Synthesis and Characterization of New Liquid Crystalline Fumarate and Maleate Monomers with Two Symmetrical Mesogens

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4-Hydroxy-4'-methoxyazobenzene and 4-hydroxy-4'-cyanoazobenzene were synthesized from phenol with *p*-anisidine and *p*-aminobenzonitrile through a diazotization reaction, respectively. They were reacted with 2-chloroethanol, 2-(2-chloroethoxy)ethanol, or 2-[2-(2-chloroethoxy)ethoxy]ethanol to produce six kinds of new mesogenic alcohols having an azobenzene group that is sensitive to the ultraviolet. Twelve kinds of new photoresponsive monomers with two symmetrical mesogens were prepared by the reaction of the mesogenic alcohols with fumaric acid or maleic acid through a Mitsunobu reaction. The resulting monomers have different length of flexible ethyleneoxy spacer tethered to azobenzene group. The length of the spacer affected their thermal stability, solubility, and phase transition temperature. Structures of the monomers were identified by FT-IR and ^{1}H-NMR spectra. Their phase transition temperatures and thermal stability were also investigated by a differential scanning calorimetry (DSC) and a thermogravimetric analysis (TGA). From an optical polarizing microscopy, all the prepared monomers except fumarate-1 and maleate-1 were found to show enantiotropic liquid crystallinity with a smectic texture like focal-conic, fan-shaped, and bâtonnet textures.

Introduction

Side chain liquid crystalline (LC) polymers containing azobenzene group have received much attention in electronic applications due to their unusual anisotropic optical and electrical properties. Especially, since they show a strong potential as reversible optical data storage materials as well as alignment layers for LC display, they have been the subject of a number of papers.[1-4]

Usually side chain LC polymers well-known as these materials have only one mesogenic side group in a repeating unit.[5-8] However, the formation of mesophase may be promoted more when one monomer unit carries more than one mesogenic side group. The corresponding copolymers retain the mesophase even at very low composition, when copolymerized with a nonmesogenic monomer because of an enhanced interaction between the mesogens having paired arrangement.[9,10]

So far azobenzene, spiropyran, fulgide, and their derivatives have been introduced into the side chain as a photoresponsive group sensitive to the light.[11,12] They induce the change of birefringence and absorbance under irradiation of a linearly polaized light. Such an optical anisotropy like dichroism and photochromism let us to apply their polymers to electronic devices. Especially, azo dye molecule is much faster than the other photoresponsive groups in the sensitivity to the light. That is why azo containing polymers are mainly used as electronic materials.

We, therefore, have studied on the synthesis and characterization of side chain LC polymers with paired azobenzene groups such as poly(malonic esters) and itaconate copolymers.[13,14] We also have investigated their applications to reversible optical information storage media through a transcis isomerization of azobenzene group.[15,16]

As a series of our works, in this research, we will describe the synthesis and charaterization of new LC fumarate and maleate monomers with paired azobenzene groups and also examine the effect of spacer on the LC behavior, thermal properties, and solubility.

Experimental Section

Materials. *p*-Anisidine (Lancaster) and *p*-aminobenzonitrile (Aldrich) were purified by recrystallization from distilled water and ethanol solution, respectively. Chloroethanol analogues (Aldrich) used as spacer unit, fumaric acid (Aldrich), maleic acid (Aldrich), triphenyl phosphine (Aldrich), and diethyl azodicarboxylate (TCI) were used as received without further purification. Tetrahydrofuran (THF) was dried over sodium hydride and freshly distilled under nitrogen atmosphere.

Instrumentation. UV absorption spectra were obtained from a Hewlett Packard 8452A diode array spectrophotometer. FT-IR spectra were recorded on a Bruker IFS 48 spectrometer. ^{1}H NMR spectra were measured by a Varian Gemini 300 spectrometer. Thermal behavior was examined by DSC and TGA (Polymer Laborotories Ltd.) at a heating rate of 10 °C under nitrogen atmosphere. Birefringent textures of the synthesized monomers were observed by a polarizing microscope (Lecia) equipped with a hot stage.

Synthesis of mesogenic alcohols (I) with *p*-methoxyazobenzene. 4-[4'-(Methoxyphenyl)azo]phenol was prepared by a well-known method. Coupling of oligoethyleneoxy spacer groups to it was carried out by our previous literature to give *p*-methoxyazobenzene containing mesogenic alcohol (I)-1, -2, or -3 with different length (n = 1, 2, 3) of ethyleneoxy spacer. The numerical value denotes the number of ethyleneoxy group used as a flexible spacer unit, which is shown in Scheme 1.[13]

