Synthesis and Thermal Properties of Side-Chain Liquid-Crystalline Copolymers Containing an Electron-Donating (Carbazolylmethylene)aniline and an Electron-Accepting (4′-Nitrobenzylidene)aniline. Effects of Alkylene Spacers on the Smectic Phase

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ABSTRACT: Side-chain liquid-crystalline copolymers containing both a mesogenic (carbazolylmethylene)aniline group as the electron donor and a mesogenic (4′-nitrobenzylidene)aniline group as the electron acceptor with alkylene spacers of different lengths were prepared. The thermal stabilization and the induction of the smectic phases were observed for the copolymers containing spacers with similar lengths. For example, the copolymer containing both a hexamethylene spacer in the carbazolyl group and a trimethylene spacer in the nitrophenyl group exhibited a smectic phase from 77 to 191 °C, though the smectic phase did not appear in both homopolymers. On the other hand, these tendencies were not seen for the copolymers with spacers of a large variation in the length, i.e., undecamethylene and ethylene spacers. Thus, it is revealed that the thermal stability and the induction of the smectic phases in the copolymers are influenced to a large extent by the degree of overlapping between the mesogenic side groups through the electron donor−acceptor interaction.

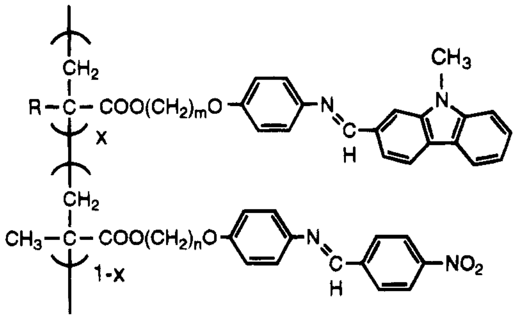
Introduction

It is known that the thermal stability of the nematic phase was caused by mixing 4-butyl-*N*-(4′-methoxybenzylidene)aniline as an electron donor and 4-pentyl-4′-cyanobiphenyl as an electron acceptor.[1] Moreover, for the similar electron donor and acceptor mixtures, the induction and the thermal stability of smectic phases were reported by Matsunaga and co-workers.[2,3]

Recently, this effect was applied to side-chain liquid-crystalline polymers which have characteristic of polymers, i.e., glass transitions and high molecular weights, and the photoelectrical properties of low molar mass mesogens.[4−18] The liquid-crystalline polymers containing electron donor and acceptor groups have great potentials in various fields, such as information storage and nonlinear optics.[5−12] These side-chain liquid-crystalline polymers have also attracted attention for fundamental studies. Liquid-crystalline copolystyrenes containing both electron-donating 4-methoxyazobenzene and electron-accepting 4-nitroazobenzene groups with the same carbon number of both alkylene spacers exhibited thermal stability of the smectic phases by the electron donor−acceptor interaction.[13,14] A new class of discotic liquid-crystalline polymer blends was prepared from polyacrylates containing electron-rich triphenylene side groups and trinitrofluorenone derivatives by charge-transfer complexation.[15,16]

In our previous papers, side-chain liquid-crystalline copolymers and polymer blends containing both a mesogenic carbazolyl group with the electron-donating character and a mesogenic nitrophenyl or cyanophenyl group with the electron-accepting character were prepared.[17,18] The induction and the thermal stability of the smectic phases for these copolymers and polymer blends were observed because of the intermolecular electron donor−acceptor interaction between the mesogenic side groups.

Chart 1. Molecular Structures of Copolymers Containing both Mesogenic Carbazolyl and Mesogenic Nitrophenyl Groups with Alkylene Spacers of Different Lengths [copoly(RmCz-MnNO$_2$)s]



Copoly(RmCz-MnNO$_2$)s

R = H (A), CH$_3$ (M)
m = 3, 6, 11
n = 2-6, 11

In this paper, we wish to report how the thermotropic properties of copolymers containing both mesogenic carbazolyl and mesogenic nitrophenyl groups are affected by alkylene spacers of different lengths. In addition, it is confirmed that the smectic phase induction in the copolymers is caused by the overlapping of the electron-donating mesogen with the electron-accepting mesogen (Chart 1). The copolymers were characterized by ^{1}H NMR spectrometry, optical polarized microscope observation, differential scanning calorimetry, and X-ray diffraction measurement.

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Table 1. Thermal Properties of 4-[(ω-Hydroxyalkyl)oxy]-N-(4′-nitrobenzylidene)anilines (HnNO$_2$'s)

n	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)
2	K 130 I	
3	K 96 (N 95)[c] I	(0.25)[e]
4	K 105 (N 107)[c] I	(0.38)[e]
5	K 83 N 94 I	0.17
6	K 118 I	
11	K 81 (S 80)[d] N 89 I	0.7

[a] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the first cooling and the second heating runs and by optical polarized microscope observation. K: crystalline. S: smectic. N: nematic. I: isotropic. [b] Measured by DSC. ΔH_i: enthalpy change from nematic to isotropic. [c] Monotropic nematic. [d] Monotropic smectic. [e] Enthalpy change from isotropic to nematic.

