Macromolecules **1995,** *28,* 8295−8301 **8295**

Synthesis and Liquid Crystallinity of Polymethacrylate Systems Containing both Electron-Donating (Quinolinylmethylene)aniline and Electron-Accepting (4′-Nitrobenzylidene)aniline Groups

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Received April 4, 1995; Revised Manuscript Received September 5, 1995[⊗]

ABSTRACT: Side-chain liquid-crystalline copolymers, polymer blends, and polymer mixtures containing a (quinolinylmethylene)aniline or a (naphthylmethylene)aniline group and a (4-nitrobenzylidene)aniline group were prepared to examine the effects of the electron-donating character of the quinoline and naphthyl groups on their thermal properties and miscibility. The thermal stability and induction of a smectic phase were caused by the electron donor−acceptor interaction for all copolymers. A miscible polymer blend was obtained from the electron-donating polymer containing the (3-quinolinylmethylene)aniline group and the electron-accepting polymer containing the (4-nitrobenzylidene)aniline group, while other 1:1 polymer blends showed phase separation. The 1:1 miscible polymer blend exhibited a smectic phase from 52 to 166 °C. Moreover, smectic phases were observed in the mixture of the electron-donating polymer containing the mesogenic 3-quinoline group with an electron-accepting low-molecular-weight compound containing the nitrophenyl group as well as in the mixture of both low-molecular-weight compounds containing the above two mesogenic groups. Thus, the (3-quinolinylmethylene)aniline group containing the nitrogen atom acted as the mesogenic electron donor, but not the (naphthylmethylene)aniline group.

Introduction

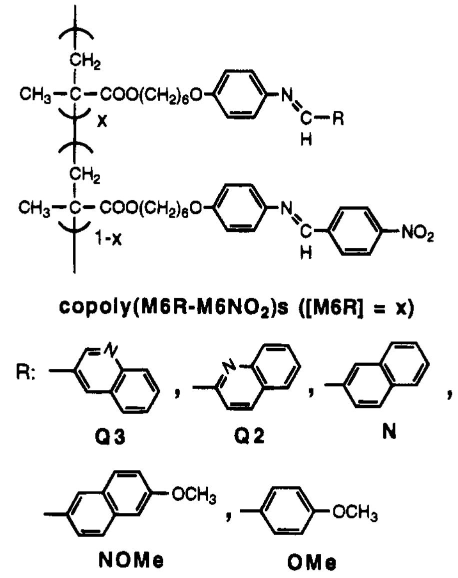
Side-chain liquid-crystalline polymer systems making use of electron donor−acceptor interactions have recently attracted attention from the viewpoint of fundamental research and of potential applications.[1−9] The systems show thermal stabilization and induction of mesophases.

Previously, we reported the thermal properties of liquid-crystalline copolymers and polymer blends containing an electron-donating (carbazolylmethylene)aniline group and an electron-accepting nitrophenyl or cyanophenyl group.[10−14] The copolymers and polymer blends showed increasing thermal stability and induction of a smectic phase. A few miscible side-chain liquid-crystalline polymer blends containing electron donor and acceptor groups were reported.[15] In addition, a novel class of liquid-crystalline complexes was also prepared from the electron-donating polymers or low-molecular-weight compounds containing the mesogenic carbazolyl group and ionic nitrostilbazoles.[16,17] It is assumed that the miscibility of the blends and the complexes might be caused by the electron-donating nature of both the carbazolyl group and nitrogen atom contained in the mesogenic group.

Stille and co-workers reported on several thermally stable polyquinolines.[18,19] The polyquinolines showed lyotropic liquid-crystalline properties.[18−20] Recently, thermotropic liquid-crystalline polyquinolines were obtained by making use of biphenylene units and alkylene spacers.[21] Low-molecular-weight liquid crystals containing quinoline groups substituted in both 2- and 6-positions exhibited thermotropic liquid crystallinity.[22,23]

In this paper, side-chain liquid-crystalline copolymers, polymer blends, and polymer mixtures containing both (2- or 3-quinolinylmethylene)aniline and (4-nitrobenzylidene)aniline groups were prepared to examine the effect of the electron-donating nature of the quinoline groups on the thermal properties and miscibility (Chart 1). The liquid crystallinity of the binary mixtures of low-molecular-weight compounds containing the same combination of the electron donor and acceptor mesogens was also studied. In addition, the thermal properties of electron donor and acceptor systems containing mesogenic (naphthylmethylene)aniline groups were also examined in the place of the quinoline group. The existence and position of the nitrogen atom in the mesogen plays an important role in the formation of an electron donor−acceptor interaction. These liquid-crystalline materials were characterized by ^{1}H NMR

Chart 1. Molecular Structures of Copoly(M6R-M6NO$_2$)s



[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

0024-9297/95/2228-8295$09.00/0

Table 1. Thermal Properties of Homopolymers (PM6R)

polymer designation	yield (%)	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_w$	phase transition temp (°C)^a	$\Delta H_i{}^b$ (kJ/mol)
PM6Q3	85	3.16	8.22	g 55 S 143 I	2.50
PM6Q2	93	2.42	5.17	g 49 N 72 I	0.58
PM6N	90	2.27	6.46	g 60 S 116 N 119 I	0.67
PM6NOMe	91	2.72	6.46	g 60 S 205 N 219 I	0.69
PM6OMe	90	3.06	11.7	g 62 N 142 I	0.82
PM6NO$_2$	84	5.23	12.0	g 56 N 120 I	0.44

^{a} Transition temperature determined by the DSC measurement at a scanning rate of 10 deg/min on the second heating run and by microscope observation. Key: g, glassy; S, smectic; N, nematic; I, isotropic. ^{b} Measured by DSC. ΔH_i, enthalpy change on clearing.

spectroscopy, polarizing microscope observation, differential scanning calorimetry, and X-ray diffraction.