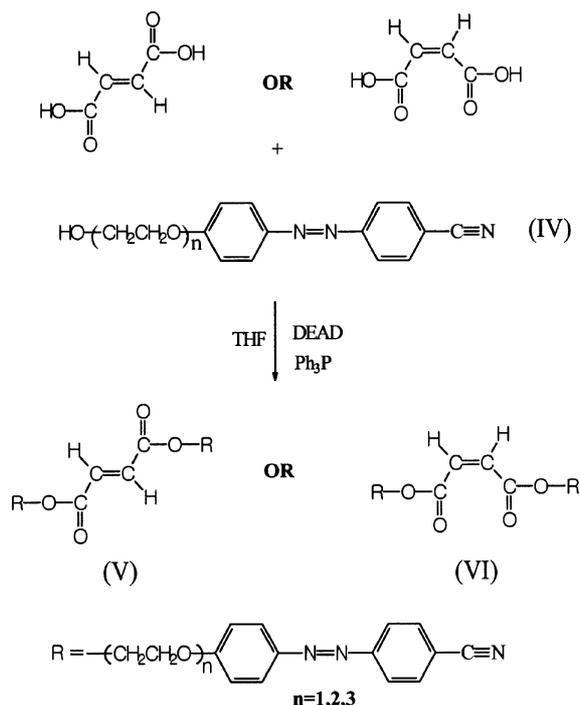**Synthesis of fumarates (II) and maleates (III) mono-**
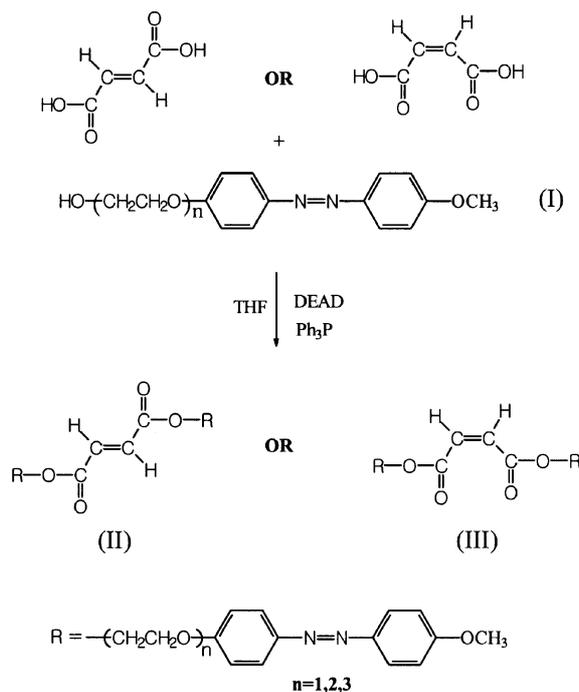
Scheme 1. Synthesis of new LC fumarates and maleates monomers with two symmetrical mesogenic groups.

Scheme 2. Synthesis of new LC fumarates and maleates monomers with two symmetrical mesogenic groups

mers with *p*-methoxyazobenzene. A mixture of *p*-methoxyazobenzene containing mesogenic alcohol (I)-1 (3 g, 0.011 mol), fumaric acid (0.685 g, 0.0059 mol), and triphenylphosphine (4.34 g, 0.0165 mol) were dissolved in THF (200 mL). A solution of diethylazodicarboxylate (2.87 g, 0.0165 mol) in THF (15 mL) was added slowly to the mixture. The resulting solution was stirred at room temperature for 24 h to carry out a Mitsunobu reaction.[17] After completion of the reaction, the solvent was removed and then the residue was dissolved in dichloromethane (200 mL). The solution was washed with a 100 mL solution of 5% sodium carbonate to extract unreacted fumaric acid and then the organic layer was collected. After evaporating dichloro-methane, the residue was dissolved in ethyl ether and stirred for 24 h to extract the triphenylphosphine oxide generated during a Mitsunobu reaction. The solid in the solution was filtered and dried under reduced pressure. The resulting crude solid was column-chromatographed on silica gel with a mixture solution of ethyl acetate and chloroform (1/3 v/v) to isolate a pure fumarate (II)-1 with paired *p*-methoxy-azobenzene groups.

Fumarate (II)-2 and -3 monomers also were synthesized by the same procedure. In addition to the fumarate monomers, even *p*-methoxyazobenzene containing maleate (III)-1, -2, and -3 were prepared by the same method as the above procedures except for using different solvents for column chromatography. The mixture solution of ethyl acetate and dichloromethane (1/10 v/v) was used as a developing solvent.

Synthesis of mesogenic alcohols (IV) with *p*-cyano-azobenzene. 4-[4'-(benzonitrile)azo]phenol (10 g, 0.045 mol) and KOH (2.95 g, 0.045 mol) was dissolved in absolute

ethanol (120 mL). Into the mixture, a solution of 2-chloroethanol (3.61 g, 0.045 mol) and KI (0.2 g, 0.0012 mol) in ethanol (20 mL) was added slowly and stirred for 20 min. The solution was refluxed for 48 h and then cooled to 0 ℃ and finally neutralized with dilute hydrochloric acid (5%). After evaporation of the solvent, crude mixture was dissolved again in chloroform. The solution was washed with water and dried over anhydrous magnesium sulfate. After removing the chloroform, crude product was column-chromatographed on silica gel to isolate a pure product and then further purified by recrystallization from methanol (mesogenic alcohol (IV)-1: yield 6.58 g, 55%). Other *p*-cyanoazobenzene containing mesogenic alcohol derivatives (IV)-2 and -3 (yield: 60 and 53%) with different length of ethyleneoxy spacer also were prepared by the same procedure except using 2-(2-chloroethoxy)ethanol or 2-[2-(2-chloroethoxy) ethoxy]ethanol instead of 2-chloroethanol, which is shown in Scheme 2.