Results and Discussion

Thermal Properties of Low Molecular Weight Compounds and Homopolymers. 4-[(ω-Hydroxyalkyl)oxy]-N-(4′-nitrobenzylidene)anilines (HnNO$_2$'s) were prepared from 4-[(ω-hydroxyalkyl)oxy]anilines and 4-nitrobenzaldehyde in high yields. Thermal properties of HnNO$_2$'s are summarized in Table 1. H3NO$_2$ and H4NO$_2$ exhibited monotropic nematic phases from 95 to 51 °C and from 107 to 85 °C, respectively. H11NO$_2$ showed a nematic phase from 81 to 89 °C on heating, while in the cooling stage, it displayed nematic and smectic phases from 88 to 80 °C and from 80 to 58 °C, respectively. The enthalpy change of isotropization for H11NO$_2$ was 0.7 kJ/mol. On the other hand, both H2NO$_2$ and H6NO$_2$ were not mesomorphic.

HnNO$_2$'s were reacted with methacryloyl chlorides in the presence of triethylamine to give methacrylate monomers, i.e., 4-[[ω-(methacryloyloxy)alkyl]oxy]-N-(4′-nitrobenzylidene)anilines (MnNO$_2$'s). Only M11NO$_2$ with an undecamethylene spacer exhibited a nematic phase between 70 and 78 °C. Other methacrylate monomers did not form mesophases, presenting the melting at 82−102 °C.

All methacrylate monomers containing a (4′-nitrobenzylidene)aniline group were prepared by solution polymerization with azobis(isobutyronitrile) as a radical initiator. The thermal properties and the molecular weights of the homopolymers (PMnNO$_2$'s) are summarized in Table 2 and Figure 1. PMnNO$_2$'s with $\bar{M}_n$'s ranging from 2.4×10^4 to 5.2×10^4 were obtained in high yields. The polymer yield and the number-average molecular weight of PMnNO$_2$'s increased with increasing carbon number of the alkylene spacer from ethylene to hexamethylene. PM2NO$_2$ and PM3NO$_2$ with short alkylene spacers showed only glass transitions at 119 and 84 °C, respectively, expressing no mesophase. PMnNO$_2$'s having from tetramethylene to hexamethylene spacers exhibited nematic phases. For PM4NO$_2$, a nematic phase was observed from 80 to 113 °C, and the enthalpy change of isotropization was 0.32 kJ/mol. On the other hand, PM11NO$_2$ with a long alkylene spacer exhibited a smectic phase from 43 to 133 °C which was characterized by focal-conic fan and homeotropic textures on the polarized microscope observation.

An X-ray diffraction pattern of the quenched PM11NO$_2$ film showed a sharp reflection at 2θ of 1.94° (d = 45.5 Å) corresponding to the thickness of the smectic layer (d) and a broad reflection at 2θ of 20.0° (d = 4.44 Å) due to the average distance between the mesogenic side group. Both polarized microscope observation and X-ray diffraction measurement indicated that the PM11NO$_2$ had a smectic A phase. A molecular model of the monomeric M11NO$_2$ in the fully stretched conformation gives the molecular length (l) of 31.5 Å. The d/l ratio of PM11NO$_2$ is 1.44. This ratio suggests that the smectic phase of PM11NO$_2$ formed an $\mathrm{S_{Ad}}$ mesophase structure.[19] The glass transition temperature of the homopolymers decreased with increasing carbon number of the alkylene spacer, while the isotropic temperature showed a reverse tendency. Longer alkylene spacers might cause stronger interactions between mesogens involved in the side chain. This tendency was also observed for side-chain liquid-crystalline polymers containing a nitrophenyl benzoate group[20] and a (carbazolylmethylene)aniline group.[21,22]

Liquid Crystallinity of Copolymers Having Mesogenic Side Groups of (4′-Nitrobenzylidene)aniline Separated by Alkylene Spacers with Different Lengths. To examine effects of the alkylene spacers on steric behaviors of mesogenic groups, copolymethacrylates containing the (4′-nitrobenzylidene)aniline group with two kinds of spacers, i.e., hexamethylene and an alkylene chosen from ethylene to undecamethylene, were prepared (Chart 2). Thermal properties of the copolymers, i.e., copoly(M6NO$_2$-MnNO$_2$)s, are summarized in Table 3. The monomer ratio (1:1) in the feed was used as the ratio (1:1) of the two monomeric units in all copolymers, because the monomer reactivity ratio is close together and the polymer yield was high. In the copolymers, it was too difficult to determine the ratio of the monomeric units by NMR because of overlappings of the absorptions.

Although PM11NO$_2$ had a smectic phase from 43 to 133 °C, copoly(M6NO$_2$-M11NO$_2$) exhibited a nematic phase from 44 to 121 °C. The enthalpy change of isotropization for the copolymer was 1.39 kJ/mol, which is smaller than that for the homopolymer (2.61 kJ/mol). As expected, a decrease in orientation of the mesophase occurred in the copolymer.

Other copoly(M6NO$_2$-MnNO$_2$)s (n = 2−5) also showed the nematic phase. It is noteworthy that the nonmesogenic PM2NO$_2$ gave mesogenic copoly(M6NO$_2$-M2NO$_2$). However, as shown in Figure 2, the glass transition temperature and the isotropic temperature of the copolymers were similar to those observed for the respective PMnNO$_2$'s.

