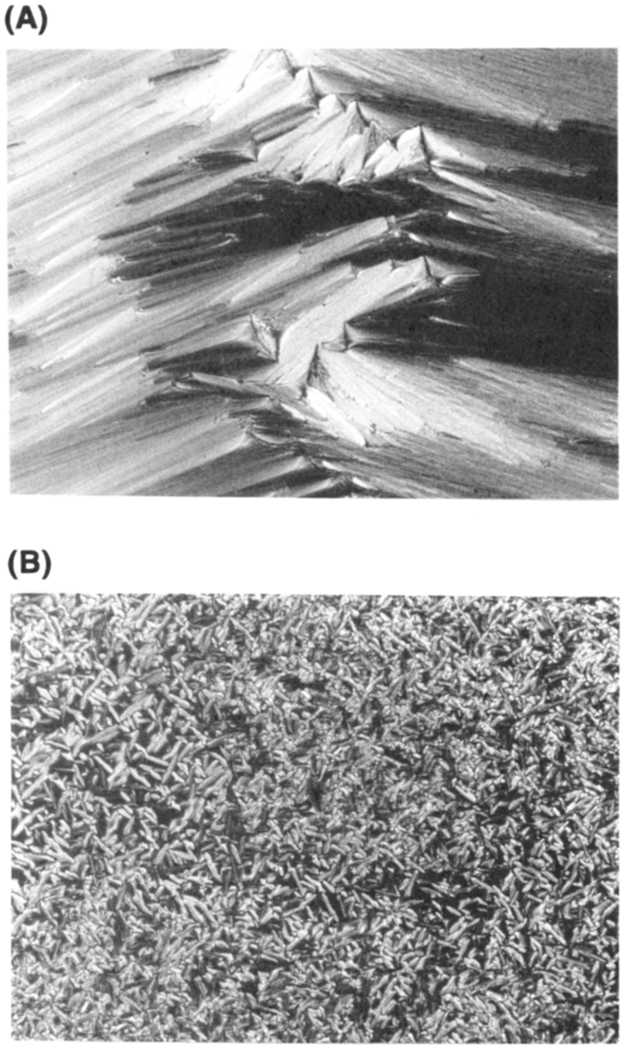


Figure 1. Optical polarized microphotographs of (A) the 1:1 mixture of HCMA and HBA-NO_2 at 83 °C and (B) the 1:1 polymer blend of PHCMA and PHBA-NO_2 at 180 °C.

and 56 to 120 °C, respectively. The 1:1 mixture of PHCMA and PHBA-NO_2 provided a miscible blend as the miscibility was revealed by the single glass transition at 69 °C and the single mesophase–isotropic transition at 190 °C in the DSC measurement (Figure 3A). This blend exhibited a focal-conic texture characteristic of a smectic phase with the polarized microscope observation (Figure 1B).

Moreover, the X-ray diffraction pattern of the quenched blend of PHCMA with PHBA-NO_2 showed two sharp reflections at 2Θ of 2.86° (d = 30.9 Å) corresponding to the thickness of the smectic layer and at 2Θ of 5.70° (d = 15.5 Å) due to the second order of the smectic layer spacing. A broad reflection at 2Θ of 20.0° (d = 4.43 Å) ascribable to the distance between the mesogenic groups (Figure 4).

A similar miscible polymer blend was obtained by mixing an electron-donating PHCMA and an electron-accepting PHBA-CN which showed a smectic phase from 66 to 148 °C. This 1:1 polymer blend exhibited a smectic phase between 67 and 180 °C. The isotropic temperature of the PHCMA and PHBA-NO_2 blend was by 10 °C higher than that of the PHCMA and PHBA-CN blend, probably because a little stronger electron donor–acceptor interactions acted in the former polymer blend than in the latter.

On the other hand, since both PHCMA and PHBA-OMe (g 65 N 137 I), are electron donors, nonmiscibility of the 1:1 polymer blend was indicated by two glass transitions at 63 and 80 °C and two mesophase–isotropic transitions at 139 and 175 °C, which correspond to the transitions of the respective homopolymers (Figure 3B).