Synthesis of fumarates (V) and maleates (VI) monomers with *p*-cyanoazobenzene. *p*-cyanoazobenzene containing mesogenic alcohol (IV)-1 (3 g, 0.011 mol), fumaric acid (0.685 g, 0.0059 mol), and triphenylphosphine (4.34 g, 0.0165 mol) were dissolved in THF (200 mL). A solution of diethylazodicarboxylate (2.87 g, 0.0165 mol) in THF (15 mL) was added slowly to the mixture. The resulting mixture was stirred at room temperature for 24 h to progress a Mitsunobu reaction. After the reaction, remaining procedures were carried out by the same method as that employed in the synthesis of *p*-methoxyazobenzene containing fumarates and maleates monmers, except using different solvents for column chromatography. In the case of fumarate (V)-1, -2,

and -3, we used the solutions of ethyl acetate and dichloromethane of 1/10, 1/10, and 1/5 in volume ratio as developing solvents, respectively. For maleate (VI)-1, -2, and -3 derivatives, we used the solutions of ethyl acetate and chloroform of 1/5, 1/10, and 1/5, respectively.

Results and Discussion

Synthesis of new thermotropic LC fumarate and maleate monomers. We synthesized new thermotropic LC fumarate and maleate monomers through Scheme 1 and 2. To synthesize new fumarate and maleate with different length of flexible ethyleneoxy spacers, azobenzene unit was first linked to the flexible spacer in which the number of ethyleneoxy units varied from 1 to 3. Through a Mitsunobu reaction,[17] two kinds of the mesogenic alcohols (I and IV) with different length of ethyleneoxy units were reacted with fumaric acid or maleic acid to produce twelve kinds of novel thermotropic LC fumarates or maleates monomers with two symmetrical mesogen groups containing azobenzene moiety.

Figure 1 shows representative ^{1}H NMR spectra of the synthesized fumarate and maleate monomers. In the case of fumarate (II)-2 with *p*-methoxyazobenzene, the peak due to hydroxyl group in the mesogenic alcohol (I)-2 disappeared at 2.2 ppm, whereas a new single peak from two hydrogens in the trans type of C=C double bond showed up at 6.9 ppm. In addition to these peaks, two kinds of hydrogens in the methylene groups adjacent to ester and phenoxy groups appeared at 4.4-4.3 and 4.2-4.1 ppm, respectively. Methoxy and methylene hydrogens close to ether had a broad peak with multiplet around 3.9 ppm. The hydrogens inside the azobenzene ring were splitted into 7.8 and 7.0 ppm, respectively (Figure 1-a). Even in the maleate (VI)-2 with *p*-cyanoazobenzene, the peak due to hydroxyl group in the mesogenic alcohol (IV)-2 disappeared, whereas a new single peak from two hydrogens in the cis type of C=C double bond appeared at 6.3 ppm. The hydrogens inside the azobenzene ring showed sharp doublet peaks at 7.9, 7.8, and 7.0 ppm, respectively. The position of methylene groups incorporated into flexible spacer group was very similar to that of the fumarate (II)-2 (Figure 1-b). Relative integration ratio between the characteristic peaks matched well with structure of the monomers as we expected.

We also confirmed structure of the monomers by the characteristic absorption bands in IR spectra. As an example, in the case of fumarate (II)-2, a broad absorption band due to hydroxy group in the mesogenic alcohol (I)-2 disappeared at 3500 cm^{-1}. On the contrary, a strong absorpton band due to new ester groups and a weak absorption due to a carbon-carbon double bond appeared at 1718 and 1641 cm^{-1}, respectively. This indicates that fumaric acid reacts with the mesogenic alcohol (I)-2 to produce new fumarate (II)-2 monomer. On the other hand, IR spectra from the fumarate (V) and maleate (VI) monomers also were very similar to those of the monomer (II) and (III) except that a strong absorption band of C≡N group appeared around 2220 cm^{-1}.

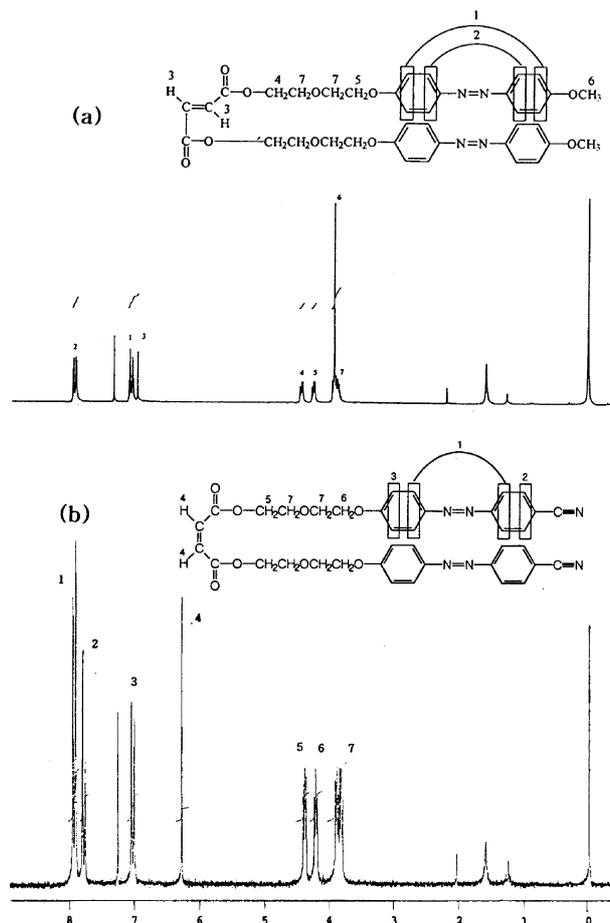Yield, melting point, and spectroscopic data for twelve

Figure 1. 300 MHz ^{1}H NMR spectrum of Fumarate (II)-2 (a) and Maleate (VI)-2 (b) monomers.

kinds of the prepared monomers are listed in Table 1 and 2.