It can be seen that the glass transition temperature and the isotropic temperature of the copolymers are close to the calculated values according to the Fox equation[23] (○) and the additive rule (□) based on the proportion of the monomeric units (1:1). Similar tendencies were reported for liquid-crystalline copolystyrenes[24,25] and copoly(vinyl ether)s[26−28] containing alkylene spacers with different lengths.

Liquid Crystallinity of Copolymers Containing Both Mesogenic Electron Donor and Acceptor Side Chains Separated by Alkylene Spacers with Different Lengths. Copolymers [copoly(RmCz-MnNO$_2$)s] containing both electron-donating mesogenic carbazolyl and electron-accepting mesogenic nitrophenyl groups, in which the alkylene spacers have different lengths, were prepared by copolymerization of the two monomers. The results of copolymerizations and thermal properties of the copolymers are summarized in Table 4.

The copolymers with high molecular weights were obtained in high yields. The proportion of individual monomeric units in the copolymer was determined by means of an ^{1}H NMR spectrum,[17] revealing that the proportion of the carbazolyl unit was in the range 0.53−0.55.

Table 2. Polymerization of 4-[[ω-(Methacryloyloxy)alkyl]oxy]-*N*-(4′-nitrobenzylidene)aniline and Thermal Properties of the Homopolymers (PMnNO₂'s)

polymer designation	polymer yield (%)	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_w$	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)	$\Delta S/R$[c]
PM2NO$_2$	79	2.39	3.58	g 119 I		
PM3NO$_2$	81	2.54	4.77	g 84 I		
PM4NO$_2$	81	3.86	8.24	g 80 N 113 I	0.32	0.10
PM5NO$_2$	83	4.23	9.19	g 70 N 122 I	0.97	0.30
PM6NO$_2$	84	5.23	12.0	g 56 N 120 I	0.44	0.19
PM11NO$_2$	85	4.12	8.48	g 43 S 133 I	2.61	0.77

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

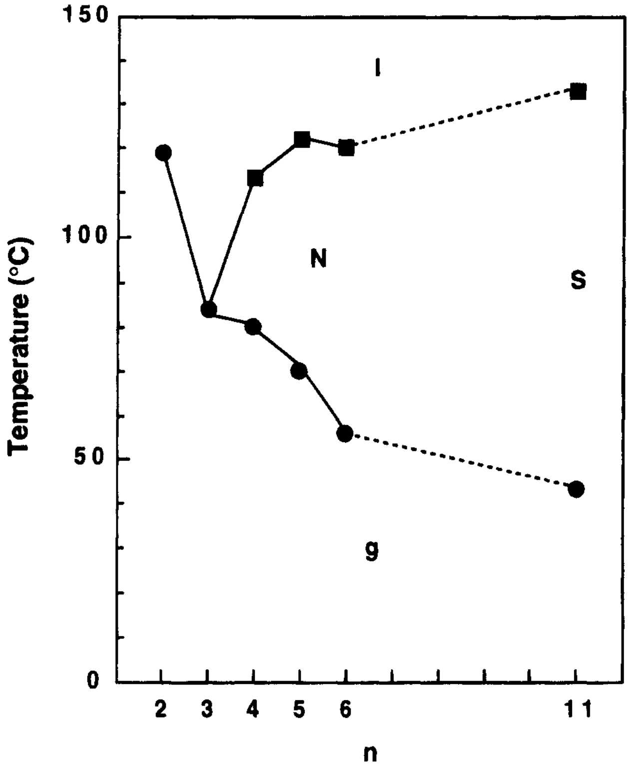
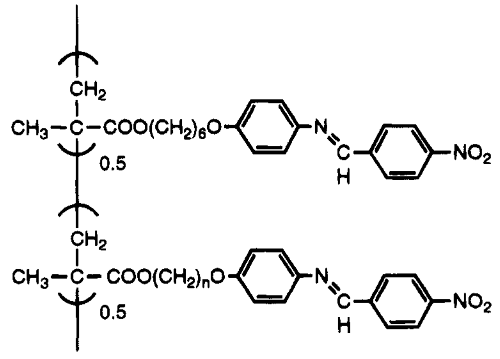


Figure 1. Dependence of the transition temperatures on carbon number of the alkylene spacer (*n*) for PMnNO$_2$'s.

Chart 2. Molecular Structures of Copolymers Containing Mesogenic Nitrophenyl Groups Separated by Alkylene Spacers with Different Lengths [copoly(M6NO₂-MnNO₂)s]



Copoly(M6NO$_2$-MnNO$_2$)s

n = 2-6, 11

Table 3. Thermal Properties of Copolymers Composed of 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-(4′-nitrobenzylidene)aniline with 4[[ω-(Methacryloyloxy)alkyl]oxy]-*N*-(4′-nitrobenzylidene)anilines [Copoly(M6NO₂-MnNO₂)s]

polymer designation	phase transition temp[a] (°C)	ΔH_i[b] (kJ/mol)	$\Delta S/R$[c]
copoly(M6NO$_2$-M2NO$_2$)	g 83 N 111 I	0.36	0.11
copoly(M6NO$_2$-M3NO$_2$)	g 73 N 102 I	0.26	0.08
copoly(M6NO$_2$-M4NO$_2$)	g 71 N 117 I	0.40	0.12
copoly(M6NO$_2$-M5NO$_2$)	g 61 N 117 I	0.64	0.20
PM6NO$_2$	g 56 N 120 I	0.44	0.19
copoly(M6NO$_2$-M11NO$_2$)	g 44 N 121 I	1.39	0.42

[a] Transition temperature (°C) determined by the DSC measurement at a scanning rate of 10 °C/min on the second heating run and by optical polarized microscope observation. g: glassy. N: nematic. I: isotropic. [b] Measured by DSC. ΔH_i: enthalpy change of isotropization. [c] $\Delta S/R$: entropy change of isotropization.