Results and Discussion

Thermal Properties of Homopolymers and Copolymers. 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(4-nitrobenzylidene)aniline (M6NO$_2$) was used as an electron acceptor monomer. Methacrylate monomers containing (quinolinylmethylene)aniline groups such as (3-quinolinylmethylene)aniline (M6Q3), (2-quinolinylmethylene)aniline (M6Q2), (2-naphthylmethylene)aniline (M6N), (6-methoxy-2-naphthylmethylene)aniline (M6NOMe), and (4-methoxybenzylidene)aniline (M6OMe) were prepared as electron donor monomers. Although M6NOMe exhibited a nematic phase from 103 to 120 °C, other monomers did not form mesophases. All polymethacrylates were prepared by solution polymerizations with AIBN as a radical initiator at 70 °C for 20 h. The molecular weights and thermal properties of homopolymers (PM6Rs) are summarized in Table 1. PM6Rs with number-average molecular weights ranging from 2.42 × 10^4 to 5.23 × 10^4 were obtained in high yields. Liquid crystallinity was seen at temperatures above the glass transition temperature to the isotropic temperature for all homopolymers. PM6N and PM6NOMe exhibited mesophases from 60 to 119 °C and from 60 to 219 °C, respectively. Both glass transition temperatures were equal, while the isotropic temperature was increased by the polar methoxy substituent. A similar tendency was observed between PM6OMe and a polymer containing a benzylideneaniline group with no terminal groups.[10] Thus, the terminal methoxy group stabilizes the mesophase.

The liquid crystallinity of PM6Q2 was remarkably different from that of PM6Q3. PM6Q2 exhibited a nematic phase from 49 to 72 °C, whereas PM6Q3 gave a smectic phase from 55 to 143 °C. Molecular models calculated by the molecular force field method (Chem 3D) of monomeric M6Q3 and M6Q2 units are depicted in Figure 1. The molecular shape of M6Q3 is linear, while the M6Q2 molecule is bent. Thus, the (3-quinolinylmethylene)aniline group is apparently more rodlike.

The results of copolymerizations of M6Q3 and M6NO$_2$ as well as thermal properties of copolymers [copoly(M6Q3-M6NO$_2$)s] are summarized in Table 2. The proportion of individual monomeric units in the copolymer was determined by ^{1}H NMR. The proportion of monomeric units in the feed was in good agreement with that in the copolymer, because the polymerization was carried out to near completion. Copoly(M6Q3-M6NO$_2$)s with fairly high molecular weights were obtained in high yields. Although the glass transition temperature was linear with the copolymer composition, the isotropic temperature showed a significant positive deviation (Figure 2A). For instance, in the copolymer with the M6Q3 content of 0.55, a smectic phase was seen from 48 to 171 °C. This isotropic temperature was 38 deg higher than the calculated value based on the copolymer composition (133 °C). Smectic phases were observed for copoly(M6Q3-M6NO$_2$)s when the M6Q3 proportions were in the range 0.35−1.0, although copoly(M6Q3-M6NO$_2$)s consisting of the M6Q3 proportion less than 0.35 exhibited nematic phases. Since the PM6Q3 and PM6NO$_2$ had smectic and nematic phases, respectively, it is reasonable to consider that the smectic phase in the copolymers with intermediate compositions was induced by electron donor−acceptor interactions between the side groups. The 3-quinoline and the 4-nitrophenyl units in the side groups are responsible for the electron-donating and -accepting properties, respectively. Similar tendencies were also seen for copoly(M6N-M6NO$_2$)s and copoly(M6NOMe-M6NO$_2$)s, as shown in Figure 2C,D.

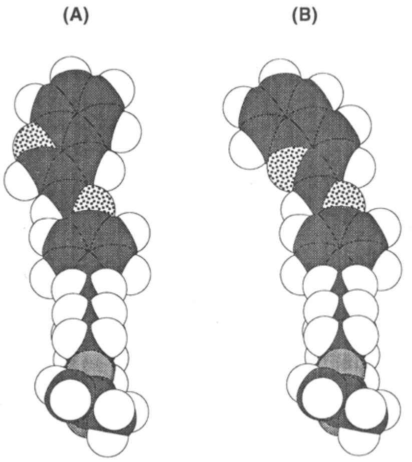


Figure 1. Molecular models calculated by the molecular force field method (Chem 3D) of (A) M6Q3 and (B) M6Q2.

