Synthesis and the Smectic Mesophase of Copolymers Containing a Mesogenic (Carbazolylmethylene)aniline Group as the Electron Donor and a (4′-Nitrobenzylidene)aniline Group as the Electron Acceptor

Yozo Kosaka

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

Takashi Kato and Toshiyuki Uryu*

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

Received December 1, 1993; Revised Manuscript Received February 23, 1994[⊗]

ABSTRACT: Side-chain liquid-crystalline copolymers containing a mesogenic (carbazolylmethylene)aniline group as an electron donor and a mesogenic (4-substituted benzylidene)aniline group with various electronegative groups were prepared. The copolymer prepared by copolymerization of 4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline with 4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)aniline exhibited smectic phases when the proportion of the mesogenic carbazolyl unit was in the range of 0.26–0.68, though the smectic phase did not appear in both homopolymers prepared from the individual monomers. The copolymer with the proportion of the carbazolyl group of 0.53 exhibited a wide smectic phase from 63 to 185 °C. For the copolymer containing mesogenic carbazolyl and nitrophenyl groups, the X-ray reflection at 30.4 Å corresponded to the thickness of the smectic layer and the broad peak centered at 4.34 Å was assigned to the distance between the layers formed by the mesogenic side groups. The same tendency on thermal behaviors was observed for the copolymer containing mesogenic carbazolyl and cyanophenyl groups, while this tendency was not seen in the copolymer having carbazolyl and (4′-methoxybenzylidene)aniline units both of which were of electron-donating nature. For the copolymers containing both an electron-donating carbazolyl group and an electron-accepting nitrophenyl or cyanophenyl group, the appearance of the smectic phase and the enhancement in thermal stability might be caused mainly by interactions between pendant electron donor and acceptor mesogens.

Introduction

In typical side-chain liquid-crystalline polymers, mesogens are attached to the polymer backbone through a flexible spacer using covalent bonding.[1] Recently, novel families of liquid-crystalline polymers were constructed by making use of intermolecular hydrogen bondings[2-4] and ionic bonding.[5,6] Intermolecular electron donor–acceptor interactions have also been utilized to form liquid crystals[7,8] and liquid-crystalline polymers.[9,10] From the viewpoint of fundamental research and of potential applications such as photo- and electrofunctional materials, the electron donor–acceptor interaction has lately attracted some attention.[11,12] Ringsdorf and co-workers have reported that the mixing of discotic liquid-crystalline triphenylene-containing polymers with electron acceptor trinitrofluorenone derivatives caused an increase in isotropic temperature, probably because the disk-shaped portions were arranged in a more thermally stable state by charge-transfer complexation.[13,14]

For side-chain liquid-crystalline copolymers, polyesters containing both 4-methoxyazobenzene and 4-cyanoazobenzene units exhibited thermal stabilization and formation of a smectic phase.[15] In addition, copolystyrene derivatives which were substituted by both electron-donating 4-methoxyazobenzene and electron-withdrawing 4-nitroazobenzene groups through flexible spacers showed smectic phases appearing within a wide range of temperature.[16,17]

Making use of an electron donor–acceptor complexation, miscible blends of polyacrylate containing a carbazolyl group as a donor with polymethacrylate containing a dinitrophenyl group as an acceptor were prepared.[18] The blends underwent a phase separation by heat treatment and exhibited photoconductive properties different from those of polymers containing a carbazole group.

In our previous paper, side-chain liquid-crystalline polyacrylates containing an alkylene-spaced carbazolyl group in the mesogenic unit were prepared.[19] The polyacrylates exhibited a mesophase when the number of carbons in the alkylene spacer was from 2 to 11. Since the content of the carbazole chromophore in such liquid-crystalline polymers is lower than that in a photoconductive polymer such as poly(vinylcarbazole), it was assumed that an enhancement in efficiency of the carbazole chromophore was needed in order to obtain photo- and electrofunctional liquid-crystalline polymers. Thus, it was attempted to synthesize liquid-crystalline carbazole-containing copolymers with electron donor–acceptor interactions.

We report the synthesis and the thermal properties of side-chain liquid-crystalline copolymers containing a mesogenic (carbazol-2-ylmethylene)aniline unit as an electron donor and (4′-nitrobenzylidene)- or (4′-cyanobenzylidene)-aniline units as an electron acceptor for the purpose of controlling the mesophase. The polymers were characterized by ^{1}H NMR spectrometry, polarized optical microscope observation, differential scanning calorimetry, and X-ray diffraction measurement.

Results and Discussion

Thermal Properties of Low Molecular Weight Compounds and Homopolymers. The thermal properties of CzH6, H6NO$_2$, H6CN, H6OMe, and H6B, having

---

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

0024-9297/94/2227-2658$04.50/0

Table 1. Thermal Properties of 4-[(6-Hydroxyhexyl)oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzH6) and 4-[(6-Hydroxyhexyl)oxy]-*N*-(4′-substituted benzylidene)anilines (H6R's)

compd designation	terminal aromatic group[a]	phase transition temp[b] (°C)
CzH6	Cz	K 126 N 142 I
$H6NO_2$	PNO_2	K 118 I
H6CN	PCN	K 102 N 127 I
H6OMe	$POCH_3$	K 121 I
H6B	PH	K 82 I

[a] Cz: 9-methylcarbazol-2-yl group. PNO_2: 4-nitrophenyl group. PCN: 4-cyanophenyl group. $POCH_3$: 4-methoxyphenyl group. PH: phenyl group. [b] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating and by optical polarizing microscopic observation. K: crystalline. N: nematic. I: isotropic.