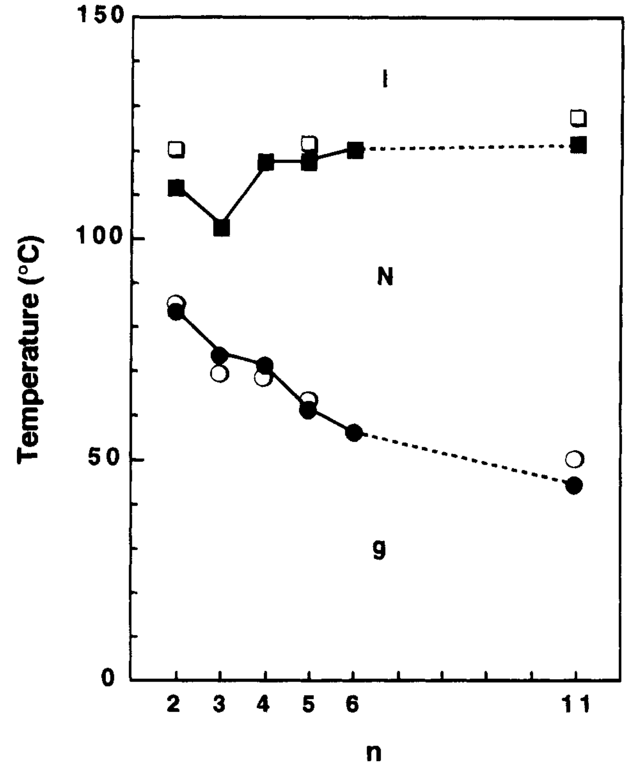


Figure 2. Dependence of the transition temperatures on carbon number of the alkylene spacer (*n*) for copoly(M6NO$_2$-MnNO$_2$)s. Open symbols represent the calculated values according to the Fox equation (○) and the additive rule (☐).

The copoly(M6Cz-M2NO$_2$) exhibited a nematic phase from 93 to 160 °C. On the other hand, the copolymers containing from trimethylene to hexamethylene spacers induced smectic phases from the glass transition to the isotropic transition temperature. For example, a copoly(M6Cz-M3NO$_2$) had a smectic phase from 77 to 191 °C (=T_i). The T_i was 59 deg higher than the calculated value (132 °C) based on the respective homopolymers without the elecron donor−acceptor interaction. It was already reported that the hexamethylene-spaced copolymer had a smectic phase.[17] The smectic phase was characterized by a focal-conic fan texture with the polarized microscope observation, as shown in Figure

Table 4. Copolymerization of 4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (M6Cz) with 4-[[ω-(Methacryloyloxy)alkyl]oxy]-*N*-(4′-nitrobenzylidene)aniline ($MnNO_2$) and Thermal Properties of the Copolymers [Copoly($M6Cz-MnNO_2$)s]

n	proportion of M6Cz 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]
2	0.55	87	3.01	9.39	g 93 N 160 I	0.31	0.09
3	0.55	90	2.46	7.60	g 77 S 191 I	1.45	0.38
4	0.55	83	3.19	9.02	g 75 S 181 I	0.90	0.24
5	0.55	86	4.17	12.9	g 66 S 197 I	1.69	0.43
6	0.53	94	2.42	5.86	g 63 S 185 I	1.29	0.34
11	0.53	91	3.35	9.87	g 48 S 179 I	2.05	0.54

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

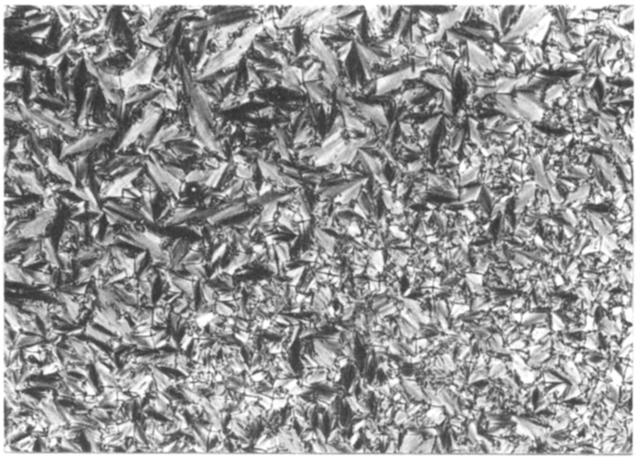


Figure 3. Optical polarized microphotograph of copoly($M6Cz-M3NO_2$) ([M6Cz] = 0.55) at 175 °C on cooling.

