578 © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *578—584(1993)* [Vol. 66, No. 2

Syntheses and Properties of New Liquid-Crystalline Polymers Having 1,3,2-Dioxaborinane Pendants

Hiroshi MATSUBARA,[††] Koji SETO,[†] Hitoshi TABUCHI,[†] Hideyuki IMAZAKI,[†] and Shigetoshi TAKAHASHI*
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567
† Research & Development Division, Nitto Kasei Co., Ltd., 3 Nishiawaji, Higashiyodogawa, Osaka 533

(Received September 16, 1992)

Polyacrylates and polymethacrylates having various 1,3,2-dioxaborinane derivatives as pendants have been synthesized and demonstrated to form chiral smectic C and/or smectic A phases which are more stable than those formed by the corresponding monomers. They provide a new family of chiral liquid crystalline side-chain polymers containing boron atoms in the pendant group.

In recent years liquid crystalline side-chain polymers have attracted great interests because of their theoretical aspects and potential applications.[1)] The principal structure of liquid crystalline side-chain polymers consists of a long main chain and a mesogenic side group attached to the main chain via a flexible spacer group. A wide variety of known mesogenic groups involve alkoxybiphenyl,[2)] cyanobiphenyl,[3)] phenyl benzoate,[4)] *N*-benzylideneaniline,[5)] and cholesteryl groups,[6)] however, few examples containing metal atoms have been reported. Liquid crystals incorporating metal atoms are of special interest since they are expected to have unique optical, magnetic, and electronic properties.[7)] Previously we found that 2,5-disubstituted 1,3,2-dioxaborinane derivatives exhibited mesomorphic properties.[8)] They have a metalloid atom, boron, however, they are fairly stable in air and for moisture, and may be expected to have unique properties. In fact, chiral dioxaborinane derivatives show large spontaneous polarization in chiral smectic C (Sc*) phases.[9)]

Then we have attempted to lead the dioxaborinane derivatives to polymeric materials and synthesized[10)] liquid crystalline side-chain polymers **1** having dioxaborinane pendants. Polymer **1** formed very stable smectic mesophases, indicating that the dioxaborinane ring is a suitable mesogenic group for liquid crystalline side-chain polymers. In this paper we wish to report the synthesis and properties of a new chiral polymer, **2**, exhibiting an Sc* phase (Fig. 1).

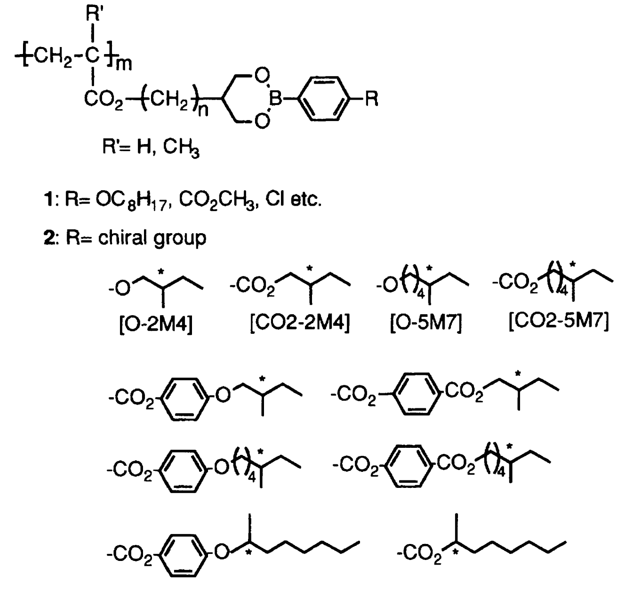


Fig. 1. Liquid-crystalline side-chain polymers having dioxaborinanes.