For copoly(M6Q2-M6NO$_2$)s, the smectic phase was induced when the M6Q2 proportions were in the range 0.28−0.70, though the homopolymers did not show the smectic phase (Figure 2B). The smectic phase was characterized by a focal-conic fan texture on the microscope observation (Figure 3A). The thermal stabilization of the mesophase is indicated by the convex curve. The mesophase temperature range of the copolymer increased to a considerable extent in the smectic region. For example, copoly(M6Q2-M6NO$_2$) ([M6Q2] = 0.51) exhibited the smectic phase from 52 to 148 °C. This isotropic temperature was 52 deg higher than the calculated value (96 °C). The entropy change on clearing ($\Delta S/R = 0.59$) for the copolymer was 3 times as high as that ($\Delta S/R = 0.20$) for the individual homopolymers, indicating that a higher orientation was caused by the electron donor−acceptor interaction. In contrast to a large difference in the liquid crystallinity between the two homopolymers, i.e., PM6Q3 and PM6Q2, the copoly(M6Q3-M6NO$_2$)s showed thermal properties similar to those of the copoly(M6Q2-M6NO$_2$)s, probably because analogous planar structures were formed in both copolymers by the electron donor−acceptor interaction.

The copoly(M6OMe-M6NO$_2$)s (Figure 2E) also showed similar behaviors by the electron donor−acceptor interaction. Since analogous behavior was observed in the copolymers containing the electron-donating (carbazolylmethylene)aniline group,[10] both (quinolinylmethylene)aniline and (naphthylmethylene)aniline groups work as electron-donating groups.

Table 2. Copolymerizations of M6Q3 with $M6NO_2$ and Thermal Properties of Copoly($M6Q3-M6NO_2$)s

proportion of M6Q3 in feed	proportion of M6Q3 in copolymer[a]	polymer yield (%)	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_w$	phase transition temp[b] (°C)	ΔH_i[c] (kJ/mol)	$\Delta S/R$[d]
0.0	0.0	84	5.23	12.0	g 56 N 120 I	0.44	0.19
0.15	0.17	85	2.58	5.79	g 46 N 141 I	1.00	0.29
0.3	0.35	88	2.85	7.23	g 55 S 158 I	1.78	0.50
0.5	0.55	87	2.70	6.04	g 48 S 171 I	2.43	0.66
0.75	0.74	90	3.68	14.0	g 50 S 173 I	2.98	0.80
1.0	1.0	85	3.16	8.22	g 55 S 143 I	2.50	0.72

[a] Determined by ^1H NMR. [b] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 deg/min on the second heating run and by microscope observation. Key: g, glassy; S, smectic; N, nematic; I, isotropic. [c] Measured by DSC. ΔH_i, enthalpy change on clearing. [d] $\Delta S/R$, entropy change on clearing.

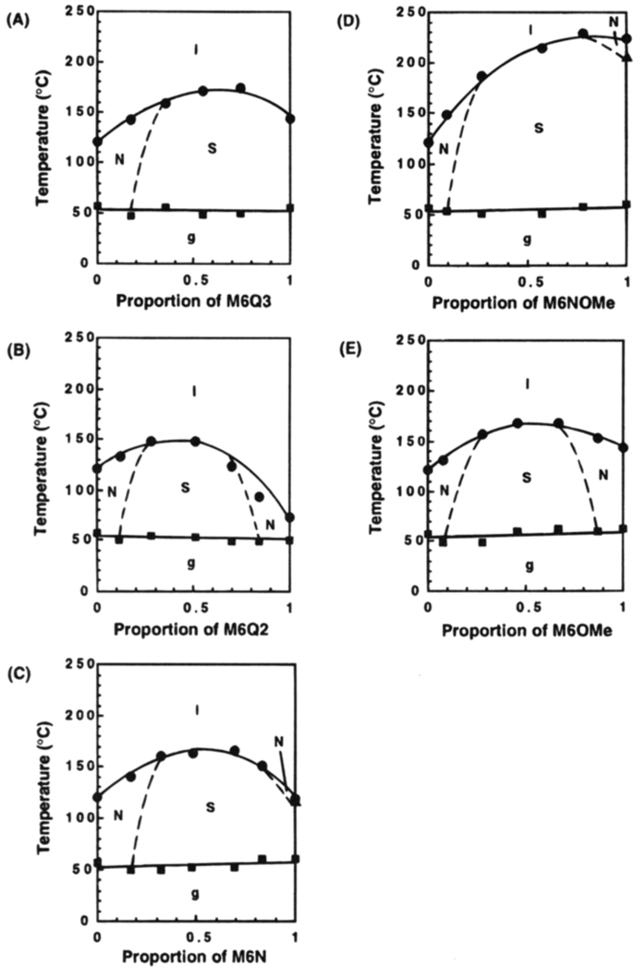


Figure 2. Dependence of phase transition temperatures on the proportion of the M6R unit for (A) copoly($M6Q3-M6NO_2$)s, (B) copoly($M6Q2-M6NO_2$)s, (C) copoly($M6N-M6NO_2$)s, (D) copoly($M6NOMe-M6NO_2$)s, and (E) copoly($M6OMe-M6NO_2$)s.