3. For copoly($M6Cz-MnNO_2$)s containing spacers from trimethylene to hexamethylene, entropy changes of clearing were about twice as high as those for the homopolymers.

A plot of the transition temperatures as a function of carbon number of the alkylene spacer in $MnNO_2$ units for copoly($M6Cz-MnNO_2$)s is presented in Figure 4A. The phase behavior of the copoly($M6Cz-MnNO_2$)s was different from that of the copoly($M6NO_2-MnNO_2$)s containing both electron-accepting groups. The glass transition behavior was almost the same as the calculated value based on the proportion of the individual homopolymers. However, the tendency on isotropic temperature showed a significant positive deviation. In the isotropic temperature of the copolymers, an odd–even effect was observed in the spacers from ethylene to hexamethylene.

For mesogenic carbazolyl-containing polyacrylates, copolymers of 4-[[3-(acryloyloxy)propyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (A3Cz) with mesogenic (4′-nitrobenzylidene)aniline-containing methacrylates ($MnNO_2$'s) were prepared. These copoly($A3Cz-MnNO_2$)s having a trimethylene spacer in the carbazolyl-containing acrylate unit exhibited thermal behaviors similar to those of the copoly($M6Cz-MnNO_2$)s, as shown in Figure 4B.

When the $MnNO_2$ unit had a short spacer from ethylene to tetramethylene, the copolymers showed the nematic phase. The copolymers having longer spacers of pentamethylene and hexamethylene in the $MnNO_2$ unit exhibited the smectic phase in the range 70–171 °C and 68–165 °C, respectively. As the spacer lengthened to undecamethylene, the copolymer again showed the nematic phase. Consequently, in order to form the smectic phase by the electron donor–acceptor interaction, it must be necessary for the length of the alkylene spacer not to be too different from each other. In addition, the fact that the entropy change of clearing for the copoly($A3Cz-M11NO_2$) was smaller than that for a homopolymer $PM11NO_2$ indicated that there was almost no electron donor–acceptor interaction between the two mesogenic units.

As the alkylene spacer length in the carbazolyl-containing unit was increased to 11, a similar but more distinct tendency was observed (Figure 4C). The copoly($A11Cz-MnNO_2$)s (n = 4–6 and 11) exhibited the smectic phase, while those of n = 2 and 3 had the nematic phase. Especially, in the case of copoly($A11Cz-M11NO_2$), a strong electron donor–acceptor interaction occurred, which is revealed by the wide mesophase temperature range for the copolymer (31–197 °C). It is assumed that since the separation by longer alkylene spacers with equivalent lengths lowered the influence originating from stiffness of the polymer backbone, the electron donor–acceptor interaction between the two mesogenic side groups was increased in the copolymers with both undecamethylene spacers.

For quenched copoly($M6Cz-MnNO_2$) (n = 3–6 and 11) films, representative X-ray diffraction patterns are shown in Figure 5. X-ray diffraction patterns of these copolymers showed sharp reflections at small angles corresponding to the thickness of the smectic layers and broad reflections at wide angles due to the average distance between the mesogenic side groups. The data calculated on the basis of the X-ray measurement are summarized in Table 5. The distances of the copolymers were shorter than those of individual homopolymers. The thicknesses of the smectic layer of the copolymers were close to the fully-stretched molecular length for the respective methacrylate monomers. These results suggested that the copolymers had smectic phases which were formed by nearly full overlapping of the electron-donating mesogenic carbazolyl group with the electron-accepting mesogenic nitrophenyl group.

Experimental Section

4-[[6-(Methacryloyloxy)hexyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (M6Cz), 4-[[3-(acryloyloxy)propyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (A3Cz), and 4-[[11-(acryloyloxy)undecyl]oxy]-*N*-[(9-methyl-2-carbazolyl)methylene]aniline (A11Cz) were prepared according to the procedure previously described.[17,21] 4-[[ω-(Methacryloyloxy)alkyl]oxy]-*N*-(4′-nitrobenzylidene)anilines were prepared according to the route shown in Scheme 1.

4-[(ω-Hydroxyalkyl)oxy]anilines (n = 2, 3, 5, 6, and 11). The synthesis of 4-[(5-hydroxypentyl)oxy]aniline is described as a representative case. 5-Chloropentanol (20.5 g, 0.17 mol) was added to a solution containing 4-nitrophenol (19.4 g, 0.14 mol) and KOH (11.7 g, 0.21 mol) in 300 mL of a mixture of ethanol and water (1:1). Then, the mixture was refluxed for 48 h to give 4-[(5-hydroxypentyl)oxy]nitrobenzene. The resulting 4-[(5-hydroxypentyl)oxy]nitrobenzene (15.8 g, 0.07 mol) was reduced with sodium sulfide nonahydrate (33.7 g, 0.14