Table 2. Thermal Properties of 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzM6) and 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(4′-substituted benzylidene)anilines (M6R's)

compd designation	terminal aromatic group[a]	phase transition temp[b] (°C)
CzM6	Cz	K 51 N 62 I
$M6NO_2$	PNO_2	K 99 I
M6CN	PCN	K 114 I
M6OMe	$POCH_3$	K 72 I
M6B	PH	K 72 I

[a] Cz: 9-methylcarbazol-2-yl group. PNO_2: 4-nitrophenyl group. PCN: 4-cyanophenyl group. $POCH_3$: 4-methoxyphenyl group. PH: phenyl group. [b] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating and by optical polarizing microscopic observation. K: crystalline. N: nematic. I: isotropic.

(carbazol-2-ylmethylene)aniline, (4′-nitrobenzylidene)aniline, (4′-cyanobenzylidene)aniline, (4′-methoxybenzylidene)aniline, and benzylideneaniline, respectively, are shown in Table 1. CzH6 and H6CN exhibit nematic phases from 126 to 142 °C and from 102 to 127 °C, respectively. The isotropic temperature of H6R's shows a tendency to increase with increasing size of the terminal groups. This tendency is also observed for the alkyl terminal compounds containing the same mesogens.[20] For H6R's with a similar size of terminal groups, only H6CN with a cyano group gives a nematic phase, while other Schiff bases $H6NO_2$ and H6OMe do not form a mesophase. Since the cyano group can participate in intermolecular hydrogen bonding with a terminal hydroxy group,[21] the formation of the mesophase may be attributed to this interaction. The phase transition behaviors of $H6NO_2$ and H6CN are almost the same as those reported by Griffin and co-workers.[22]

CzH6 and H6R's were reacted with methacryloyl chloride in the presence of triethylamine to give five methacrylate monomers, i.e., 4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzM6) and 4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)aniline ($M6NO_2$), -*N*-(4′-cyanobenzylidene)aniline (M6CN), -*N*-(4′-methoxybenzylidene)aniline (M6OMe), and -*N*-benzylideneaniline (M6B). The thermal properties of the methacrylate monomers are given in Table 2. Only CzM6 exhibited a nematic phase from 52 to 62 °C, while other monomers did not show a mesophase. These results suggest that the carbazolyl group substituted by a *N*-methanylylidenephenyleneamine group in the 2-position functions as a more potent mesogenic group to form liquid crystals than other groups examined in this experiment. Taking into account the mesophase temperature range of the three compounds, i.e., methacrylate, hydroxy, and alkyl terminal groups, the methacrylate monomer had the lowest liquid crystallinity, which was attributable to the steric effects of the bulky methacrylate group.

Table 3. Polymerization and Thermal Properties of Poly[4-[[(6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline] (PCzM6) and Poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-substituted benzylidene)aniline] (PM6R)[a]

polymer designation[b]	polymer yield (%)	$\bar{M}_n$[c] × 10^4	$\bar{M}_w$[c] × 10^4	phase transition temp[d] (°C)	ΔH_i[e] (kJ/mol)
PCzM6	94	2.55	7.68	g 79 N 172 I	0.34
$PM6NO_2$	84	1.62	4.25	g 45 N 111 I	0.37
PM6CN	92	5.47	13.6	g 53 S 146 I	1.42
PM6OMe	88	3.40	7.47	g 56 N 123 I	0.58
PM6B	90	9.71	48.4	g 35 I	

[a] Radical polymerization in a benzene or DMF solution using 3 mol % AIBN as a radical initiator at 70 °C for 20 h. [b] PCzM6: poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline]. $PM6NO_2$: poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)aniline]. PM6CN: poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-cyanobenzylidene)aniline]. PM6OMe: poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-(4′-methoxybenzylidene)aniline]. PM6B: poly[4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-benzylideneaniline]. [c] Determined by GPC using THF as an eluent and standard polystyrene as reference. [d] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating and by optical polarizing microscopic observation. g: glassy. S: smectic. N: nematic. I: isotropic. [e] Measured by DSC. ΔH_i: enthalpy change from mesophase to isotropic.

All polymethacrylates were prepared by solution polymerization with AIBN as the radical initiator. An acrylate monomer containing a nitrophenyl group was hardly polymerized by AIBN, while the methacrylate monomer containing the same nitrophenyl group was polymerized by AIBN in high yields, probably because more stable polymer radicals were formed from the methacrylate double bonds. Since the intensity of the C–H proton peak of the Schiff base linkage in ^1H NMR spectrum of the polymer corresponded to that expected, the relatively labile C=N bond in the polymer was not decomposed during polymerization. In addition, the aromatic proton absorptions due to carbazolyl groups and phenylene groups showed the existence of the designed mesogenic unit. The thermal properties and molecular weights of homopolymers (PCzM6 and PM6R's) are summarized in Table 3. Number-average molecular weights of the homopolymers were more than 1.6 × 10^4. Except for PM6B without para-substitution, PCzM6, PM6OMe, and $PM6NO_2$ exhibited nematic phases which were confirmed by the observation of threaded textures by optical microscopy, and no peaks corresponding to the smectic layer were observed in the X-ray measurements.