The smectic order possessed by the copoly(M6Q2-$M6NO_2$) was revealed by X-ray measurement. X-ray diffraction of the copolymer film quenched from the liquid-crystalline state showed two sharp reflections at 2Θ of 3.10° (d = 28.5 Å) and 2Θ of 6.26° (d = 14.1 Å) corresponding to the smectic layer spacing and its second-order reflection, respectively (Figure 4A). A broad reflection at 2Θ of 20.04° (d = 4.43 Å) is assignable to the distance between the mesogenic side groups. The smectic layer spacing was close to the molecular lengths of the monomeric unit in the fully stretched conformations (26.0 and 25.5 Å for M6Q2 and $M6NO_2$, respectively). Both the polarizing microscope observation and X-ray diffraction study suggested that this copolymer had a S_{A1} mesophase structure. Similar results were obtained for other copolymers, as listed in Table 3.

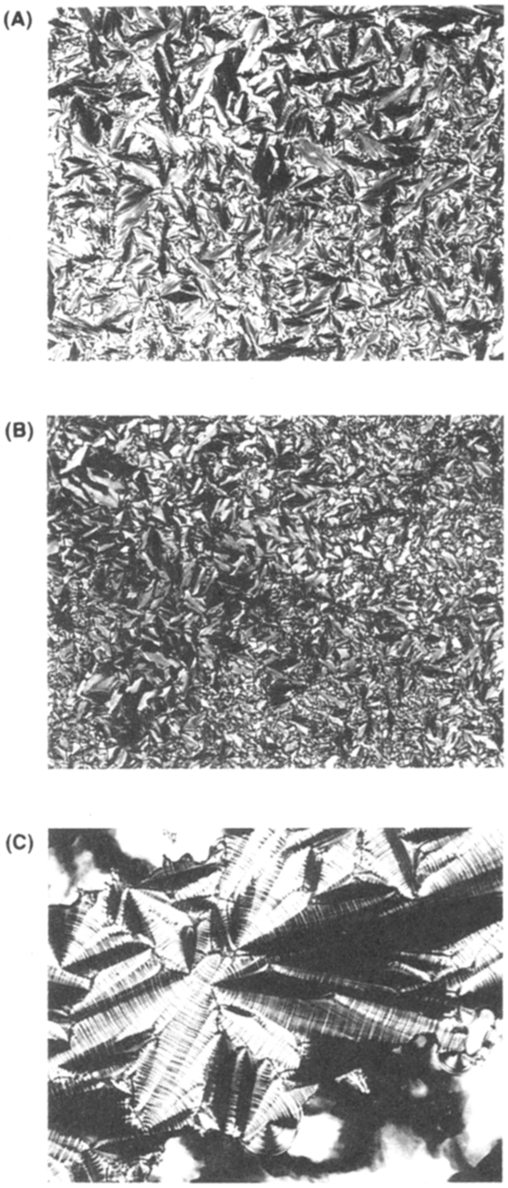


Figure 3. Optical polarized microphotographs of (A) copoly($M6Q2-M6NO_2$) ([M6Q2] = 0.51) at 140 °C, (B) the 1:1 polymer blends of PM6Q3 and $PM6NO_2$ at 150 °C, and (C) the 1:1 binary mixture of HNOMe with HNO_2 at 38 °C on cooling.

Liquid-Crystalline Properties of Polymer Blends and Polymer Mixtures. The liquid-crystalline behavior revealed in the copolymers also appeared in polymer blends.[11,13] A miscible polymer blend was obtained by blending PM6Q3 and $PM6NO_2$, as shown in Figure 5A. The DSC thermogram represents a glass transition at

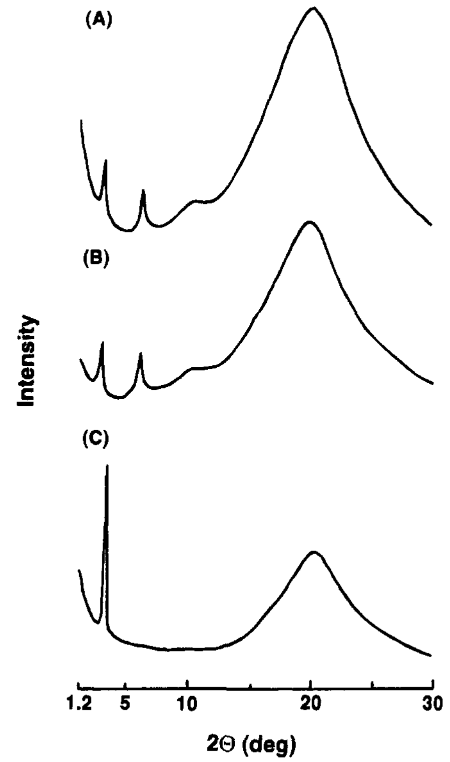


Figure 4. Wide-angle X-ray diffraction patterns of quenched films: (A) copoly(M6Q2-M6NO$_2$) ([M6Q2] = 0.51); (B) the 1:1 polymer blends of PM6Q3 and PM6NO$_2$; (C) the 1:1 polymer mixture of PM6Q3 and HNO$_2$.