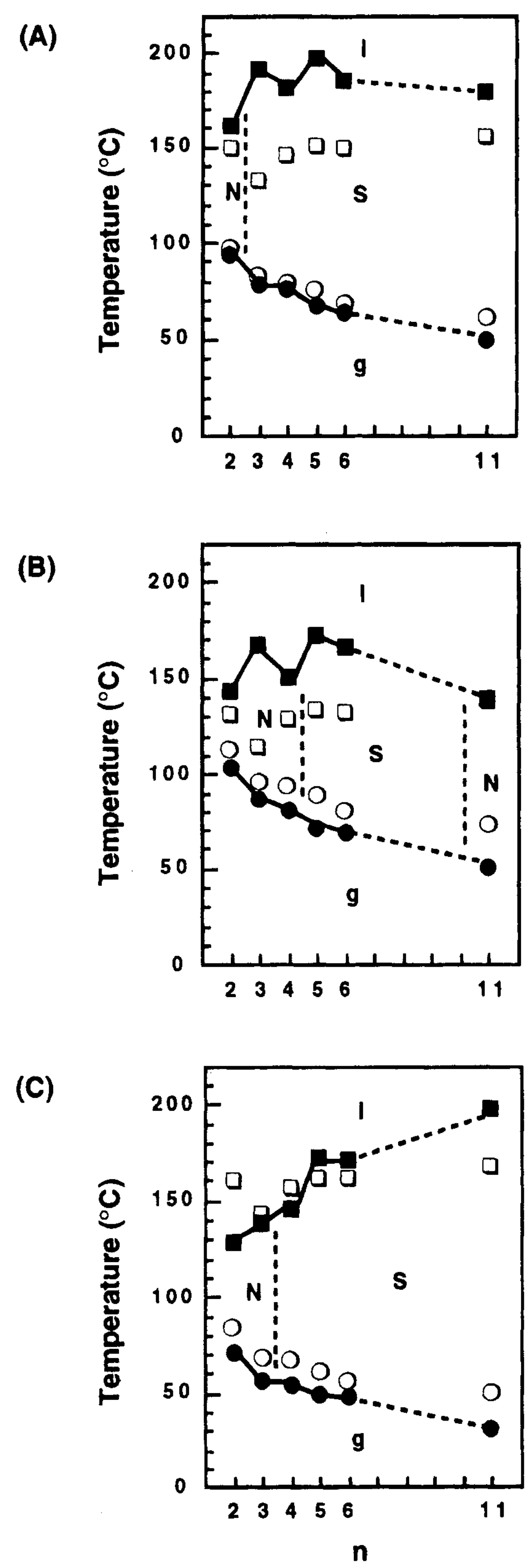


Figure 4. Dependence of the transition temperatures on carbon number of the alkylene spacer (n) for (A) copoly(M6Cz-MnNO$_2$)s, (B) copoly(A3Cz-MnNO$_2$)s, and (C) copoly(A11Cz-MnNO$_2$)s. Open symbols represent the calculated values according to the Fox equation (○) and the additive rule (□).

mol) in 300 mL of 50% ethanol at refluxing temperature for 20 h to give 7.8 g of 4-[(5-hydroxypentyl)oxy]aniline. Yield: 31%. Mp: 87.9 °C. For other 4-[(ω-hydroxyalkyl)oxy]anilines: (n = 2) yield 30%, mp 63.8 °C; (n = 3) yield 45%, mp 79.4 °C; (n = 6) yield 52%, mp 75.7 °C; (n = 11) yield 35%, mp 89.9 °C.

4-[(Tetrahydro-2-pyranyl)oxy]-1-chlorobutane. 3,4-Dihydro-2-pyran was added to a mixture of 4-chlorobutane (54.5 g, 0.5 mol) and concentrated HCl (0.5 mL) at 0 °C. After the resulting mixture was stirred at room temperature for 20 h, the solution was neutralized with KOH (0.9 g) and then filtered. The product was distilled under reduced pressure. Yield: 64%. Bp: 105–107 °C (6 mmHg) [lit.[29] bp: 99–101 °C (4 mmHg)].

4-[(4-Hydroxybutyl)oxy]nitrobenzene. 4-[[4-[(Tetrahydro-2-pyranyl)oxy]butyl]oxy]nitrobenzene was synthesized by the reaction of 4-[(tetrahydro-2-pyranyl)oxy]-1-chlorobutane (53 g, 0.27 mol) and 4-nitrophenol (31.3 g, 0.22 mol) in the same way as 4-[(5-hydroxypentyl)oxy]nitrobenzene. After the