On the other hand, for PM6CN, focal-conic and homeotropic textures characteristic of the smectic phase were observed with the polarized microscope. In the X-ray diffraction of the quenched PM6CN film, a sharp peak at $2\Theta = 2.20°$ (layer distance = 40.1 Å) appeared as well as a broad peak at $2\Theta = 19.7°$. These results suggest that PM6CN had a smectic A phase.

For similar liquid-crystalline polymethacrylates containing such mesogenic groups as phenylbenzoate, azobenzene, and biphenylene groups with the same terminal groups such as nitro, cyano, and methoxy groups, smectic phases dominated.[1,23,24] However, the liquid-crystalline polymethacrylates containing the benzylideneaniline group with the exception of the (cyanobenzylidene)aniline group all exhibited nematic phases, probably because interactions between mesogenic side groups were weak.

Table 4. Copolymerization of 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene)aniline (CzM6) with 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(4′-methoxybenzylidene)aniline (M6OMe) and Thermal Properties of Copolymers [Copoly(CzM6-M6OMe)s][a]

proportion of CzM6		polymer			phase transition		
in feed	in copolymer[b]	yield (%)	$\bar{M}_n{}^c \times 10^4$	$\bar{M}_w{}^c \times 10^4$	temp[d] (°C)	$\Delta H_i{}^e$ (kJ/mol)	$\Delta S/R^f$
0.0	0.0	88	3.40	7.47	g 56 N 123 I	0.58	0.18
0.25	0.23	88	3.98	11.3	g 59 N 141 I	0.52	0.15
0.50	0.47	90	2.69	7.75	g 68 N 150 I	0.55	0.12
0.75	0.78	90	3.68	11.7	g 72 N 163 I	0.39	0.11
1.0	1.0	94	2.55	7.68	g 79 N 172 I	0.34	0.09

[a] Radical polymerization in a benzene solution using 3 mol % AIBN as a radical initiator at 70 °C for 20 h. [b] Determined by ^{1}H NMR. [c] Determined by GPC using THF as an eluent and standard polystyrene as reference. [d] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating and by optical polarizing microscopic observation. g: glassy. N: nematic. I: isotropic. [e] Measured by DSC. ΔH_i: enthalpy change from nematic to isotropic. [f] $\Delta S/R$: entropy change from nematic to isotropic.

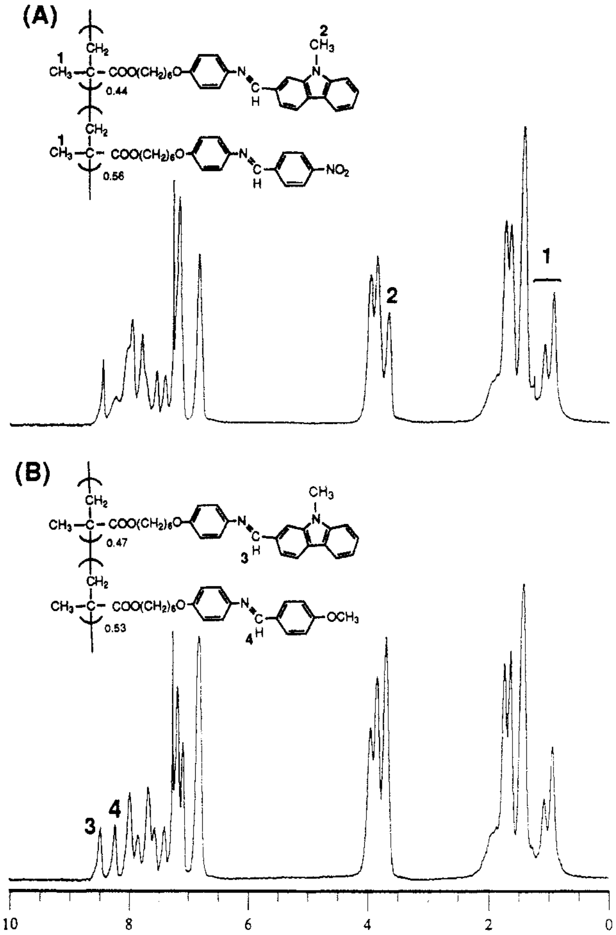


Figure 1. ^{1}H NMR spectra of copolymers (A) copoly(CzM6–M6NO$_2$) ([CzM6] = 0.44) and (B) copoly(CzM6-M6OMe) ([CzM6] = 0.47) in a chloroform-*d* solution at 22 °C.