Table 3. Results of X-ray Measurements of Homopolymers and Polymer Systems Containing Electron Donor and Acceptor Groups

polymer designation	d_1[b] (Å)	d_2[c] (Å)
homopolymers		
PM6Q3	27.8 (3.18)	4.44 (19.98)
PM6Q2		4.60 (19.30)
PM6NOMe	29.6 (2.98)	4.49 (19.74)
PM6OMe		4.51 (19.66)
PM6NO$_2$		4.63 (19.17)
copolymers[d]		
copoly(M6Q3-M6NO$_2$)	29.2 (3.02)	4.46 (19.80)
copoly(M6Q2-M6NO$_2$)	28.5 (3.10)	4.43 (20.04)
copoly(M6N-M6NO$_2$)	29.2 (3.02)	4.45 (19.92)
copoly(M6NOMe-M6NO$_2$)	29.6 (2.98)	4.41 (20.12)
copoly(M6OMe-M6NO$_2$)	29.0 (3.04)	4.36 (20.34)
polymer blend (1:1)[e]		
PM6Q3-PM6NO$_2$	28.9 (3.06)	4.45 (19.92)
polymer mixture (1:1)[e]		
PM6Q3-HNO$_2$	26.4 (3.34)	4.34 (20.44)

[a] 2Θ values (deg) in parentheses. [b] The smectic layer spacing. [c] Distance between the mesogenic side groups. [d] [M6R] ≈ 0.5. [e] Mole ratio.

52 °C and a liquid crystal–isotropic transition at 166 °C, indicating that the miscible blend was formed. A non-liquid-crystalline miscible polymer blend was prepared by mixing a polymethacrylate containing a 9-carbazolyl group with a polymethacrylate containing a (3,5-dinitrobenzoyl)oxy group.[24]

However, phase separations were observed for the polymer blends of PM6NO$_2$ and PM6Q2, PM6N, PM6NOMe, or PM6OMe by microscopic and DSC studies. For example, as seen in Figure 5B, the DSC thermogram of the PM6NO$_2$-PM6OMe blend exhibited three endothermic peaks at 121, 140, and 162 °C corresponding to the isotropic transitions of PM6NO$_2$, PM6OMe, and the miscible 1:1 polymer blend.

The reason that the PM6Q3 formed the miscible blend but not the PM6Q2 might be ascribable to the more linear structure and possibly stronger electron-donating property of the former than the latter. The polymer blend had the smectic phase represented by a focal-conic fan texture (Figure 3B). Therefore, it was found that the (3-quinolinylmethylene)aniline group acts as an electron donor like the (carbazolylmethylene)aniline group.[10-14]

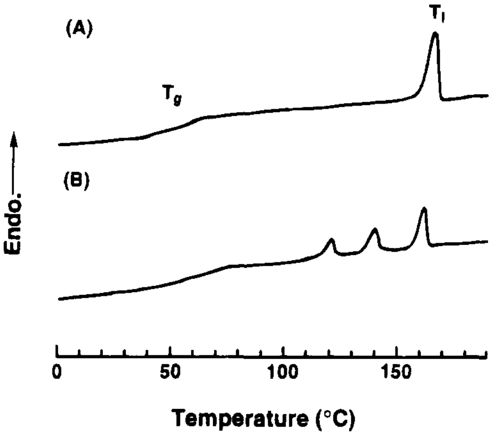


Figure 5. DSC thermograms of the 1:1 polymer blends on the second heating run at a scanning rate of 10 deg/min: (A) PM6Q3 and PM6NO$_2$; (B) PM6OMe and PM6NO$_2$.

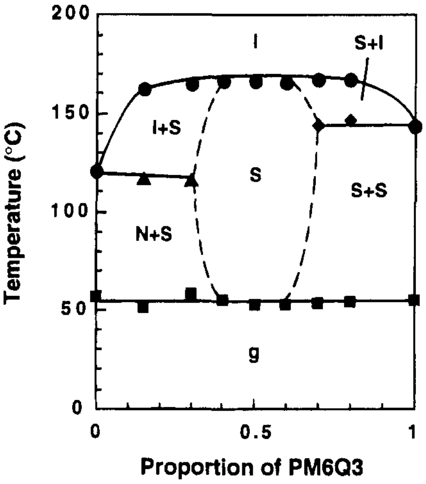


Figure 6. Dependence of phase transition temperatures on the proportion of the PM6Q3 unit for the polymer blends of PM6Q3 and PM6NO$_2$.

As shown in Figure 4B, for the 1:1 polymer blend of PM6Q3 and PM6NO$_2$, the smectic layer spacing was 28.9 Å. The spacing was almost the same as that of the copoly(M6Q3-M6NO$_2$) ([M6Q3] = 0.55), indicating that this polymer blend had a mesophase structure similar to that of the copolymer containing the same mesogens.

The phase diagram for the polymer blends of PM6Q3 and PM6NO$_2$ is given in Figure 6. A single smectic phase appeared in the polymer blends near equimolar compositions. In the polymer blends containing PM6Q3 in the proportion less than 0.3, the phase separation provided mixtures of PM6NO$_2$ and the 1:1 miscible polymer blend. Moreover, the polymer blends in the PM6Q3 proportion of more than 0.7 showed a similar tendency. These results suggest that the electron donor–acceptor interaction acted between the equimolar electron donor and acceptor groups.