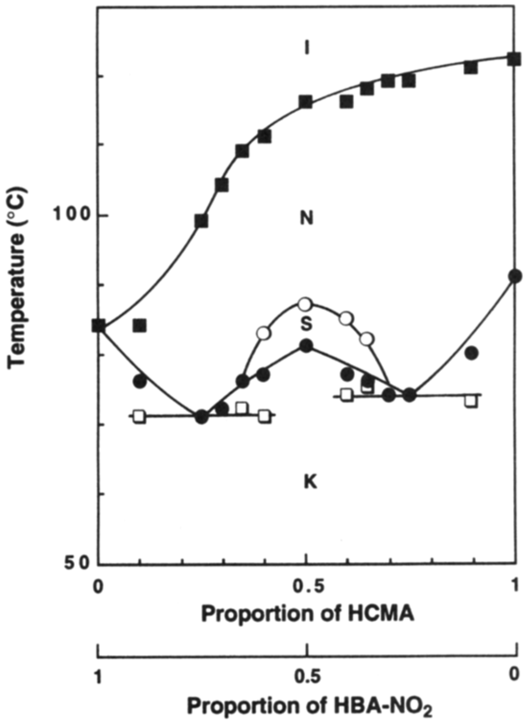


Figure 2. Phase diagram for the binary mixture of HCMA and HBA-NO_2 as a function of the proportion of HCMA.

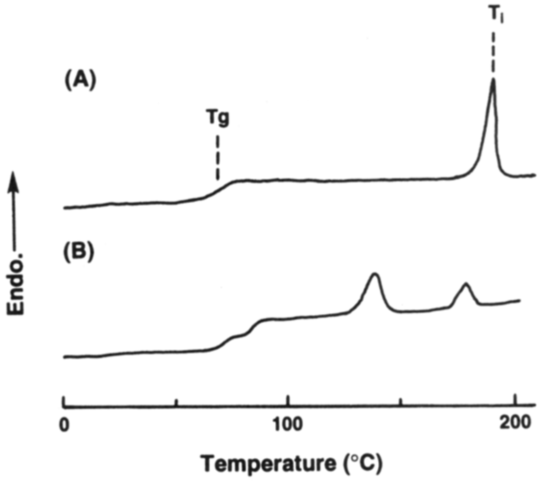


Figure 3. DSC thermograms of the 1:1 polymer blends of (A) PHCMA and PHBA-NO_2, and (B) PHCMA and PHBA-OMe on the second heating run at a scanning rate of 10 °C/min.

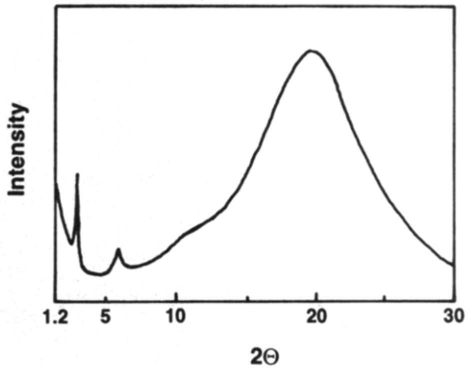


Figure 4. Wide-angle X-ray diffraction pattern of a quenched 1:1 polymer blend of a PHCMA and PHBA-NO_2 film.

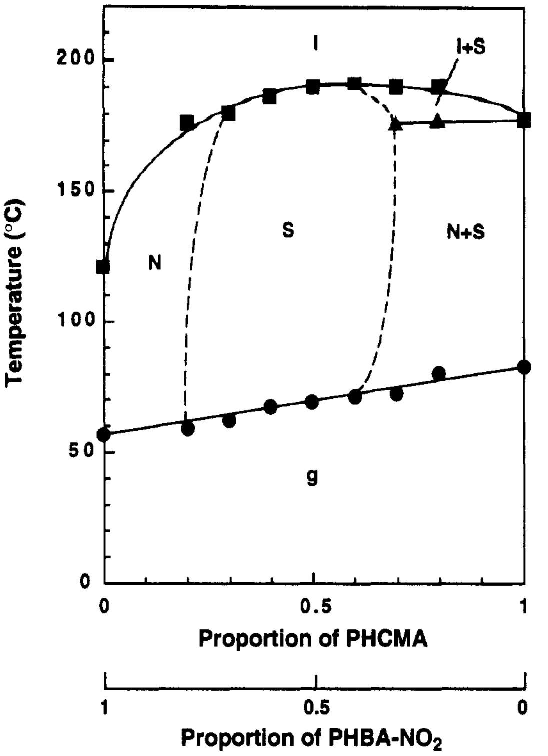


Figure 5. Dependence of phase transition temperatures on the proportion of the PHCMA unit of the polymer blend of PHCMA and PHBA-NO_2.