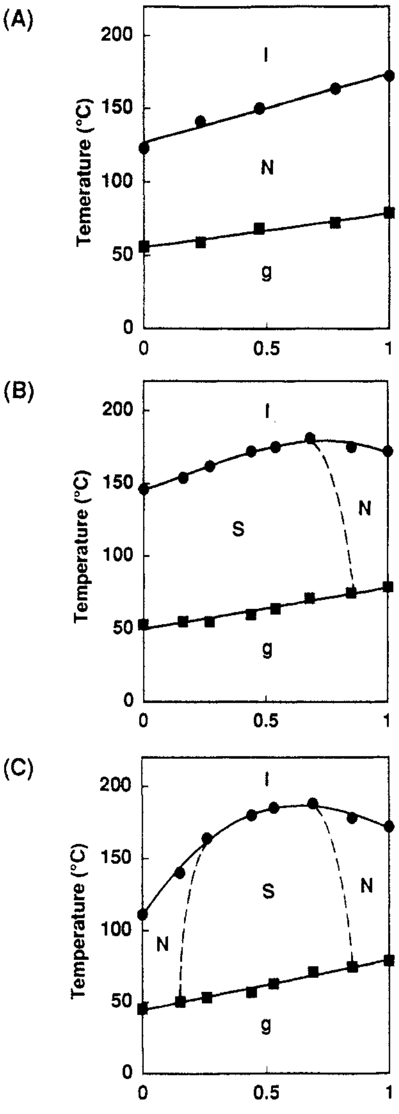


Figure 2. Dependence of phase transition temperatures on the proportion of the CzM6 unit of copolymers: (A) copoly(CzM6–M6OMe); (B) copoly(CzM6–M6CN); (C) copoly(CzM6–M6NO$_2$).

Liquid Crystallinity of Copolymers. Copolymerizations of the carbazolyl-containing monomer CzM6 with the (methoxybenzylidene)aniline-containing M6OMe were carried out with AIBN as the radical initiator. The result of copolymerizations and thermal properties of the copolymers [copoly(CzM6–M6OMe)s] are summarized in Table 4. Copoly(CzM6–M6OMe)s with fairly high molecular weights were obtained in high yields.

The proportion of individual monomeric units in the copolymer was determined by use of ^{1}H NMR spectra (Figure 1). For copolymers composed of CzM6 and M6OMe, the absorptions at 8.20 and 8.46 ppm due to the CH=N protons of the latter (4) and the former (3), respectively, were used for the determination. As described later, for copolymers of CzM6 with M6CN [copoly(CzM6–M6CN)], M6NO$_2$ [copoly(CzM6–M6NO$_2$)], or M6B [copoly(CzM6–M6B)], the peak intensity at 3.61 ppm (2) due to the CH$_3$ group bonded to the carbazolyl group was compared with the intensity at 0.94–1.29 ppm (1) due to the CH$_3$ group in the methacrylate backbone.

All copoly(CzM6–M6OMe)s showed nematic phases. As shown in Figure 2A, both glass transition temperature and isotropic temperature changed linearly with the copolymer composition, and hence there were almost no significant interactions between the two kinds of mesogenic units in the copoly(CzM6–M6OMe)s.

On the other hand, copoly(CzM6–M6CN)s composed of CzM6 and M6CN exhibited smectic phases when the

Table 5. Copolymerization of 4-[[(6-(Methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzM6) with 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(4′-cyanobenzylidene)aniline (M6CN) and Thermal Properties of Copolymers [Copoly(CzM6–M6CN)s][a]

proportion of CzM6		polymer			phase transition		
in feed	in copolymer[b]	yield (%)	$\bar{M}_n{}^c \times 10^4$	$\bar{M}_w{}^c \times 10^4$	temp[d] (°C)	$\Delta H_i{}^e$ (kJ/mol)	$\Delta S/R^f$
0.0	0.0	92	5.47	13.6	g 53 S 146 I	1.42	0.41
0.15	0.16	90	3.05	6.42	g 55 S 154 I	1.24	0.35
0.30	0.27	92	3.15	10.1	g 55 S 162 I	1.09	0.30
0.50	0.44	92	2.80	6.94	g 60 S 172 I	1.09	0.30
0.60	0.54	92	2.92	8.18	g 64 S 175 I	1.11	0.30
0.70	0.68	94	2.89	13.7	g 71 S 181 I	1.06	0.28
0.85	0.85	90	2.35	6.37	g 75 N 175 I	0.70	0.19
1.0	1.0	94	2.55	7.68	g 79 N 172 I	0.34	0.09

[a] Radical polymerization in a benzene or DMF solution using 3 mol % AIBN as a radical initiator at 70 °C for 20 h. [b] Determined by ^{1}H NMR. [c] Determined by GPC using THF as an eluent and standard polystyrene as reference. [d] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating and by optical polarizing microscopic observation. g: glassy. S: smectic. N: nematic. I: isotropic. [e] Measured by DSC. ΔH_i: enthalpy change from mesophase to isotropic. [f] $\Delta S/R$: entropy change from mesophase to isotropic.