A miscible polymer mixture was also obtained by mixing the electron-donating PM6Q3 and a low-molecular-weight electron-accepting 4-(hexyloxy)-*N*-(4-ni-

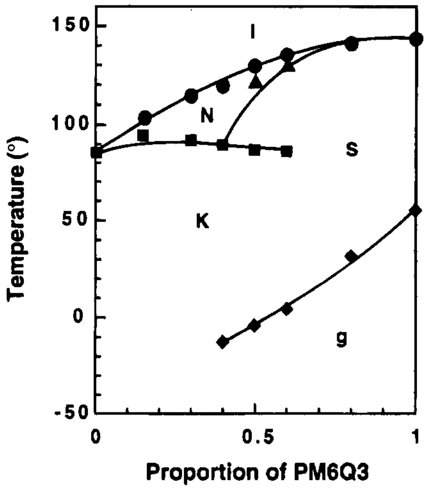


Figure 7. Dependence of phase transition temperatures on the proportion of the PM6Q3 unit for the polymer mixtures of PM6Q3 with HNO_2.

trobenzylidene)aniline (HNO_2). The 1:1 polymer mixture of PM6Q3 and HNO_2 exhibited a smectic phase from 87 to 122 °C followed by a nematic phase from 122 to 129 °C. In addition, the X-ray diffraction pattern of the quenched polymer mixture film showed a sharp peak at 2Θ of 3.34° (d = 26.4 Å) corresponding to the smectic layer spacing as well as a broad diffraction at 2Θ of 20.44° (d = 4.34 Å) due to the distance between the mesogenic side groups (Figure 4C and Table 3). The spacing was close to the molecular lengths of the fully-stretched M6Q3 and HNO_2 molecules which were calculated to be 26.3 and 20.7 Å, respectively.

It is noteworthy that the glass transition temperature decreased from +55 to −13 °C with the increasing proportion of HNO_2 for the polymer mixture when the PM6Q3 proportion exceeded 0.4 (Figure 7). The remarkable decrease in the T_g might be due to a decrease in the magnitude of mobile segments caused by the formation of the electron donor and acceptor complex. When the proportion of PM6Q3 was less than 0.6, crystal regions originating from the low-molecular-weight compound were observed. Similar behavior was reported for mixtures of electron-donating polymers and electron-accepting low-molecular-weight compounds.[11,25]

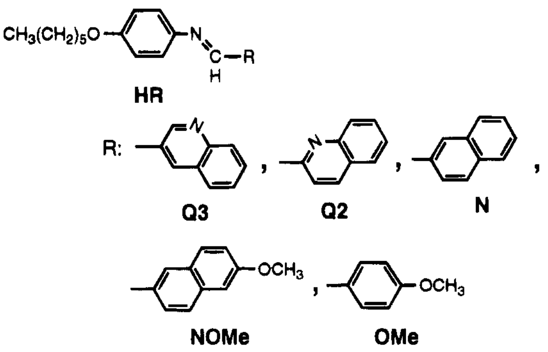
Electron Donor and Acceptor Mixtures of Both Low-Molecular-Weight Compounds. Binary mixtures consisting of both low-molecular-weight compounds were examined as the model of electron donor−acceptor interactions. 4-(Hexyloxy)-*N*-(R-substituted-methylene)anilines [HR; R = Q3 (3-quinoline), Q2 (2-quinoline), N (2-naphthyl), and NOMe (6-methoxy-2-naphthyl)] and -*N*-(4-methoxybenzylidene)aniline (HOMe) were synthesized as model compounds for electron donors (Chart 2). HNO_2 was used as the model compound for an electron acceptor. The thermal properties of HR, HNO_2, and the 1:1 (mole ratio) binary mixtures of HR with HNO_2 are summarized in Table 4. HNOMe exhibited a nematic phase from 119 to 178 °C. HN and HOMe displayed monotropic nematic phases, whereas both HQ3 and HQ2 did not form mesophases.

By creating electron donor−acceptor interactions, all 1:1 binary mixtures of HR with HNO_2 expressed smectic A and nematic phases. For instance, the 1:1 binary mixture of HQ3 with HNO_2 showed a smectic A phase from 64 to 101 °C followed by a nematic phase from 101 to 102 °C, although both compounds were not mesomorphic. Ordered smectic phases were observed for the 1:1 binary mixtures of HR (R = NOMe, N, and OMe) with HNO_2. A smectic E phase was seen for the 1:1 binary mixture of HNOMe with HNO_2. The smectic phase was characterized by a paramorphotic arced focal-conic fan texture with the polarized microscope observation (Figure 3C). Thus, for model systems, the thermal stability and induction of the smectic phase were also caused by the electron donor−acceptor interaction.

As the phase diagram for the binary mixtures of HQ3 with HNO_2 is represented in Figure 8, the smectic phase was induced in considerably wide proportions near equimolar compositions by the electron donor−acceptor interaction. When the HQ3 proportions were less than 0.5, nematic phases were observed. The thermal stability of the mesophase was shown by the convex curve. In the 1:1 binary mixture of HQ3 with HNO_2, the isotropic temperature was 12 deg higher than the calculated value based on the composition, with the remarkable decrease in the melting temperature occurring. The quinoline groups therefore act as electron donors in analogy with the (carbazolylmethylene)aniline group.