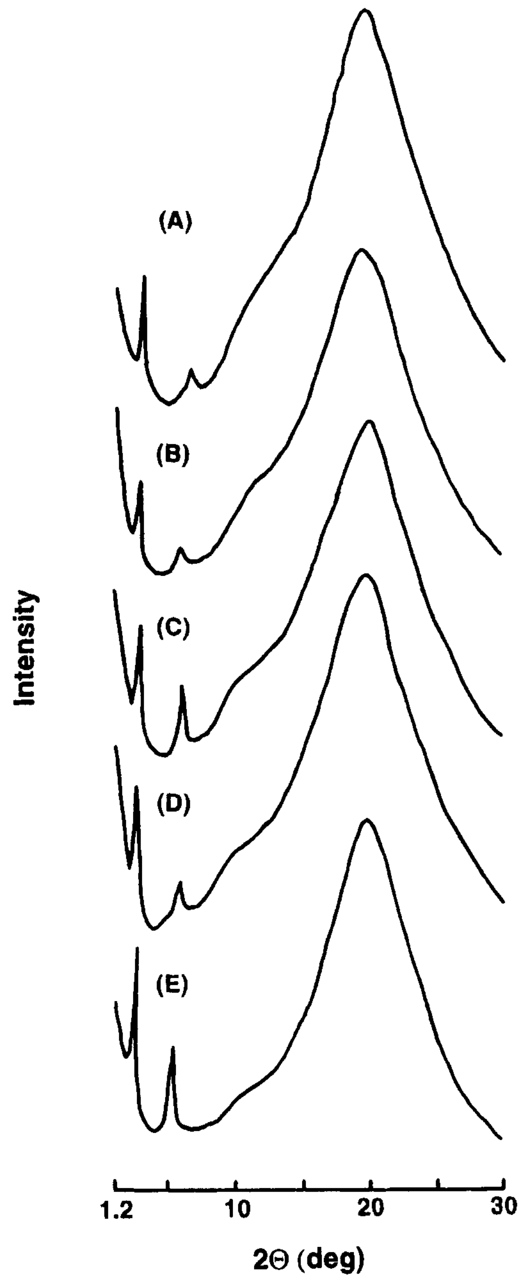


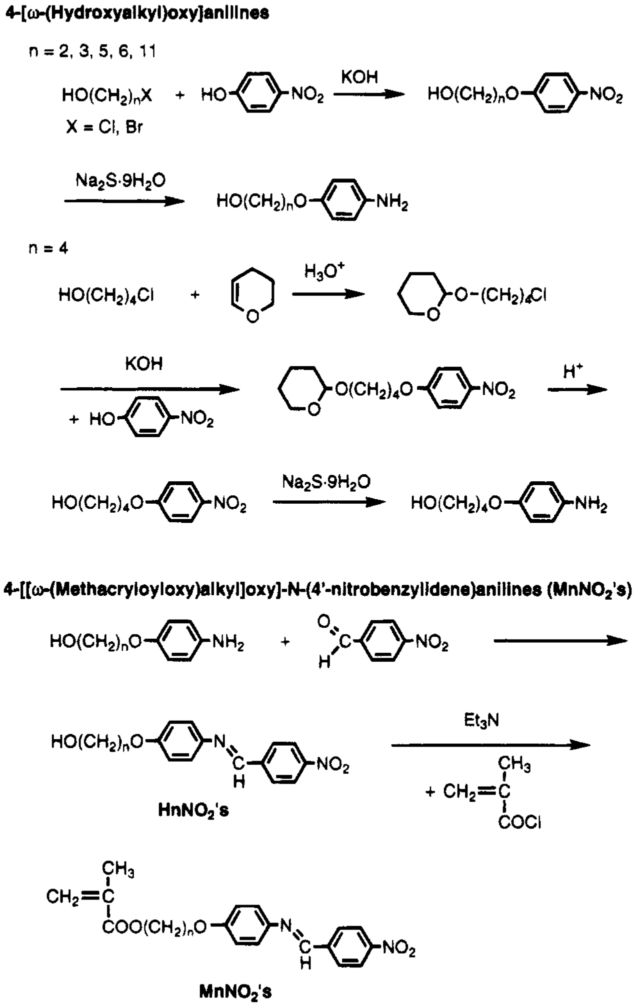
Figure 5. Wide-angle X-ray diffraction patterns of quenched copoly(M6Cz-MnNO$_2$) films: (A) n = 3; (B) n = 4; (C) n = 5; (D) n = 6; (E) n = 11.

Table 5. Results of X-ray Measurements of Copolymers [Copoly(M6Cz-MnNO$_2$)s]

copolymer designation	d_1[a] (Å)	d_2[b] (Å)
copoly(M6Cz-M3NO$_2$)	27.8	4.50
copoly(M6Cz-M4NO$_2$)	29.8	4.48
copoly(M6Cz-M5NO$_2$)	29.0	4.39
copoly(M6Cz-M6NO$_2$)	30.4	4.34
copoly(M6Cz-M11NO$_2$)	33.4	4.37

[a] Thickness of the smectic layer. [b] Distance between the mesogenic side groups.

Scheme 1. Synthetic Route of 4-[[ω-(methacryloyloxy)alkyl]oxy]-*N*-(4′-nitrobenzylidene)anilines (MnNO₂'s)



resulting product was dissolved in hot ethanol, concentrated H_2SO_4 (10 mL) was added dropwise. The mixture was refluxed under stirring for 0.5 h. After cooling, the precipitate was filtered and successively washed with ethanol and water. The product was recrystallized from toluene to provide 4-[(4-hydroxybutyl)oxy]nitrobenzene. Yield: 47%. Mp: 75.0 °C.

4-[(4-Hydroxybutyl)oxy]aniline. 4-[(4-Hydroxybutyl)oxy]aniline was synthesized by the same way as 4-[(5-hydroxypentyl)oxy]aniline. The resulting product was recrystallized from toluene. Yield: 60%. Mp: 54.7 °C.