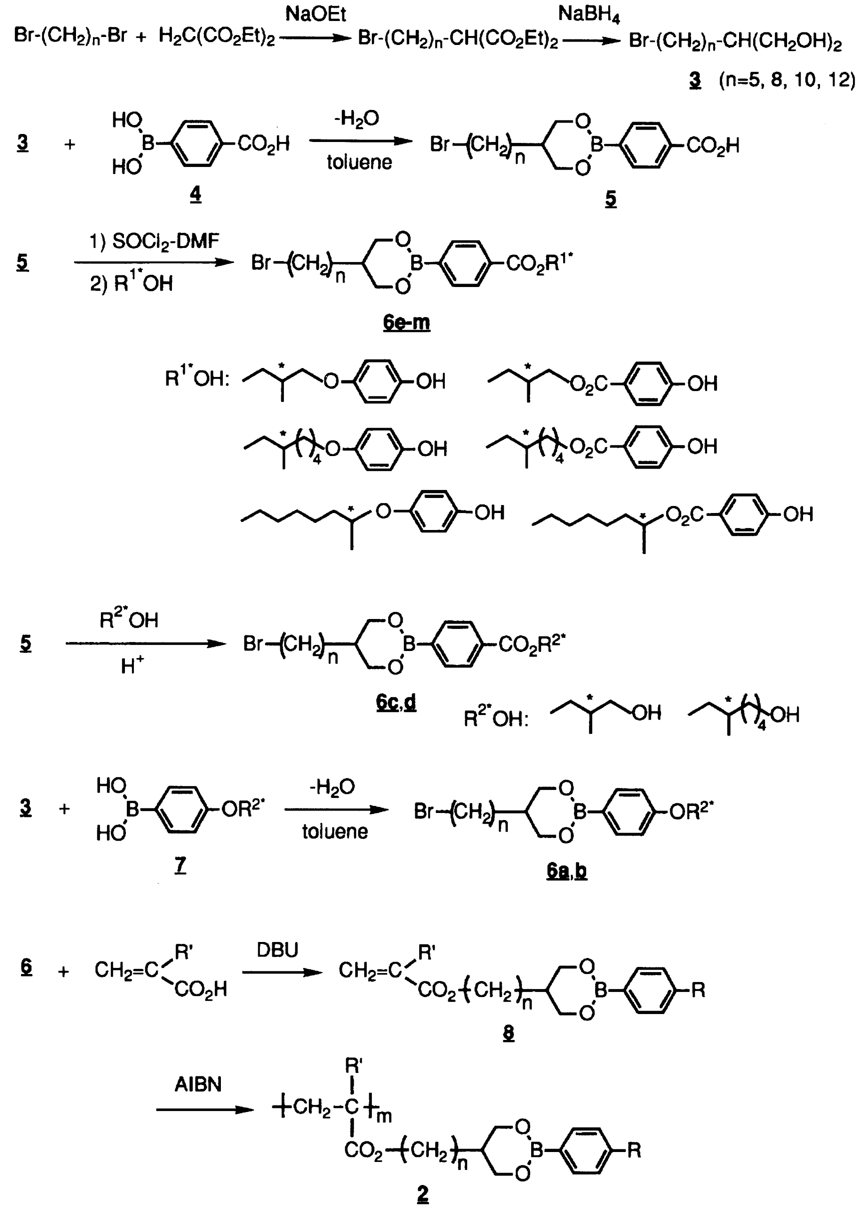
Results and Discussion

Synthesis and Characterization of Chiral Polymer 2. The synthetic procedure leading to the target polymer **2** is outlined in Scheme 1. 2-(ω-Bromoalkyl)-1,3-propanediol **3** was prepared by the alkylation of diethylmalonate followed by reduction of the ester groups with a large excess of sodium borohydride.[11)] Mesogenic groups **6e**—**m** having a three-ring system were prepared by the esterification of carboxylic acids **5** via the acyl chlorides. The carboxylic acids **5** were also converted to **6c** and **6d** by esterification with chiral alcohols R^{2*}OH in the presence of an acid catalyst. Compounds **6a** and **6b** incorporating chiral alkoxyl groups were prepared by simple condensation between **3** and chiral boronic acids **7** in toluene. Mesogenic groups **6** were transformed into the acylate or methacrylate monomers **8** by a literature method.[12)] Polymers **2** were successfully synthesized from **8** by radical polymerization at 60°C for 6 h using 2,2'-azobisisobutyronitrile (AIBN) as an initiator, and purified by reprecipitation from benzene-methanol. Though the conversion of **8** to polymer **2** was as low as ca. 10% under the above conditions, a large amount of unreacted monomer was recovered after the polymerization reaction, indicating that any side reactions did not occur during the reaction under the above conditions. The low reactivity of **8** toward polymerization may be due to the sterically large substituent on the acrylic monomers.