Chart 2. Molecular Structures of HRs and HNO_2

(A) Electron-Donating Compounds



(B) Electron-Accepting Compound

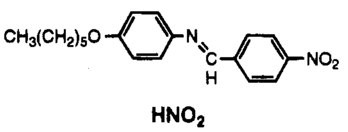


Table 4. Thermal Properties of HR and Their 1:1 Mixtures with HNO_2

compd and 1:1 mixture	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)
HQ3	K 96 I	
HQ2	K 71 I	
HN	K 85 (N 68)[c] I	(0.35)[d]
HNOMe	K 119 N 178 I	0.63
HOMe	K 100 (N 95)[c] I	(0.53)[d]
HNO_2	K 85 I	
HQ3/HNO_2	K 64 S_A 101 N 102 I	0.77
HQ2/HNO_2	K 55 S_A 78 N 86 I	0.65
HN/HNO_2	K (S_X 29)[c] 60 S_A 98 N 103 I	0.70
HNOMe/HNO_2	K 74 (S_E 41)[c] S_A 131 N 142 I	0.65
HOMe/HNO_2	K 73 S_X 76 S_A 105 N 109 I	0.83

[a] Transition temperature determined by the DSC measurement at a scanning rate of 10 deg/min on the first cooling and second heating runs and by optical polarized microscope observation. Key: K, crystalline; S_E, smectic E; S_A, smectic A; N, nematic; I, isotropic. S_X is an unidentified smectic phase. [b] Measured by DSC. ΔH_i, enthalpy change on clearing. [c] Monotropic. [d] Enthalpy change from isotropic to nematic.

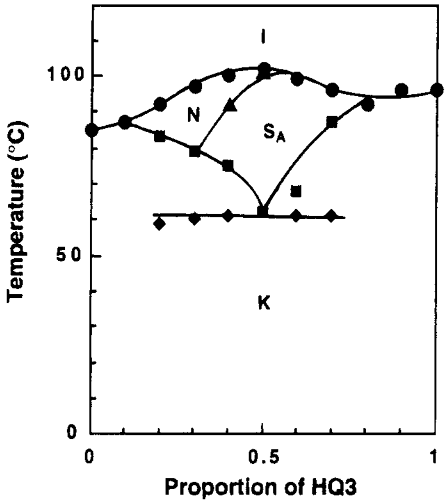


Figure 8. Phase diagram for the binary mixtures of HQ3 and HNO_2 as a function of the proportion of HQ3.

Conclusion

Electron donor and acceptor systems composed of (3-quinolinylmethylene)aniline and (4-nitrobenzylidene)-aniline groups exhibit thermally stable liquid-crystalline states and enhanced miscibility in blends. For the copolymers, the polymer blends, and the low-molecular-weight blends containing similar mesogenic groups, the existence and position of the nitrogen atom played an important role in causing the electron donor–acceptor interaction between the groups.

Experimental Section

Aldehyde compounds such as 2-quinolinecarboxaldehyde, 3-quinolinecarboxaldehyde (Aldrich Chemical Co.), 2-naphthaldehyde, and 6-methoxy-2-naphthaldehyde (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. 4-[(6-Hydoxyhexyl)oxy]aniline,[26] 4-[[6-methacryloyloxy)oxy]-*N*-(4-nitrobenzylidene)aniline ($M6NO_2$),[10] and 4-[[6-(methacryloyloxy)-hexyl]oxy]-*N*-(4′-methoxybenzylidene)aniline[10] were prepared according to literature procedures.

Monomers were prepared according to the literature.[10] As a representative case, the synthesis of 4-[[6-(methacryloyloxy)-hexyl]oxy]-*N*-(3-quinolinylmethylene)aniline (M6Q3) is described.

4-[(6-Hydroxyhexyl)oxy]-*N*-(3-quinolinylmethylene)-anilines. 4-[(6-Hydroxyhexyl)oxy]aniline (2.7 g, 13 mmol) was dissolved in 30 mL of ethanol. After an equimolar amount of a 3-quinolinecarboxaldehyde (2.0 g, 13 mmol) was added to the ethanol solution, the mixture was heated at 70 °C for 2 h. The product was purified by recrystallization from ethanol. Yield: 93%. Mp: 122.1 °C. ^1H NMR ($CDCl_3$): δ 1.45 (4H, m), 1.65 (2H, m), 1.82 (3H, m), 3.68 (2H, t), 4.00 (2H, t), 6.94 (2H, d), 7.30 (2H, d), 7.60 (1H, t), 7.78 (1H, t), 7.92 (1H, d), 8.16 (1H, d), 8.55 (1H, s), 8.68 (1H, s), 9.48 (1H, s).