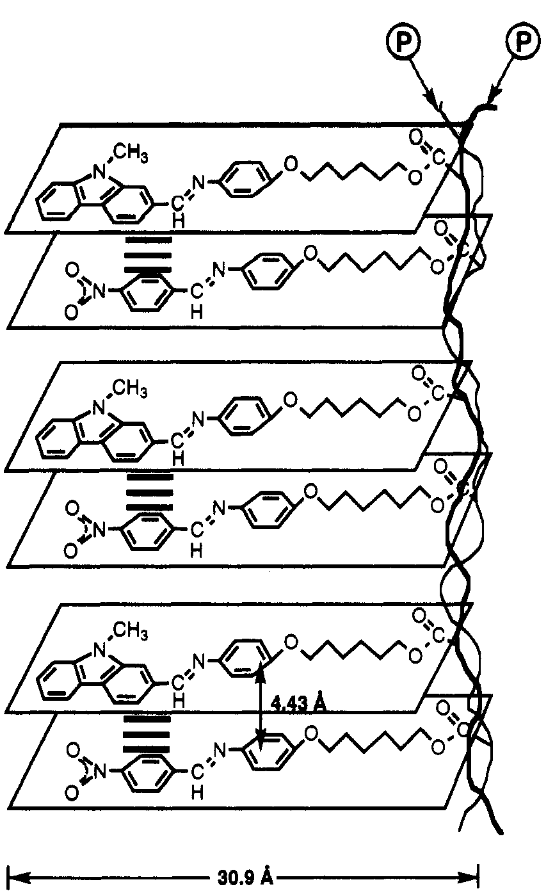


Figure 6. Schematic illustration of a proposed mesophase structure in the 1:1 polymer blend of PHCMA and PHBA-NO_2.

In the previous paper,[18] we reported that a copolymer containing both a mesogenic electron-donating (carbazolylmethylene)aniline group and a mesogenic electron-accepting (nitrobenzylidene)aniline group exhibited a smectic phase by intra- and intermolecular electron donor–acceptor interactions. The present experiment revealed that the intermolecular electron donor–acceptor interaction is one of the interactions highly aligning the two kinds of liquid-crystalline polymers as well as the interaction between mesogenic groups.

The formation of non-liquid-crystalline miscible polymer blends by electron donor–acceptor interactions was previously reported for the blend of a polyacrylate containing a carbazolyl group and a polymethacrylate containing a dinitrophenyl group.[19] In addition, a non-liquid-crystalline electron-donating polymer was mixed with electron-accepting 2,4,7-trinitrofluorenone to produce a liquid-crystalline discoid polymer.[13]

In Figure 5, for the polymer blend of PHCMA and PHBA-NO_2, the phase diagram representing the dependence of the phase transition on the proportion of PHCMA is shown. Two peaks were observed at 177 and 190 °C for the polymer blends of the PHCMA proportion of more than 0.7 in the DSC measurement. These peaks might correspond to the isotropic transitions of PHCMA and the 1:1 polymer blend of PHCMA and PHBA-NO_2 with optical polarized microscope observation. When the proportion of PHCMA was less than 0.7, a single glass transition and a single mesophase–isotropic transition were observed. Polymer blends composed of the PHCMA proportion from 0.3 to 0.6 exhibited the smectic phase, while those of the proportion of less than 0.3 exhibited the nematic phase. Similar to the case of the model compounds, the induction of the smectic phase in the PHCMA proportions centered at 0.5 supports that the 1:1 electron donor–acceptor complex is formed by mixing the two kinds of homopolymers.