The polymers are obtained as colorless solids and are soluble in common organic solvents such as benzene, chloroform and tetrahydrofuran. The ^{1}H NMR spectra of polymer **2f** as well as the corresponding monomer

---

[††] Present address: Department of Chemistry, College of Integrated Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 591.



Scheme 1. Synthetic Route to Polymer **2**.

8f are shown in Fig. 2. Monomer **8f** exhibited olefinic protons in the region of $\delta=5.8$—6.4, whereas in the spectrum of **2f** they completely disappeared. The other proton signals were still observed at the almost same positions as the monomer though they were somewhat broadened. Polymer **2f** showed also the same IR spectra as the corresponding monomer **8f** except absorptions due to the olefinic group of **8f**. These spectral data indicate that the dioxaborinane structure remains intact after the radical polymerization with AIBN and polymer **2** has the structure shown in Fig. 1.

The molecular weights of polymer **2** were determined by GPC with a polystyrene standard, and the results are summarized in Table 1. Polymer **2** has an average molecular weight in the range of 20000—40000 which corresponds to an average degree of polymerization of 40—80. Polymethacrylate **2o** has about ten times larger molecular weight than that of the polyacrylate analogue. Absolute average molecular weights of the polymers were determined by a light scattering experiment in order to check the date obtained by the GPC method though samples of achiral polymers were employed. The results listed in Table 2 show a good agreement between the molecular weights obtained by the two methods.

Thermal Properties. The identification of mesophases has been made on the basis of optical textures. Smectic A (S_A) phases were identified by the appearance of a focal comic texture on cooling from an isotropic liquid. In Sc* phases, a broken fan texture was observed.

Thermal properties of mesogenic group **6** and monomer **8** are listed in Tables 3 and 4, respectively.