4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(3-quinolinylmethylene)aniline (M6Q3). A methacryloyl chloride (3.4 g, 32.7 mmol) solution in 30 mL of chloroform was added to a solution containing 4-[(6-hydroxyhexyl)oxy]-*N*-(3-quinolinylmethylene)aniline (3.8 g, 10.9 mmol) and triethylamine (5.5 g, 54.5 mmol) in 50 mL of chloroform at 0 °C. The reaction was continued for 12 h. After workup, the product was purified by recrystallization three times from ethanol to provide M6Q3. Yield: 64%. Mp: 78.5 °C. ^1H NMR ($CDCl_3$): δ 1.51 (4H, m), 1.74 (2H, m), 1.86 (2H, m), 1.95 (3H, s), 4.00 (2H, t), 4.17 (2H, t), 5.56 (1H, s), 6.11 (1H, s), 6.96 (2H, d), 7.31 (2H, d), 7.60 (1H, t), 7.78 (1H, t), 7.93 (1H, d), 8.16 (1H, d), 8.55 (1H, s), 8.69 (1H, s), 9.48 (1H, s). For M6Q2: 60% yield; mp 87.8 °C; ^1H NMR ($CDCl_3$) δ 1.51 (4H, m), 1.74 (2H, m), 1.86 (2H, m), 1.95 (3H, s), 3.98 (2H, t), 4.19 (2H, t), 5.56 (1H, s), 6.11 (1H, s), 6.96 (2H, d), 7.40 (2H, d), 7.60 (1H, t), 7.76 (1H, t), 7.87 (1H, d), 8.16 (1H, d), 8.24 (1H, d), 8.37 (1H, d), 8.82 (1H, s). For M6N: 50% yield; mp 84.1 °C; ^1H NMR ($CDCl_3$) δ 1.50 (4H, m), 1.73 (2H, m), 1.83 (2H, m), 1.95 (3H, s), 3.99 (2H, t), 4.17 (2H, t), 5.55 (1H, s), 6.11 (1H, s), 6.94 (2H, d), 7.38 (2H, d), 7.54 (2H, m), 7.89 (3H, m), 8.16 (1H, d), 8.18 (1H, s), 8.65 (1H, s). For M6NOMe: 25% yield; mp 103.3 °C; ^1H NMR ($CDCl_3$) δ 1.50 (4H, m), 1.71 (2H, m), 1.83 (2H, m), 1.95 (3H, s), 3.97 (3H, t), 4.00 (2H, d), 4.20 (2H, d), 5.56 (1H, s), 6.11 (1H, s), 6.94 (2H, d), 7.19 (2H, m), 7.32 (2H, d), 7.81 (2H, m), 8.11 (2H, m), 8.60 (1H, s).

Model Compounds. Using the same procedure as that of 4-[(6-hydroxyhexyl)oxy]-*N*-(3-quinolinylmethylene)anilines, 4-(hexyloxy)-*N*-(3-quinolinylmethylene)aniline (HQ3) was synthesized from 4-(hexyloxy)aniline and 3-quinolinecarboxaldehyde. Yield: 89%. Mp: 94.5 °C. ^1H NMR ($CDCl_3$): δ 0.92 (3H, t), 1.35 (4H, m), 1.47 (2H, m), 1.82 (2H, m), 4.00 (2H, t), 6.95 (2H, d), 7.30 (2H, d), 7.60 (1H, t), 7.75 (1H, t), 7.92 (1H, d), 8.16 (1H, d), 8.55 (1H, s), 8.69 (1H, s), 9.47 (1H, s). For HQ2: 66% yield; mp 101.6 °C; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t), 1.36 (4H, m), 1.48 (2H, m), 1.82 (2H, m), 4.02 (2H, t), 6.97 (2H, d), 7.35 (2H, d), 7.59 (1H, t), 7.76 (1H, t), 7.87 (1H, d), 8.15 (1H, d), 8.24 (1H, d), 8.37 (1H, d), 8.82 (1H, s). For HN: 75% yield; mp 85.1 °C; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t), 1.36 (4H, m), 1.48 (2H, m), 1.82 (2H, m), 4.00 (2H, t), 6.95 (2H, d), 7.37 (2H, d), 7.54 (2H, m), 7.88 (3H, m), 8.15 (1H, d), 8.18 (1H, s), 8.64 (1H, s). For HNOMe: 93% yield; mp 117.7 °C; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t), 1.36 (4H, m), 1.48 (2H, m), 1.81 (2H, m), 3.95 (3H, s), 3.98 (2H, t), 6.94 (2H, d), 7.20 (2H, m), 7.26 (2H, d), 7.80 (2H, m), 8.11 (2H, m), 8.60 (1H, s).

Polymerizations. Polymerizations of M6R and $M6NO_2$ were carried out in benzene or DMF with azobis(isobutyronitrile) (AIBN) (3 mol %) as an initiator at 70 °C for 20 h under vacuum. The resulting polymers were purified by reprecipitation using the tetrahydrofuran–methanol system.

Preparation of Binary Mixtures of HR with HNO_2. Binary mixtures of HR with HNO_2 were prepared by evaporation of chloroform solutions of these mixtures, followed by drying under vacuum.

Preparation of Polymer Blends of PM6R and $PM6NO_2$. The polymer blends of PM6R and $PM6NO_2$ were prepared by melting these polymers at an isotropic temperature under a nitrogen atmosphere.

Characterization. ^1H NMR spectra were recorded on a JEOL JNM-GX270 spectrometer in chloroform-*d* or DMF-d_7 solution. Molecular weights of the resulting polymers were determined with an HLC-802A (Tosoh Co.) using tetrahydrofuran as an eluent and polystyrene standards. Differential scanning calorimetry (Perkin-Elmer DSC-7) was used to determine the phase transition temperatures at heating and cooling rates of 10 deg/min. For the low-molecular-weight compounds, the onset point of the endotherms was taken as the transition and melting temperatures. For other cases, the peak temperature of endotherms was taken as the transition temperature. A polarizing microscope equipped with a Mettler FP-82 hot stage and a temperature programmer FP-80 was also used to observe phase transitions. X-ray diffraction was measured with a Rigaku RINT 1500 X-ray diffractometer.

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MA950462A