The isotropic temperature of the blend containing the PHCMA proportion of more than 0.2 was in the range of 177–190 °C which was approximately 60° and 10° higher than that of PHBA-NO_2 and PHCMA, respectively. In addition, the enthalpy change of isotropization for the 1:1 polymer blend was three times as high as that of the individual homopolymers. This phenomenon also reveals that the degree of orientation was raised by the electron donor–acceptor interaction in the polymer blend. The polymer blends of PHCMA and PHBA-NO_2 exhibited wider mesophase transition temperature ranges compared to the mixtures of HCMA and HBA-NO_2, probably because of the thermal stability of polymers by the balance between stiffness of polymer backbones and side groups. A similar behavior was seen in such a comparison of a copolystyrene containing both methoxyazobenzene and nitroazobenzene groups with a binary mixture of the low-molecular-weight compounds containing the same mesogenic groups.[11]

The thickness (30.9 Å) of the smectic layer for the polymer blend was almost equivalent to that of the copolymer containing both monomeric units (30.4 Å).[18] Since this distance is close to the molecular lengths of the fully-stretched respective methacrylate monomers, i.e., 28.0 Å (HCMA) and 25.5 Å (HBA-NO_2), the thickness of the smectic layer seems to correspond to the length of the side groups. Accordingly, it was concluded that the PHCMA–PHBA-NO_2 blend had a S_{A1} mesophase structure in which the electron-donating mesogenic (carbazolylmethylene)aniline group overlapped the electron-accepting mesogenic (nitrobenzylidene)aniline groups, as illustrated in Figure 6.

The distance between the mesogenic groups (4.43 Å) was shorter than that of both homopolymers, i.e., 4.64 Å (PHCMA) and 4.63 Å (PHBA-NO_2),[18] probably because of the electron donor–acceptor interactions between the mesogenic groups.

Thus, these phenomena may suggest that this electron interaction is a kind of weak charge transfer between the

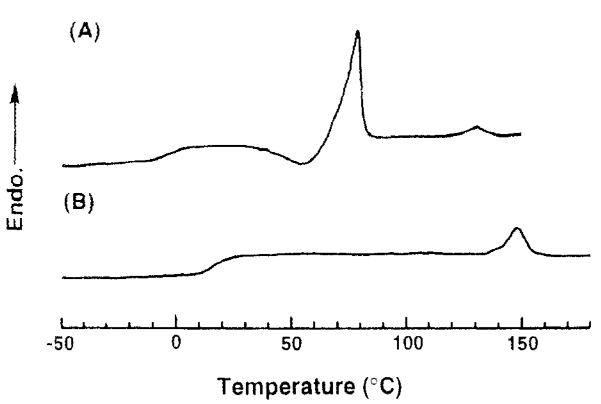


Figure 7. DSC thermograms of the polymer mixtures of PHCMA and HBA-NO_2 of the PHCMA proportion of (A) 0.4 and (B) 0.6 on the second heating run at a scanning rate of 10 °C/min.

electron-donating carbazolyl group and the electron-accepting nitrophenyl group.

Although a miscible blend was obtained by mixing an electron-donating polymer with an electron-accepting low-molecular-weight compound, its thermal behaviors were different from those of the mixtures of the two kinds of polymers and of the two kinds of low-molecular-weight compounds. For a mixture consisting of the PHCMA proportion of 0.4 and the HBA-NO_2 proportion of 0.6, the DSC thermogram denoted two endothermic peaks corresponding to the crystalline–nematic and nematic–isotropic transitions at 78 and 130 °C and a glass transition at −5 °C, respectively (Figure 7A).

On the other hand, for a mixture containing the PHCMA proportion of 0.6, a single glass transition originating from the polymer and a single nematic–isotropic transition appeared at 17 and 148 °C, respectively (Figure 7B). Taking into account these thermal behaviors and the polarized microscopic observation, the PHCMA and HBA-NO_2 mixtures produced miscible blends. Similar behaviors were reported on a blend of a low-molecular-weight liquid crystal having a cyanophenyl group and a side-chain liquid-crystalline polysiloxane having a methoxyphenyl group.[20]

The phase diagram of the mixture of PHCMA with HBA-NO_2 is presented in Figure 8. When the PHCMA proportion exceeded 0.25, a remarkable decrease in the glass transition temperature occurred. For instance, the T_g of PHCMA was 82 °C, while that of the blend in the PHCMA proportion of 0.5 was 8 °C. The remarkable decrease in the T_g might be ascribed to an increase in bulkiness of the polymer side group which was caused by the formation of electron donor–acceptor complexes between the polymethacrylate and HBA-NO_2, because it is well-known that as the ester group of polymethacrylate is bulkier, the T_g is generally lower.[21]

Experimental Section

(9-Methyl-2-carbazolyl)carbaldehyde,[22] poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline] (PHCMA),[18,23] and poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-X-substituted benzylidene)aniline] (PHBA-X; X = NO_2, CN, OMe)[18] were prepared according to the procedure described in the literature.