Polymerization. We, unfortunately, failed to prepare the corresponding homo and copolymers from the fumarate and maleate LC monomers due to their solubility and steric hindrance between two bulky symmetrical mesogens. Of course, although they have good solubility in chloroform and dichloromethane, they are not suitable as solvents because chain transfer reaction from the solvents to radicals occurs very quickly during radical polymerization. In addition, 1,2-disubstituted ethylenes with bulky groups like the prepared new monomers is very hard to undergo radical polymerization because they have much more sterical hindrance than monosubstituted and 1,1-disubstituted ethylenes.[18,19]

Liquid crystalline behavior and thermal properties. We investigated LC behavior of the prepared monomers by means of DSC and optical polarizing microscopy. The phase transition temperatures are summarized in Table 3 and 4, where numerical value denotes the number of ethyleneoxy spacer unit. As shown in Table 3, we can not observe liquid crystalline behavior for the fumarate (II)-1 and maleate (III)-1 monomers having the shortest spacer unit (n = 1). It seems that the length of the ethyleneoxy group is too short to act as a flexible spacer, which is responsible for stacking the mesogenic side chains. On the other hand, in the monomers with two or three ethyleneoxy spacers, we can observe their

Table 1. Characterization Data for Fumarate and Maleate Monomers with *p*-Methoxyazobenzene Group

samples[a]	yield (%)	m.p.[b] (°C)	IR (KBr) (cm^{-1})	^{1}H NMR[c] (δ)
Fum(II)-1	45%	197 °C	1712 (C=O), 1641 (C=C), 1602, 1500 (Ar C=C), 1243 (C-O)	7.9 (d, Ar-H, 8H), 7.0 (d, Ar-H, 8H), 6.9 (s, HC=CH, 2H), 4.6-4.5 (t, O-CH$_2$-C, 4H), 4.3-4.2 (t, C-CH$_2$-O, 4H), 3.9 (s, CH$_3$O-Ar, 6H)
Fum(II)-2	50%	140 °C	1718 (C=O), 1641 (C=C), 1595, 1499 (Ar C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.0 (d, Ar-H, 8H), 6.9 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.2-4.1 (t, C-CH$_2$-O, 4H), 3.8 (s, CH$_3$O-Ar, 6H), 3.8-3.7 (m, C-CH$_2$O-CH$_2$-C, 8H)
Fum(II)-3	50%	145 °C	1721 (C=O), 1641 (C=C), 1594, 1500 (Ar C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.0 (d, Ar-H, 8H), 6.9 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.2-4.1 (t, C-CH$_2$O-Ar, 4H), 3.9-3.8 (m, CH$_3$O-Ar, -OCH$_2$CH$_2$O-, 14H), 3.7-3.6 (m, C-CH$_2$O-C, C-OCH$_2$-C, 8H)
Mal(III)-1	35%	177 °C	1712 (C=O), 1641(C=C), 1593, 1498 (Ar C=C), 1253 (C-O)	7.9 (d, Ar-H, 8H), 7.0 (d, Ar-H, 8H), 6.3 (s, HC=CH, 2H), 4.6-4.5 (t, O-CH$_2$-C, 4H), 4.3-4.2 (t, C-CH$_2$-O, 4H), 3.8 (s, CH$_3$O-Ar, 6H)
Mal(III)-2	30%	148 °C	1732 (C=O), 1641 (C=C), 1596, 1499 (Ar C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.0 (d, Ar-H, 8H), 6.3 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.2-4.1 (t, C-CH$_2$-O, 4H), 3.8 (s, CH$_3$O-Ar, 6H), 3.9-3.8 (m, C-CH$_2$O-CH$_2$-C, 8H)
Mal(III)-3	35%	116 °C	1728 (C=O), 1641 (C=C), 1594, 1499 (Ar C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.0 (d, Ar-H, 8H), 6.3 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.2-4.1 (t, C-CH$_2$O-Ar, 4H), 3.9-3.8 (m, CH$_3$O-Ar, -OCH$_2$CH$_2$O-, 14H), 3.7-3.6 (m, C-CH$_2$O-C, C-OCH$_2$-C, 8H)

[a]Numerical value denotes the number of the ethyleneoxy spacer length. [b]Peak maximum position in the DSC endotherm. [c]In CDCl$_3$.