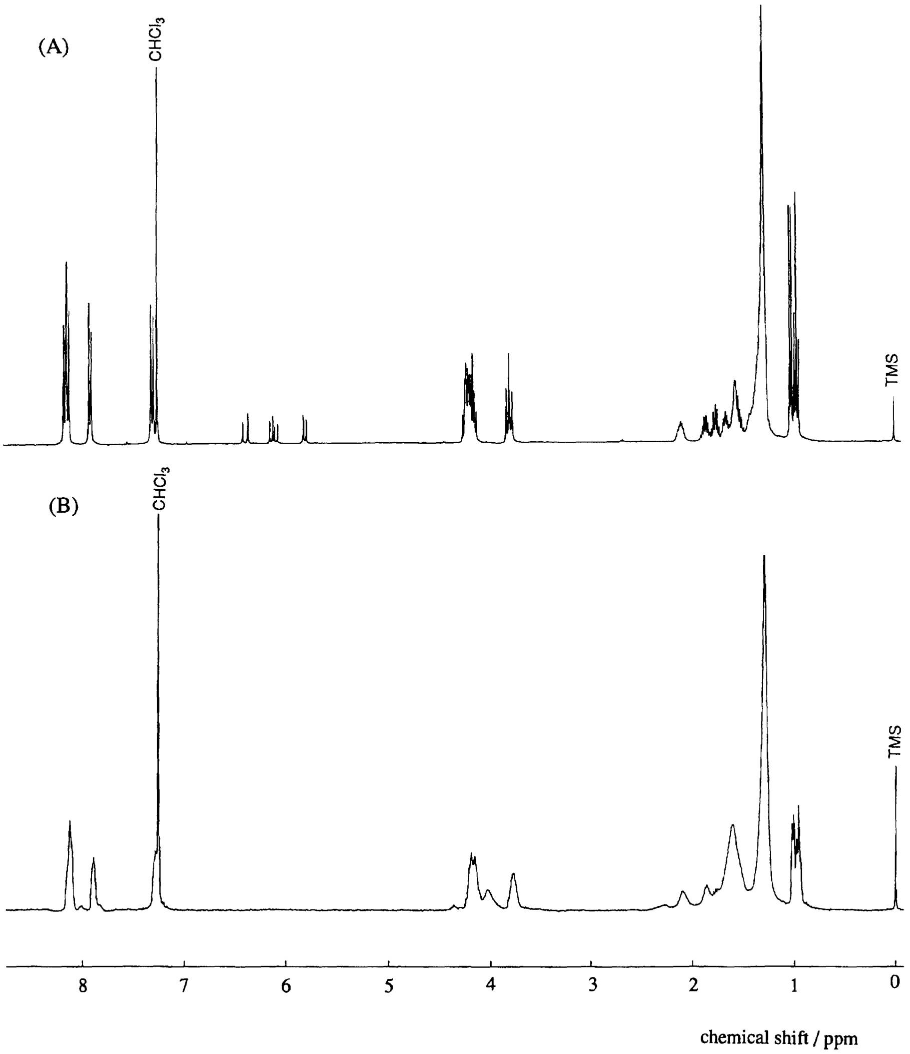


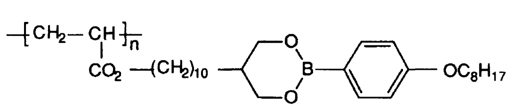
Fig. 2. ^{1}H NMR Spectra of Monomer **8f** (A) and Polymer **2f** (B).

Table 1. Average Molecular Weights of Polymer **2**[a)]

	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_n}/\overline{M_w}$
2a	21000	33000	1.57
2c	17000	28000	1.65
2f	13000	21000	1.62
2h	15000	24000	1.60
2o	125000	258000	2.06

a) Determined by GPC method on the basis of polystyrene standards.

Table 2. Average Molecular Weights of Polymer **11**



11

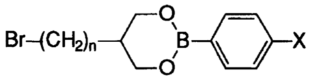
	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_n}/\overline{M_w}$
Light scattering method	7800±800	16400±1200	1.87
GPC method	7300	13700	1.88

The mesogenic groups **6a**—**d** having a two-ring system showed no mesophases except **6b**, however, **6e**—**m** constructed with three rings exhibited a stable smectic phase. For all of them an enantiotropic S_A phase was observed. Furthermore compounds **6f**, **6i**, and **6m** exhibited an enantiotropic Sc* phase, and compound **6h** a monotropic Sc* phase. It seems that the stability of mesophases depends on the length of spacer groups. For example, among compounds which have the same mesogenic group, formation of stable Sc* phases was observed for compounds **6f** (n=10) and **6i** (n=12) which have longer spacer groups, while **6g** (n=5) did not form an Sc* phase.

However, thermal stabilities of the mesophases formed by **6** are somewhat lower than those of compound **12** reported previously (Chart 1).[9a,13] This may be due to the large bromine atom on the terminal alkyl group which diminishes effective molecular orientation and packing in mesophases.

Monomer **8** showed thermal behaviors similar to compound **6**. Displacement of the bromine atom by an acrylic group did not give essential effects on the meso-

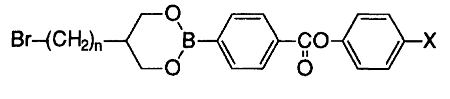
Table 3. a) Phase Transition[a] of Mesogenic Groups Having a Two-Ring System. b) Phase Transition of Mesogenic Groups Having a Three-Ring System



6a-d

(a)

	n	X[b]	K	Sc*	S_A	I
6a	10	O-2M4	● 39.5			●
6b	10	O-5M7	● 37.0		● (31.4)[c]	●
6c	10	CO_2-2M4	● 35.2			●
6d	10	CO_2-5M7	● 38.3			●



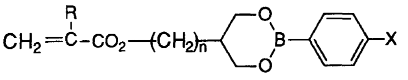
6e-m

(b)

	n	X[d]	K	Sc*	S_A	I
6e	10	O-2M4	● 112.9		● 114.0	●
6f	10	CO_2-2M4	● 75.5	● 84.3	● 106.3	●
6g	5	CO_2-2M4	● 74.3		● 109.6	●
6h	8	CO_2-2M4	● 68.0	● (57.6)	● 106.0	●
6i	12	CO_2-2M4	● 63.2	● 65.9	● 99.0	●
6j	10	O-1M7	● 59.8		● 81.4	●
6k	10	CO_2-1M7	● 69.8		● 72.6	●
6l	10	O-5M7	● 88.7		● 119.9	●
6m	10	CO_2-5M7	● 70.2	● 79.1	● 109.1	●

a) K: Crystal; Sc*: chiral smectic C; S_A: smectic A; I: isotropic liquid. b) 2M4=(S)-2-methylbutyl; 5M7=(S)-5-methylheptyl, see Fig. 1. c) Monotropic transition. d) 1M7=(R)-1-methylheptyl.