4-(Hexyloxy)-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (HCMA). The (carbazolylmethylene)aniline derivative was prepared by reacting 4-(hexyloxy)aniline (0.97 g, 5 mmol) with (9-methyl-2-carbazolyl)carbaldehyde (1.05 g, 5 mmol) in 10 mL of dry ethanol at 70 °C for 2 h. The product was purified by recrystallization from ethanol to provide HCMA. Yield: 85%. Mp: 91.1 °C. ^{1}H NMR ($CDCl_3$) for HCMA: δ 0.94 (3H, t), 1.38 (4H, m), 1.51 (2H, m), 1.82 (2H, m), 3.93 (3H, s), 4.00 (2H, t), 6.96 (2H, d), 7.26 (2H, d), 7.29 (1H, t), 7.43 (1H, d), 7.53 (1H, t), 7.70 (1H, d), 8.06 (1H, s), 8.13 (1H, d), 8.16 (1H, d), 8.68 (1H, s).

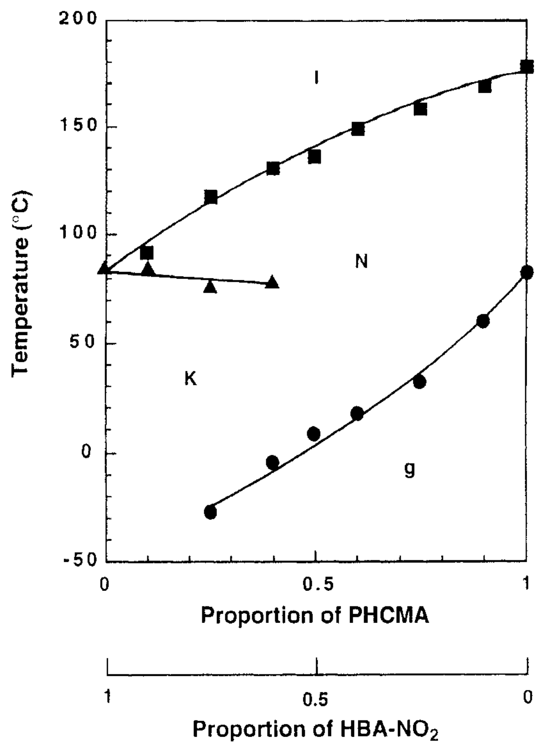


Figure 8. Phase diagram of the polymer mixtures of PHCMA and HBA-NO_2 as a function of the proportion of the PHCMA unit.

4-(Hexyloxy)-*N*-(4′-substituted benzylidene)aniline (HBA-X). The synthesis of 4-(hexyloxy)-*N*-(4′-nitrobenzylidene)aniline (HBA-NO_2) is described as a representative case. 4-(Hexyloxy)aniline (0.97 g, 5 mmol) was mixed with *p*-nitrobenzaldehyde (0.76 g, 5 mmol) in 10 mL of dry ethanol. After the mixture was heated at 70 °C for 2 h, the product was purified by recrystallization from ethanol to provide HBA-NO_2. Using the same procedure, (4′-cyanobenzylidene)- (HBA-CN) and (4′-methoxybenzylidene)aniline (HBA-OMe) and nonsubstituted (HBA-H) benzylideneaniline derivatives were obtained. Yield: HBA-NO_2, 89%; HBA-CN, 86%; HBA-OMe, 84%; HBA-H, 83%. Mp: HBA-NO_2, 83.6 °C; HBA-CN, 101.2 °C; HBA-OMe, 97.5 °C; HBA-H, 50.2 °C. ^{1}H NMR ($CDCl_3$): HBA-NO_2, δ 0.93 (3H, t), 1.37 (4H, m), 1.48 (2H, m), 1.82 (2H, m), 4.00 (2H, t), 6.96 (2H, d), 7.31 (2H, d), 8.06 (2H, d), 8.31 (2H, d), 8.59 (1H, s); HBA-CN, δ 0.92 (3H, t), 1.36 (4H, m), 1.46 (2H, m), 1.81 (2H, m), 3.99 (2H, t), 6.95 (2H, d), 7.27 (2H, d), 7.74 (2H, d), 7.99 (2H, d), 8.53 (1H, s); HBA-OMe, δ 0.93 (3H, t), 1.36 (4H, m), 1.48 (2H, m), 1.80 (2H, m), 3.89 (3H, s), 3.98 (2H, t), 6.92 (2H, d), 6.99 (2H, d), 7.20 (2H, d), 7.84 (2H, d), 8.42 (1H, s); HBA-H, δ 0.93 (3H, t), 1.36 (4H, m), 1.48 (2H, m), 1.82 (2H, m), 3.99 (2H, t), 6.94 (2H, d), 7.25 (2H, d), 7.47 (3H, t), 7.90 (2H, d), 8.50 (1H, s).