Table 2. Characterization Data for Fumarate and Maleate Monomers with *p*-Cyanoazobenzene Group

samples[a]	yield (%)	m.p.[b] (°C)	IR (KBr) (cm^{-1})	^{1}H NMR[c] (δ)
Fum(V)-1	40%	241 °C	2224 (C≡N), 1720 (C=O), 1641 (C=C), 1225 (C-O)	7.9 (d, Ar-H, 8H), 7.8 (d, Ar-H, 4H), 7.0 (d, Ar-H, 4H), 6.9 (s, HC=CH, 2H), 4.6-4.5 (t, O-CH$_2$-C, 4H), 4.4-4.3 (t, C-CH$_2$-O, 4H)
Fum(V)-2	49%	141 °C	2224 (C≡N), 1727 (C=O), 1641 (C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.8 (d, Ar-H, 4H), 7.0 (d, Ar-H, 4H), 6.9 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.3-4.2 (t, C-CH$_2$-O, 4H), 3.9-3.8 (m, C-CH$_2$O-CH$_2$-C, 8H)
Fum(V)-3	54%	90 °C	2224 (C≡N), 1720 (C=O), 1641 (C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.8 (d, Ar-H, 4H), 7.0 (d, Ar-H, 4H), 6.9 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.3-4.2 (t, C-CH$_2$O-Ar, 4H), 3.9-3.8 (t, C-CH$_2$O-C, 4H), 3.8-3.7 (m, O-CH$_2$CH$_2$OCH$_2$-C, 12H)
Mal(VI)-1	25%	237 °C	2224 (C≡N), 1717(C=O), 1642 (C=C), 1253 (C-O)	7.9 (d, Ar-H, 8H), 7.8 (d, Ar-H, 4H), 7.0 (d, Ar-H, 4H), 6.3 (s, HC=CH, 2H), 4.6-4.5 (t, O-CH$_2$-C, 4H), 4.3-4.2 (t, C-CH$_2$-O, 4H)
Mal(VI)-2	30%	96 °C	2223 (C≡N), 1721 (C=O), 1641 (C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.8 (d, Ar-H, 4H), 7.0 (d, Ar-H, 4H), 6.3 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.2-4.1 (t, C-CH$_2$-O, 4H), 3.9-3.8 (m, C-CH$_2$O-CH$_2$-C, 8H)
Mal(VI)-3	30%	63 °C	2225 (C≡N), 1731 (C=O), 1648 (C=C), 1254 (C-O)	7.9 (d, Ar-H, 8H), 7.8 (d, Ar-H, 4H), 7.0 (d, Ar-H, 4H), 6.3 (s, HC=CH, 2H), 4.4-4.3 (t, O-CH$_2$-C, 4H), 4.3-4.2 (t, C-CH$_2$O-Ar, 4H), 3.9-3.8 (t, C-CH$_2$O-C, 4H), 3.7-3.6 (m, O-CH$_2$CH$_2$OCH$_2$-C, 12H)

[a]Numerical value denotes the number of the ethyleneoxy spacer length. [b]Peak maximum position in the DSC endotherm. [c]In CDCl$_3$.

LC phase transition temperatures on both heating and cooling cycles. The melting and LC phase transition temperatures of the fumarate and maleate monomers were lowered as the length of the spacer group was increased. Even the fumarate (V) and maleate (VI) monomers with *p*-cyano-azobenzene group exhibited the same phenomenon, which is shown in Table 4.

As shown in Table 3 and 4, the degree of supercooling between heating and cooling cycles has a large value up to 40 °C. Such a phenomenon might be due to the rapid cooling rate (average rate: 30 °C/min) of the equipment and also to the complicated structural change with temperature of the monomers. It, however, is not clear yet and need to examine in more detail.

Figure 2 is representative DSC thermograms of new fumarate and maleate monomers. The fumarate (II)-2 with *p*-methoxyazobenzene showed enantiotropic behavior in which

Table 3. Phase Transition Temperatures of New LC Fumarate and Maleate Monomers with *p*-Methoxyazobenzene Group

| samples	phase transition temperature (°C)			
	on heating cycle[a]	on cooling cycle[a]	on heating cycle[b]	on cooling cycle[b]
Fum(II)-1	205 i	150 k	197 i	175 k
Fum(II)-2	k 125 s 144 i	i 123 s 105 k	k 120 s 140 i	i 100 s 90 k
Fum(II)-3	k 120 s 151 i	i 120 s 95 k	k 117 s 145 i	i 108 s 96 k
Mal(III)-1	180 i	155 k	178 i	150 k
Mal(III)-2	k 130 s 150 i	i 92 s 77 k	k 133 s 148 i	i 89 s 79 k
Mal(III)-3	k 103 s 120 i	i 95 s 65 k	k 95 s 116 i	i 77 s 70 k

[a]Observed by optical polarizing microscope. [b]Detected by DSC thermogram.

LC phase appeared in the range of 140-120 °C on heating cycle and 100-90 °C on cooling, respectively (Figure 2-a).

Table 4. Phase Transition Temperatures of New LC Fumarate and Maleate Monomers with *p*-Cyanoazobenzene Group

samples	phase transition temperature (°C)			
	on heating cycle[a]	on cooling cycle[a]	on heating cycle[b]	on cooling cycle[b]
Fum(V)-1	224 i	164 k	241 i	155 k
Fum(V)-2	k * s 144 i	i 134 s 122 k	k * s 141 i	i 129 s 115 k
Fum(V)-3	k 83 s 102 i	i 65 s 44 k	k 78 s 90 i	i * s 30 k
Mal(VI)-1	200 i	137 k	237 i	162 k
Mal(VI)-2	k 80 s 103 i	i 90 s 62 k	k 75 s 96 i	i 85 s 60 k
Mal(VI)-3	k 73 s 87 i	i 68 s 46 k	k 51 s 63 i	i 60 s 42 k