4-[(ω-Hydroxyalkyl)oxy]-*N*-(4′-nitrobenzylidene)anilines (H*n*NO₂'s). The mixture of 4-[(ω-hydroxyalkyl)oxy]aniline (0.03 mol) and 4-nitrobenzaldehyde (4.5 g, 0.03 mol) was heated at 70 °C for 1 h. The resulting product was purified by recrystallization from ethanol to provide H*n*NO$_2$: ($n = 2$) yield 78%, mp 130.1 °C; ($n = 3$) yield 81%, mp 96.3 °C; ($n = 4$) yield 86%, mp 105.4 °C; ($n = 5$) yield 87%, mp 83.1 °C; ($n = 6$) yield 93%, mp 118.3 °C; ($n = 11$) yield 90%, mp 81.1 °C.

4-[[ω-(Methacryloyloxy)alkyl]oxy]-*N*-(4′-nitrobenzylidene)anilines (M*n*NO₂'s). A methacryloyl chloride (10.4 g, 0.1 mol) solution in 50 mL of chloroform was added to a solution containing H*n*NO$_2$ (0.03 mol) and triethylamine (15.2 g, 0.15 mol) in 150 mL of chloroform at 0 °C. The reaction was continued for 12 h at room temperature. After the workup procedure, the product was purified by recrystallization three times from ethanol to provide M*n*NO$_2$: ($n = 2$) yield 47%, mp 89.7 °C; ($n = 3$) yield 49%, mp 101.7 °C; ($n = 4$) yield 50%, mp 82.4 °C; ($n = 5$) yield 51%, mp 88.9 °C; ($n = 6$) yield 52%, mp 98.7 °C; ($n = 11$) yield 56%, mp 70.4 °C. ^{1}H NMR ($CDCl_3$) for M4NO$_2$: δ 1.92 (2H, m), 1.96 (2H, m), 4.05 (2H, t), 4.25 (2H, t), 5.57 (1H, s), 6.12 (1H, s), 6.96 (2H, d), 7.30 (2H, d), 8.06 (2H, d), 8.32 (2H, d), 8.58 (1H, s).

Polymerizations. Polymerizations of RmCz's with M*n*NO$_2$'s were carried out in a DMF solution 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 a tetrahydrofuran–diethyl ether system.

Characterization. ^{1}H NMR spectra were recorded on a GE Omega 400WB NMR spectrometer in a chloroform-*d* solution. Molecular weights of the resulting polymers were obtained with a HLC-802A (Tosoh Co.) using tetrahydrofuran as an eluent and standard polystyrenes as the 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 the 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) Park, J. W.; Bak, C. S.; Labes, M. M. *J. Am. Chem. Soc.* **1975**, *97*, 4398.
(2) Araya, K.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3079.
(3) Araya, K.; Matsunaga, Y. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 153.
(4) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
(5) McArdle, C. B. Ed. *Side Chain Liquid Crystal Polymers*; Blackie: Glasgow, 1989, p 330.
(6) Chapoy, L. L. Ed. *Recent Advances in Liquid Crystalline Polymer*; Elsevier: London, 1985; p 323.
(7) Meredith, G. R.; VanDusen, J. G.; Williams, D. J. *Macromolecules* **1982**, *15*, 1385.
(8) Griffin, A. C.; Bhatti, A. M.; Hung, R. S. L. *SPIE* **1986**, *682*, 65.
(9) Griffin, A. C.; Bhatti, A. M.; Hung, R. S. L. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 129.
(10) Griffin, A. C.; Bhatti, A. M. *Spec. Publ. R. Soc. Chem.* **1989**, 295.
(11) Robello, D. R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1.
(12) Smith, D. A. M.; Coles, H. J. *Liq. Cryst.* **1993**, *14*, 937.
(13) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Liq. Cryst.* **1991**, *9*, 47.
(14) Schleeh, T.; Imrie, C. T.; Rice, D. M.; Karasz, F. E.; Attard, G. S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1859.
(15) Ringsdorf, H.; Wüstefeld, R.; Zerta, E.; Ebert, M.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 914.
(16) Bengs, H.; Renkel, R.; Ringsdorf, H.; Baehr, C.; Ebert, M.; Wendorff, J. H. *Makromol. Chem., Rapid. Commun.* **1991**, *12*, 439.
(17) Kosaka, Y.; Kato, T.; Uryu, T. *Macromolecules* **1994**, *27*, 2658.
(18) Kosaka, Y.; Uryu, T. *Macromolecules* **1994**, *27*, 6286.
(19) Imrie, C. T.; Schleeh, T.; Karasz, F. E.; Attard, G. S. *Macromolecules* **1993**, *26*, 539.
(20) Lorenz, R. *Liq. Cryst.* **1991**, *9*, 127.
(21) Kosaka, Y.; Kato, T.; Uryu, T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 711.
(22) Lux, M.; Strohriegl, P.; Höcker, H. *Makromol. Chem.* **1987**, *188*, 811.
(23) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(24) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Macromolecules* **1992**, *25*, 1278.
(25) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Macromolecules* **1994**, *27*, 1578.
(26) Percec, V.; Lee, M. *Macromolecules* **1991**, *24*, 4963.
(27) Percec, V.; Lee, M. *Polymer* **1991**, *32*, 2862.
(28) Percec, V.; Lee, M. *Polym. Bull.* **1991**, *25*, 131.
(29) Ando, M.; Uryu, T. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2584.

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