Table 6. Copolymerization of 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzM6) with 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)aniline ($M6NO_2$) and Thermal Properties of Copolymers [Copoly($CzM6–M6NO_2$)s][a]

proportion of CzM6		polymer			phase transition		
in feed	in copolymer[b]	yield (%)	$\bar{M}_n{}^c \times 10^4$	$\bar{M}_w{}^c \times 10^4$	temp[d] (°C)	$\Delta H_i{}^e$ (kJ/mol)	$\Delta S/R^f$
0.0	0.0	84	1.62	4.25	g 45 N 111 I	0.37	0.11
0.15	0.16	84	2.10	5.51	g 50 N 140 I	0.86	0.25
0.30	0.26	86	2.51	6.97	g 53 S 164 I	1.13	0.31
0.50	0.44	90	2.27	5.67	g 57 S 180 I	1.26	0.33
0.60	0.53	94	2.42	5.86	g 63 S 185 I	1.28	0.34
0.70	0.69	92	2.75	6.27	g 71 S 188 I	1.09	0.28
0.85	0.85	92	2.40	6.48	g 75 N 178 I	0.64	0.17
1.0	1.0	94	2.55	7.68	g 79 N 172 I	0.34	0.09

[a] Radical polymerization in a benzene or DMF solution using 3 mol % AIBN as a radical initiator at 70 °C for 20 h. [b] Determined by ^{1}H NMR. [c] Determined by GPC using THF as an eluent and standard polystyrene as reference. [d] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating and by optical polarizing microscopic observation. g: glassy. S: smectic. N: nematic. I: isotropic. [e] Measured by DSC. ΔH_i: enthalpy change from mesophase to isotropic. [f] $\Delta S/R$: entropy change from mesophase to isotropic.

CzM6 proportion was in the range from 0 to 0.68 (Table 5). The copolymer had the nematic phase when the CzM6 proportion exceeded 0.68. Since the homopolymers of M6CN and CzM6 had the smectic and nematic liquid crystallinities, 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 two different kinds of side groups, i.e., the electron-donating carbazolyl group and the electron-withdrawing cyanophenyl group.

In Figure 2B, the phase transition temperatures of the copoly(CzM6–M6CN)s are plotted against the proportion of the CzM6 unit. Although the glass transition temperature was linear with the copolymer composition, the isotropic temperature showed a significant positive deviation. For instance, in the copolymer with the CzM6 proportion of 0.54, the isotropic temperature (175 °C) was 15 °C higher than the calculated value based on the copolymer composition (160 °C).

Copolymerizations of CzM6 with a nitro-substituted monomer $M6NO_2$ as well as thermal properties of the copolymers are summarized in Table 6. In the copoly($CzM6–M6NO_2$)s, the induction of a smectic mesophase explicitly took place. The DSC thermograms of copoly($CzM6–M6NO_2$) and individual homopolymers demonstrated the existence of the glass transition at 40–70 °C and of the nematic–isotropic or smectic–isotropic transition at 100–180 °C (Figure 3). In addition, upon observation by a polarized optical microscope, the homopolymers PCzM6 and $PM6NO_2$ exhibited the threaded textures that are characteristic of nematic phases, while the copolymers having the CzM6 proportion of 0.26–0.68 showed focal-conic fan textures characteristic of smectic phases (Figure 4). Accordingly, it was revealed that the smectic liquid crystallinity was induced by the existence of electron donor–acceptor interactions in the copoly($CzM6–M6NO_2$).

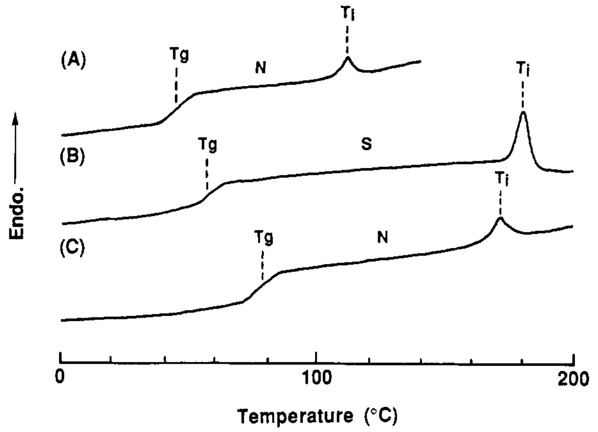


Figure 3. DSC thermograms of homo- and copolymers on the second heating run at a scanning rate of 10 °C/min: (A) $PM6NO_2$; (B) copoly($CzM6–M6NO_2$) ([CzM6] = 0.44); (C) PCzM6.

Stabilization of the smectic phase was also caused by the electron donor–acceptor interaction. As shown in Figure 2C, the mesophase temperature range of copoly($CzM6–M6NO_2$)s was enlarged to a considerable extent in the smectic region. A copoly($CzM6–M6NO_2$) with a CzM6 content of 0.53 had a smectic phase from 63 to 185 °C (=T_i). The T_i was 42 °C higher than the calculated value (143 °C) for a copolymer without the electron donor–acceptor interaction. A similar increase in the isotropic temperature was observed for a side-chain liquid-crystalline copolystyrene derivative containing methoxyazoben-

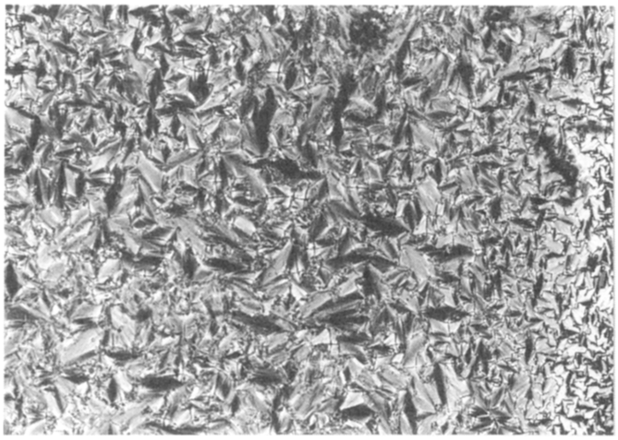


Figure 4. Optical polarizing microphotograph of copoly(CzM6–M6NO_2) ([CzM6] = 0.44) at 170 °C on cooling.