[a]Observed by optical polarizing microscope. [b]Detected by DSC thermogram. *We failed to observe the phase transition temperature.
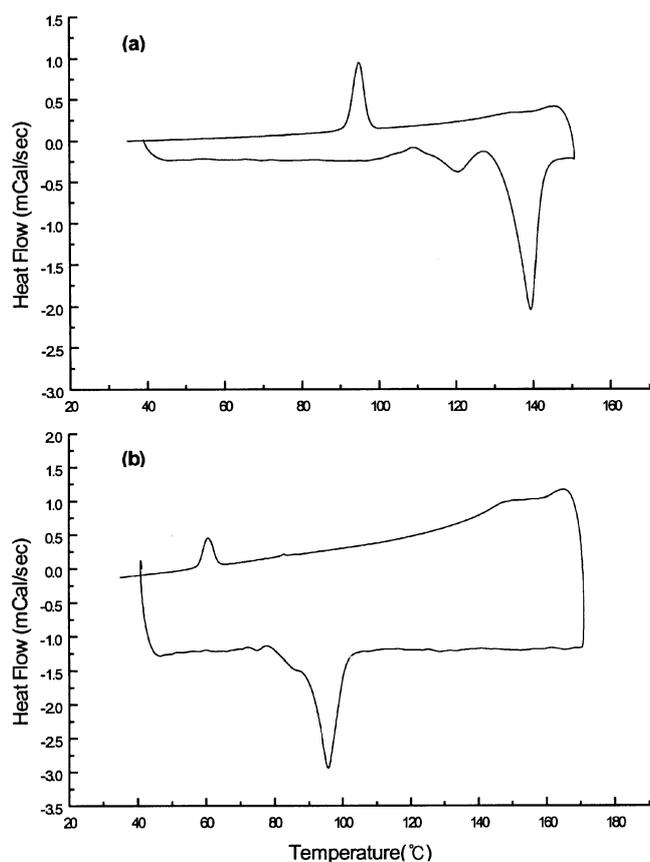
Figure 2. DSC thermograms of Fumarate (II)-2 (a) and Maleate (VI)-2 (b) monomers .

The maleate (VI)-2 with *p*-cyanoazobenzene developed LC textures between 96 and 75 °C on heating cycle and between 85 and 60 °C on cooling cycle (Figure 2-b).

On the heating scans, the large enthalpy peak results from melting of the fully crystallized monomers. However, the cold crystallization peak appears to be much smaller than the melting peak because of the rapid cooling rate (average rate: 30 °C/min). That is, due to the rapid cooling scheme of the equipment, the recrystallization would not be completed. Consequently, it shows lower degree of crystallinity, viz., lower heat of crystallization.
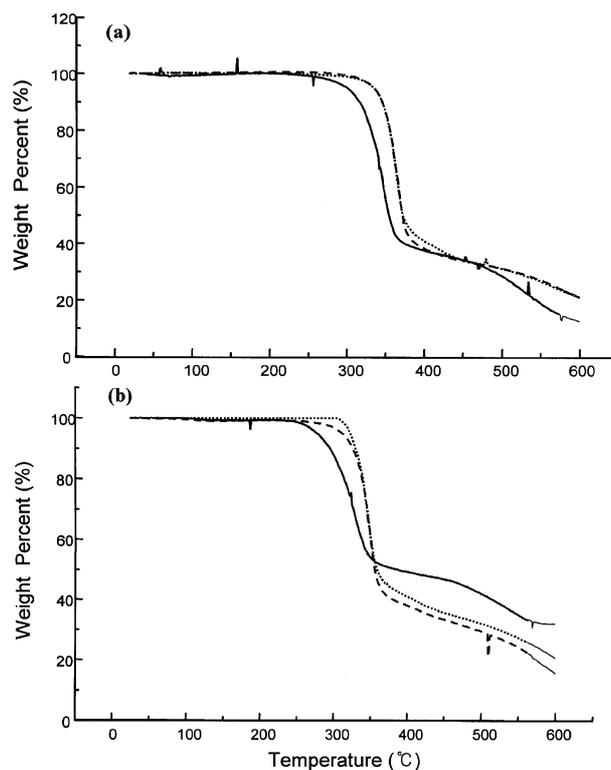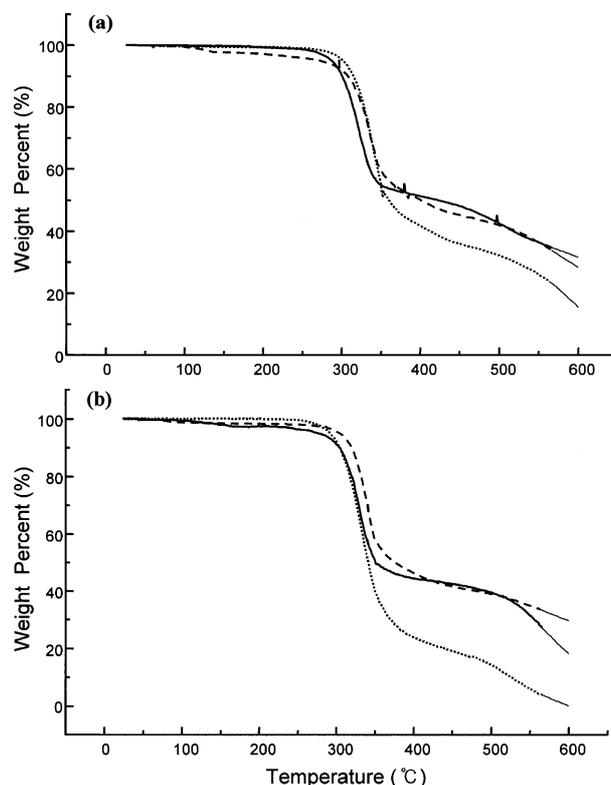
Figure 3 and 4 show TGA thermograms for the fumarate

Figure 3. TGA thermograms of *p*-methoxyazobenzene containing fumarate (a) and maleate (b) monomers: (——), Fum(II)-1; (----), Fum(II)-2; (······), Fum(II)-3; (——), Mal(III)-1; (----), Mal(III)-2; (······), Mal(III)-3.