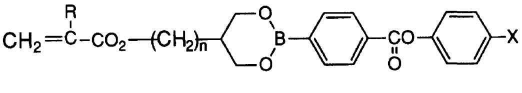
Table 4. Phase Transition of Monomers 8



8a-d and 8o

(a)

	n	R	X[a]	K	Sc*	S_A	I
8a	10	H	O-2M4	● 57.4			●
8b	10	H	O-5M7	● 47.9			●
8c	10	H	CO_2-2M4	● 54.3			●
8d	10	H	CO_2-5M7	● 26.6			●
8o	10	Me	O-2M4	● 55.7			●

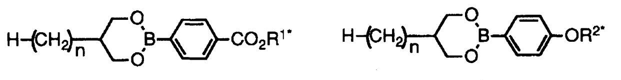


8e-n

(b)

	n	R	X[a]	K	Sc*	S_A	I
8e	10	H	O-2M4	● 86.4		● 108.4	●
8f	10	H	CO_2-2M4	● 53.4	● 61.5	● 98.4	●
8g	5	H	CO_2-2M4	● 74.3		● 109.8	●
8h	8	H	CO_2-2M4	● 67.9	● (57.6)	● 106.0	●
8i	12	H	CO_2-2M4	● 63.2	● 65.9	● 99.0	●
8j	10	H	O-1M7	● 46.1		● 73.3	●
8k	10	H	CO_2-1M4	● 34.2		● 66.6	●
8l	10	H	O-5M7	● 89.3		● 135.3	●
8m	10	H	CO_2-5M7	● 71.2	● 74.4	● 108.0	●
8n	10	Me	CO_2-2M4	● 57.1	● (49.9)	● 85.3	●

a) See Table 3.

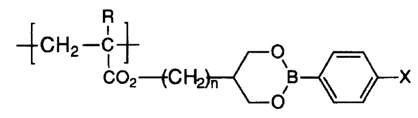


12a **12b**

Chart 1.

morphic properties. All of compound **8** formed a stable S_A phase, and **8f**, **8i**, and **8m** exhibited an enantiotropic Sc* phase. As compared with acrylate ester **8f**, methacrylate analogue **8n** showed a higher melting point, whereas a lower clearing point for **8n** was observed. The transition temperatures of polymer **2** were summarized in Table 5. The glass transition temperatures were determined on heating on the first scan with a differential scanning calorimeter. All of **2** showed an enantiotropic S_A phase, and the phases were much more stable than those of the corresponding monomers. In polymers the mesogenic groups bound to the polymer chain are oriented forcibly and often attain situation favorable to forming layer structures.[14] In fact stable Sc* phases were observed for **2e**—**2i** and **2m**, although some of their corresponding mononers showed no Sc* phases. Compounds consiting of three rings with an (S)-2-methylbutyl, 2M4, group exhibited a stable Sc* phase, whose thermal stability was extremely increased in comparison with that of the monomers. Polymers **2f**—**2h** could form Sc* phases even at temperatures as high as ca. 130°C. Nevertheless, polymers having the other chiral groups did not exhibit Sc* phases except **2m**. It has been reported[15] that chiral liquid crystalline polymers containing phenyl benzoate mesogens exhibit theremally less stable S_A phases than the corresponding monomers, whereas the Sc* phases formed by the polymers are more stable than those of the monomers. These thermal behaviors of phenyl benzoate mesogens are in sharp contrast to our result obtained in the present work. Liquid crystals containing dioxaborinane rings incline to form stable smectic phases.[8b,16] As already pointed out, the mesogenic groups whose free motion is limited to some extent by polymer main chains are oriented forcibly in polymers and the possible orientation of the mesogenic groups may be strongly influenced by the nature of polymer main chain. Polymethacrylate **2n** showed a high glass transition temperature and formed no Sc* phase, though the corresponding monomer **8n** exhibited an Sc* phase. Hahn et al. observed the formation of Sc* phase for some polysiloxanes having dioxaborinane derivatives consisting of two rings.[17] In contrast, Table 5 shows that no Sc* phases appeared for the polymers having two-ring systems, and for the polymethacrylate, as described above, even with a three-ring systems. It is well-known that the main chain flexibility of liquid crystalline polymers affects the transition temperatures.[14] The flexibility of main