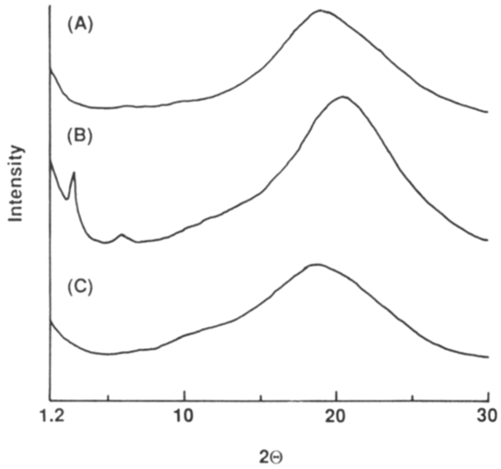


Figure 5. Wide-angle X-ray diffraction patterns of quenched homo- and copolymer films: (A) PM6NO_2; (B) copoly(CzM6–M6NO_2) ([CzM6] = 0.53); (C) PCzM6.

Table 7. Results of X-ray Measurements of Homo- and Copolymers

polymer designation	d_1[a] (Å)	d_2[b] (Å)	l[c] (Å)
PCzM6		4.64	28.0
PM6NO_2		4.63	25.5
PM6CN	40.1	4.50	26.1
copoly(CzM6–M6NO_2) ([CzM6] = 0.53)	30.4	4.34	
copoly(CzM6–M6CN) ([CzM6] = 0.54)	30.4	4.46	

[a] Thickness of the smectic layer. [b] Distance between the mesogenic side group layer. [c] Calculated fully-stretched conformation, including the backbone.

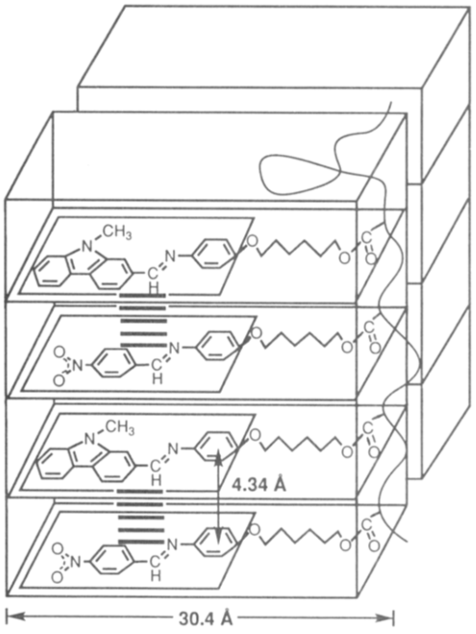


Figure 6. Schematic illustration of a proposed mesophase structure in copoly(CzM6–M6NO_2).

zene and nitroazobenzene groups.[16,17] In addition, the entropy change ($\Delta S/R$) from the smectic phase to the isotropic melt was about 3 times as high as that from the nematic–isotropic in the homopolymers (Table 6). An analogous smectic phase induction was found in the mixtures of low molecular weight compounds containing the carbazolyl and nitrophenyl groups.[20] However, in the present study, it was assumed that the incorporation of the carbazolyl and nitrophenyl groups into the side-chain mesogenic units might enhance interactions between the two groups, because the mesogenic groups had planar structures which easily overlapped.

For copoly(CzM6–M6NO_2) ([CzM6] = 0.53) and the two homopolymers, X-ray diffraction patterns are shown in Figure 5. The results obtained by X-ray measurements are summarized in Table 7. It was revealed that, in the X-ray diffraction of the copolymer, a sharp reflection at 2Θ of 2.90° (d = 30.4 Å) was close to molecular lengths of the fully-stretched CzM6 and M6NO_2 molecules which were calculated to be 28.0 and 25.5 Å, respectively. Accordingly, it was concluded that the copolymer had a smectic structure. A broad reflection at 2Θ of 20.4° (d = 4.34 Å) was assignable to the distance between layers formed by the mesogenic side groups. The distance for copoly(CzM6–M6NO_2) ([CzM6] = 0.53) was approximately 0.3 Å shorter than that for the homopolymers. The X-ray diffraction data indicated that the copoly(CzM6–M6CN) ([CzM6] = 0.54) had a smectic structure almost equivalent to that of the copoly(CzM6–M6NO_2) ([CzM6] = 0.53).