Figure 4. TGA thermograms of *p*-cyanoazobenzene containing fumarate (a) and maleate (b) monomers: (——), Fum(V)-1; (----), Fum(V)-2; (······), Fum(V)-3; (——), Mal(VI)-1; (----), Mal(VI)-2; (······), Mal(VI)-3.

Table 5. Solubility of New LC Fumarate and Maleate Monomers with *p*-Methoxyazobenzene Group[a]

samples	solvent											
	CHCl$_3$	DMF	benzene	ethyl acetate	THF	CH$_2$Cl$_2$	acetone	dioxane	MeOH	ethyl ether	n-hexane	CCl$_4$
Fum(II)-1	◎	×	×	×	×	△	×	×	×	×	×	×
Fum(II)-2	◎	△	×	×	×	○	×	×	×	△	×	×
Fum(II)-3	◎	△	×	×	×	○	×	×	×	△	×	×
Mal(III)-1	◎	×	×	×	×	△	×	×	×	×	×	×
Mal(III)-2	◎	×	×	×	×	○	×	×	×	△	×	×
Mal(III)-3	◎	×	×	×	×	○	×	×	×	△	×	×

[a]◎, very soluble; ○, soluble; △, slightly soluble; ×, insoluble.

Table 6. Solubility of New LC Fumarate and Maleate Monomers with *p*-Cyanoazobenzene Group[a]

samples	solvent											
	CHCl$_3$	DMF	benzene	ethyl acetate	THF	CH$_2$Cl$_2$	acetone	dioxane	MeOH	ethyl ether	n-hexane	CCl$_4$
Fum(V)-1	◎	×	×	×	×	△	×	×	×	×	×	×
Fum(V)-2	◎	△	×	△	○	○	×	×	×	×	×	×
Fum(V)-3	◎	△	○	○	○	○	×	○	×	×	×	×
Mal(VI)-1	◎	×	×	×	△	△	×	×	×	×	×	×
Mal(VI)-2	◎	△	△	△	○	○	○	△	×	×	×	×
Mal(VI)-3	◎	△	○	○	○	○	○	○	×	×	×	×

[a]◎, very soluble; ○, soluble; △, slightly soluble; ×, insoluble.

and maleate monomers with *p*-methoxy or *p*-cyanoazobenzene group. In the case of all monomers, initial decomposition temperature increased with increase in the length of the ethyleneoxy spacer. It means that the increase of the flexible spacer unit improves their thermal stabilities resulting from the interaction between the bulky mesogenic side chains. In addition, the increase of the spacer length enhances not only the flexibility of the corresponding monomers but also their solubilities (Table 5 and 6).

Figure 5 and 6 show liquid crystalline textures of new monomers. They were measured by optical polarizing microscope with a hot stage in the range of LC phase transition temperatures, which are listed in Table 3 and 4. The LC structures of all the prepared monomers had a typical smectic phase like focal-conic, fan-shaped, or bâtonnet texture.[20] Especially, homeotropic smectic textures (Figure 6-B and -D) from Mal (VI)-2 and -3, which were prepared by shearing between two glass plates, are birefringent and can include schlierens with point singularities like a nematic texture.[21] Figure 5-E shows a crystalline spherulite of Fum (II)-2 taken at 85 °C on the cooling cycle.

Solubility.   The solubility was measured in 3% solution. All the monomers with *p*-methoxyazobenzene group were soluble only in chloroform and dichloromethane, but they were not soluble in most of solvents such as ethyl ether, benzene, THF, methanol, n-hexane, and so on (Table 5). However, the monomers with *p*-cyanoazobenzene group showed better solubility than those with *p*-methoxyazobenzene (Table 6). Especially, the fumarate (V)-3 and maleate (VI)-3 were soluble in many kinds of solvents. Table 5 and 6 indicate that the increase of the spacer length enhances the solubility.