Preparation of Binary Mixtures of HCMA with HBA-Xs. The binary mixture of HCMA with HBA-X was prepared by evaporation of the mixture from a THF solution, after the binary mixture was mixed by stirring for 2 h at room temperature. The resulting product was dried under vacuum.

Characterization. A 400-MHz ^{1}H NMR spectrum was recorded on a GE Omega 400WB NMR spectrometer in a chloroform-*d* solution. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used to determine phase transition temperatures at heating and cooling rates of 10 °C/min. For the low-molecular-weight compounds and the binary mixtures of HCMA with HBA-X, the onset point of the endotherm was taken as the transition and the melting temperatures. For the polymer mixtures composed of two kinds of polymers or a polymer and a HBA-X, the peak temperature of the endotherm was taken as the transition temperature. An optical polarizing microscope equipped with a Mettler FP-82 hot stage and a temperature programmer FP-80 was used to observe phase transitions. X-ray diffraction was measured with a Rigaku RINT 1500 X-ray diffractometer.

References and Notes

(1) McArdle, C. B., Ed. *Side Chain Liquid Crystal Polymers*; Blackie: Glasgow, U.K., 1989.

(2) Chapoy, L. L., Ed. *Recent Advances in Liquid Crystalline Polymer*; Elsevier: London, 1985.

(3) Kato, T.; Fréchet, J. M. J. *Macromolecules* **1989**, *22*, 3818.

(4) Kumar, U.; Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.

(5) Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Fréchet, J. M. J. *Macromolecules* **1992**, *25*, 6836.

(6) Ujiie, S.; Iimura, K. *Macromolecules* **1992**, *25*, 3174.

(7) Rodriguez, D. N.; Guillon, D.; Skouilos, A.; Frere, Y.; Gramair, P. *Makromol. Chem.* **1992**, *193*, 3117.

(8) Hessel, V.; Ringsdorf, H.; Festag, R.; Wendorff, J. H. *Makromol. Chem., Rapid. Commun.* **1993**, *14*, 707.

(9) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.

(10) Reck, B.; Ringsdorf, H. *Liq. Cryst.* **1990**, *8*, 247.

(11) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Liq. Cryst.* **1991**, *9*, 47.

(12) Schleeh, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1859.

(13) Ringsdorf, H.; Wüstefeld, R.; Zerta, E.; Ebert, M.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 914.

(14) Park, J. W.; Bak, C. S.; Labes, M. M. *J. Am. Chem. Soc.* **1975**, *97*, 4398.

(15) Oh, C. S. *Mol. Cryst. Liq. Cryst.* **1977**, *42*, 11.

(16) Araya, K.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3079.

(17) Praefcke, K.; Singer, D.; Kohne, B.; Ebert, M.; Liebmann, A.; Wendorff, J. H. *Liq. Cryst.* **1991**, *10*, 147.

(18) Kosaka, Y.; Kato, T.; Uryu, T. *Macromolecules* **1994**, *27*, 2658.

(19) Uryu, T.; Ohkawa, H.; Furuichi, H.; Oshima, R. *Macromolecules* **1988**, *21*, 188.

(20) Ringsdorf, H.; Schmidt, H.-W.; Schneller, A. *Makromol. Chem., Rapid. Commun.* **1982**, *3*, 745.

(21) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989; p VI-217.

(22) Lux, M.; Strohiegel, P.; Höcker, H. *Makromol. Chem.* **1987**, *188*, 811.

(23) Kosaka, Y.; Kato, T.; Uryu, T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 711.