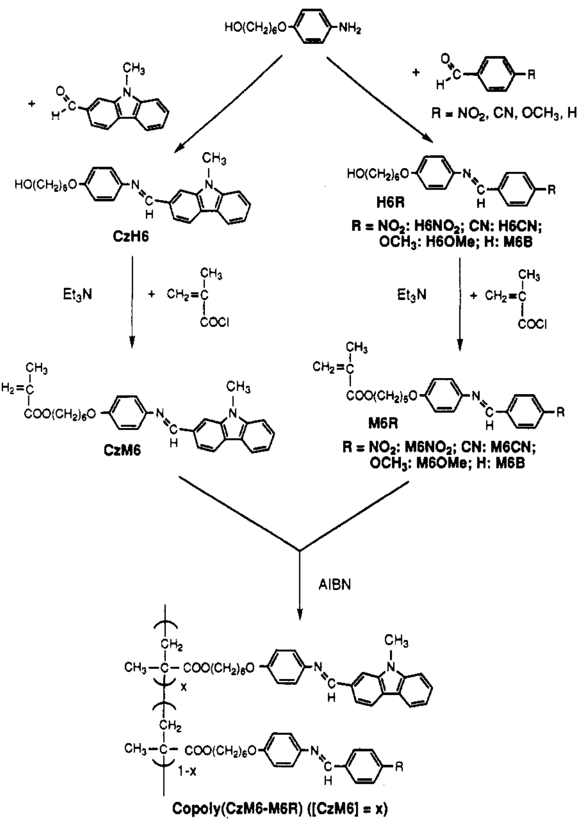
Thus, the thermal stability and the induction of the smectic phase in the copolymer containing a (carbazolylmethylene)aniline group as an electron donor and a (4′-nitrobenzylidene)aniline group as an electron acceptor were caused by interactions between the electron donor and acceptor mesogenic side groups, because both mesogenic side groups easily formed the planar structures, as shown in Figure 6.

Experimental Section

The monomers were prepared according to the route shown in Scheme 1. 4-Nitrobenzaldehyde (Wako Chemical Industries, Ltd.), 4-cyanobenzaldehyde, 4-methoxybenzaldehyde, and benzaldehyde (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. 4-[(6-Hydroxyhexyl)oxy]aniline,[19] (9-methylcarbazol-2-yl)carbaldehyde,[25] 4-[(6-hydroxyhexyl)oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzH6),[19] and 4-[[6-(methacryloyloxy)hexyl]oxy]-*N*-[(9-methylcarbazol-2-yl)methylene]aniline (CzM6)[19] were prepared according to the procedures described in the literature.

4-[(6-Hydroxyhexyl)oxy]-*N*-(4′-substituted benzylidene)anilines (H6R's). 4-[(6-Hydroxyhexyl)oxy]aniline (6.23 g, 0.03 mol) was dissolved in 30 mL of ethanol. After an equimolar amount of a corresponding para-substituted benzaldehyde (0.03 mol) was added to the ethanol solution, the mixture was heated at 70 °C for 2 h. The product was purified by recrystallization from ethanol to provide H6R's. Yield: H6NO_2, 93%; H6CN, 91%; H6OMe, 88%; H6B, 83%. Mp: H6NO_2, 118.3 °C; H6CN, 101.8 °C; H6OMe, 121.1 °C; H6B, 81.6 °C. ^{1}H NMR ($CDCl_3$): H6NO_2, δ 1.35 (1H, t), 1.51 (4H, m), 1.63 (2H, m), 1.83 (2H, m), 3.68 (2H, m), 4.00 (2H, t), 6.95 (2H, d), 7.30 (2H, d), 8.05 (2H, d), 8.31 (2H, d), 8.58 (1H, s); H6CN, δ 1.35 (1H, t), 1.50 (4H, m), 1.62 (2H, m), 1.83 (2H, m), 3.67 (2H, m), 4.00 (2H, t), 6.94 (2H,

Scheme 1. Synthetic Route of Copolymers



d), 7.28 (2H, d), 7.75 (2H, d), 7.99 (2H, d), 8.52 (1H, s); H6OMe, δ 1.33 (3H, t), 1.51 (4H, m), 1.64 (2H, m), 1.82 (2H, m), 3.68 (2H, m), 3.88 (3H, s), 3.99 (2H, t), 6.92 (2H, d), 6.98 (2H, d), 7.20 (2H, d), 7.84 (2H, d), 8.41 (1H, s); H6B, δ 1.36 (1H, t), 1.50 (4H, m), 1.63 (2H, m), 1.82 (2H, m), 3.67 (2H, m), 4.00 (2H, t), 6.93 (2H, d), 7.23 (2H, d), 7.47 (3H, s), 7.90 (2H, d), 8.49 (1H, s).