UV-VIS spectroscopy.   Figure 7 displays UV-VIS absorption spectrum in the chloroform solution (41 μmol/L) of
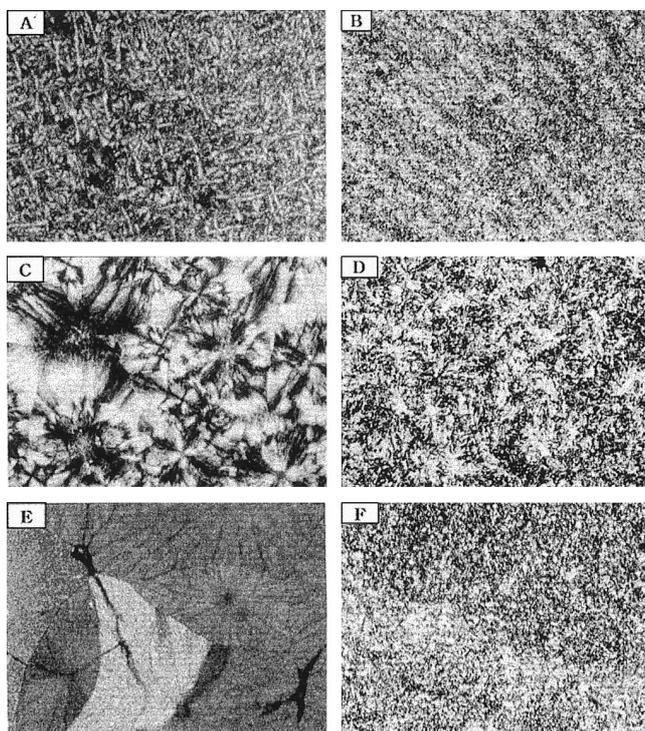

Figure 5. Optical polarizing micrographs of *p*-methoxyazobenzene containing fumarates and maleates (italic, on heating cycle; bold, on cooling cycle): A(×100), Fum(II)-2 at 120 °C; B(×100), Mal(III)-2 at 80 °C; C(×100), Fum(II)-3 at 115 °C; D(×200), Mal(III)-3 at 92 °C; E(×100), Fum(II)-2 at 85 °C (crystalline spherulite); F(×100), Mal(III)-3 at *107* °C.
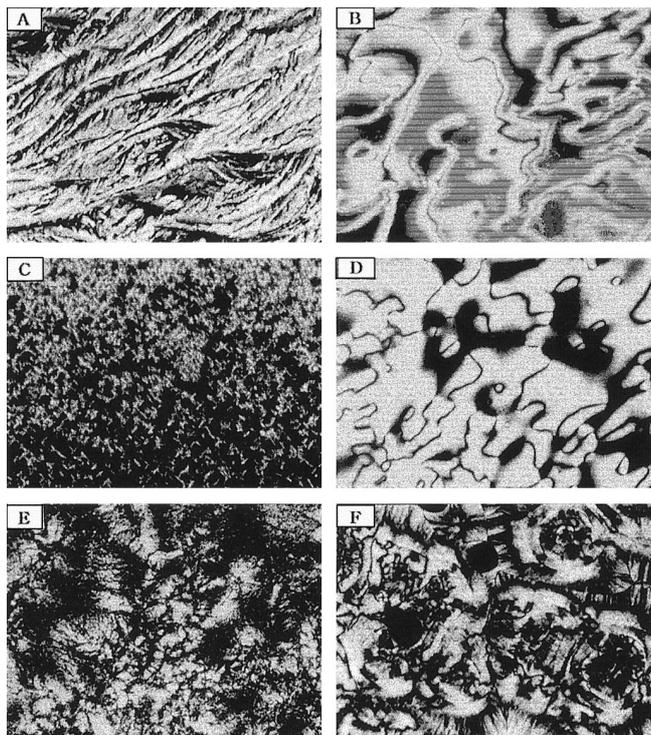
Figure 6. Optical polarizing micrographs of *p*-cyanoazobenzene containing fumarates and maleates (italic, on heating cycle; bold, on cooling cycle): A(×100), Fum(V)-2 at 128 °C; B(×100), Mal(VI)-2 at 82 °C; C(×100), Fum(V)-3 at 65 °C; D(×200), Mal(VI)-3 at 68 °C; E(×100), Fum(V)-3 at *95* °C; F(×100), Mal(VI)-3 at 62 °C.
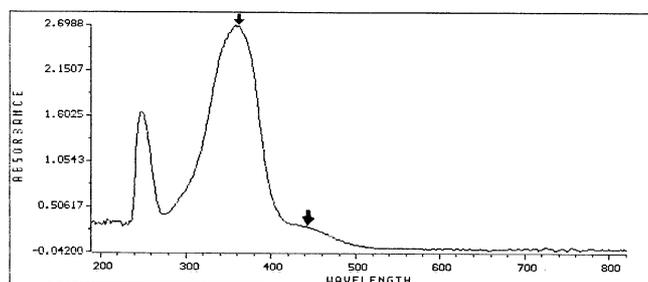

Figure 7. UV-VIS absorption spectrum of the solution of Fum(II)-2 with *p*-methoxyazobenzene group in chloroform (41 μmol/L).

fumarate (II)-2 before UV irradiation at room temperature. The absorption band of $\pi \rightarrow \pi^*$ transition due to the stable trans conformation of azobenzene appeared strongly at 358 nm, and the absorbance of $n \rightarrow \pi^*$ transition due to the *cis* conformation appeared weakly around 450 nm. This implies that azobenzene exists as the stable trans form at room temperature.

It has been reported that azobenzene molecule aligns perpendicular to the plane of linearly polarized light. Such a photo-induced orientation let us to write, erase, and rewrite optical information on the side chain LC or amorphous poly-

mer films containing azobenzene group.[7,15]

We have examined the possibility of the application of the synthesized new LC monomers to electronic materials. Lately, we found that the polymer films from the blends of poly(methyl methacrylate) with the monomers could be used as reversible optical data storage media. Detailed results will be published elsewhere soon.

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