4-[[6-(Methacryloxyloxy)hexyl]oxy]-*N*-(4′-substituted benzylidene)aniline (M6R's). A methacryloyl chloride (5.2 g, 0.05 mol) solution in 40 mL of chloroform was added to a solution containing H6R (0.034 mol) and triethylamine (10.4 g, 0.1 mol) in 130 mL of chloroform at 0 °C. The reaction was continued for 12 h. After the work-up procedure, the product was purified by recrystallization three times from ethanol to provide M6R. Yield: M6NO$_2$, 52%; M6CN, 52%; M6OMe, 45%; M6B, 43%. Mp: M6NO$_2$, 98.7 °C; M6CN, 113.6 °C: M6OMe, 72.3 °C; M6B, 71.7 °C. ^{1}H NMR (CDCl$_3$): M6NO$_2$, δ 1.53 (4H, m), 1.75 (2H, m), 1.83 (2H, m), 1.96 (3H, s), 4.01 (2H, t), 4.18 (2H, t), 5.56 (1H, s), 6.11 (1H, s), 6.95 (2H, d), 7.30 (2H, d), 8.06 (2H, d), 8.32 (2H, d), 8.59 (1H, s); M6CN, δ 1.52 (4H, m), 1.73 (2H, m), 1.83 (2H, m), 1.95 (3H, s), 4.00 (2H, t), 4.17 (2H, t), 5.56 (1H, s), 6.11 (1H, s), 6.94 (2H, d), 7.28 (2H, d), 7.75 (2H, d), 7.99 (2H, d), 8.53 (1H, s); M6OMe, δ 1.51 (4H, m), 1.73 (2H, m), 1.82 (2H, m) 1.95 (3H, s), 3.89 (3H, s), 3.98 (2H, t), 4.17 (2H, t), 5.56 (1H, s), 6.11 (1H, s), 6.91 (2H, d), 6.98 (2H, d), 7.20 (2H, d), 7.83 (2H, d), 8.41 (1H, s); M6B, δ 1.51 (4H, m), 1.72 (2H, m), 1.82 (2H, m), 1.96 (3H, s), 3.99 (3H, t), 4.18 (3H, t), 5.56 (1H, s), 6.11 (1H, s), 6.93 (2H, d), 7.23 (2H, d), 7.47 (3H, t), 7.90 (2H, d), 8.49 (1H, s).

Polymerization. Polymerizations of CzM6 and M6R were carried out in a benzene or DMF solution with azobis(isobutyronitrile) (AIBN; 3 mol %) as an initiator at 70 °C for 20 h under vacuum. The resulting polymer was purified by reprecipitation using a chloroform–diethyl ether system.

Characterization. A 400-MHz ^{1}H NMR spectrum was recorded on a GE Omega 400WB NMR spectrometer in a chloroform-*d* solution. The molecular weight of the resulting polymer was obtained with a HLC-802A (Tosoh Co.) using tetrahydrofuran as an eluent and standard polystyrene as reference. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used to determine phase transition temperatures at the heating and cooling rates of 10 °C/min. For the low molecular weight compounds, the onset point of endotherms was taken as the transition and melting temperatures. For the polymers, the peak temperature of endotherms 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 also 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: Glascow, Scotland, 1989.
(2) Kato, T.; Fréchet, J. M. J. *Macromolecules* **1989**, *22*, 3819.
(3) Kumar, U.; Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.
(4) Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Fréchet, J. M. J. *Macromolecules* **1992**, *25*, 6836.
(5) Ujiie, S.; Iimura, K. *Macromolecules* **1992**, *25*, 3174.
(6) Rodriguez, D. N.; Guillon, D.; Skouilos, A.; Frere, Y.; Gramain, P. *Makromol. Chem.* **1992**, *193*, 3117.
(7) Araya, K.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3079.
(8) Demus, D.; Pelzel, G.; Sharma, N. K.; Weissflog, W. *Mol. Cryst. Liq. Cryst.* **1981**, *76*, 241.
(9) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
(10) Finkelman, H.; Kiechle, U.; Rehage, G. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 343.
(11) Koide, N.; Ogura, S.; Aoyama, Y. *Mol. Cryst. Liq. Cryst.* **1991**, *198*, 323.
(12) Ford, W. T.; Bautista, M.; Zhao, M.; Reeves, R. J.; Powell, R. C. *Mol. Cryst. Liq. Cryst.* **1991**, *198*, 351.
(13) Ringsdorf, H.; Wustefeld, R.; Zerta, E.; Ebert, M.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 914.
(14) Bengs, H.; Renkel, R.; Ringsdorf, H.; Baehr, C.; Ebert, M.; Wendorff, J. H. *Makromol. Chem., Rapid. Commun.* **1991**, *12*, 439.
(15) Reck, B.; Ringsdorf, H. *Liq. Cryst.* **1990**, *8*, 247.
(16) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Liq. Cryst.* **1991**, *9*, 47.
(17) Schleeh, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1859.
(18) Uryu, T.; Ohkawa, H.; Furuichi, T.; Oshima, R. *Macromolecules* **1988**, *21*, 188.
(19) Kosaka, Y.; Kato, T.; Uryu, T. *J. Polym. Sci., Part A: Polym. Chem.*, in press.
(20) Kosaka, Y.; Uryu, T., unpublished data.
(21) Allerhand, A.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1963**, *85*, 866.
(22) Griffin, A. C.; Vaidya, S. R. *Mol. Cryst. Liq. Cryst.* **1989**, *173*, 85.
(23) Finkelmann, H.; Happ, M.; Portugal, M.; Ringsdorf, H. *Makromol. Chem.* **1978**, *179*, 2541.
(24) Lorenz, R. *Liq. Cryst.* **1991**, *9*, 127.
(25) Lux, M.; Strohiegel, P.; Höcker, H. *Makromol. Chem.* **1987**, *188*, 811.