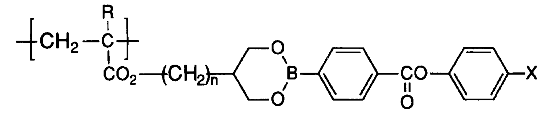
Table 5. Phase Transition of Polymers **2**



2a-d and 2o

(a)

	n	R	X[a)]	G[b)]		Sc*		SA		I
2a	10	H	O-2M4	•	46.6			•	82.9	•
2b	10	H	O-5M7	•	39.5			•	72.6	•
2c	10	H	CO$_2$-2M4		*c)			•	67.0	•
2d	10	H	CO$_2$-5M7	•	38.7			•	55.5	•
2o	10	Me	O-2M4	•	70.8			•	76.5	•



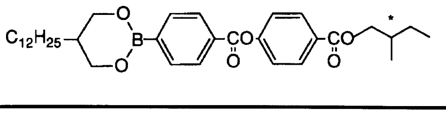
2e-n

(b)

	n	R	X[a)]	G		Sc*		SA		I
2e	10	H	O-2M4	•	64.6	•	82.2	•	136.2	•
2f	10	H	CO$_2$-2M4	•	44.9	•	127.6	•	177.6	•
2g	5	H	CO$_2$-2M4	•	61.6	•	130.8	•	145.6	•
2h	8	H	CO$_2$-2M4	•	54.6	•	133.2	•	157.8	•
2i	12	H	CO$_2$-2M4	•	45.6	•	93.7	•	161.3	•
2j	10	H	O-1M7	•	47.1			•	109.4	•
2k	10	H	CO$_2$-1M7	•	60.7			•	103.9	•
2l	10	H	O-5M7	•	63.7			•	130.1	•
2m	10	H	CO$_2$-5M7	•	61.8	•	76.3	•	110.4	•
2n	10	Me	CO$_2$-2M4	•	151.9			•	169.2	•

a) See Table 3. b) G: glassy state. c) Glassy transition temperature was below room temperature.

Table 6. Magnitude of Spontaneous Polarization



13

	Ps/nC cm^{-2}
2f	—
8f	1.0
6f	0.2
13	9.6

chains increases in the order; polymethacrylate<polyacrylate<polysiloxane. As the flexibility increases, the thermal stability of mesophases is generally increased. The result obtained here reveals again that the flexibilities of main chains are very important for the formation of mesophases.

Spontaneous Polarizations. The magnitude of spontaneous polarizations (Ps) for polymer **2f**, monomer **8f**, and mesogenic group **6f** was measured on the basis of the dynamic response to a changing external electric field, and the results are summarized in Table 6. They showed small Ps relatively to compound **13** reported previously,[9a,18)] since the terminal group (bromine or acrylate) disordered the orientation of molecular dipole in the Sc* phase. Experiments to switch polymer **2f** in electric fields could not yet be performed successfully. This may be attributable to the extremely high viscosity of polymer **2f** in comparison with **8f** and **6f**.[16)] The similar phenomenon has been reported by Scherowsky et al.[19)]

Experimental

Measurements of transition temperatures and observation of mesophases were made using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 control unit. The transition temperatures were also performed with a Shimadzu DSC-50 differential scanning carolimeter. The rate of heating and cooling was fixed to 5°C min^{-1}. IR spectra were obtained with a Hitachi 295 Infrared Spectrophotometer. ^{1}H NMR spectra were recorded on a Brucker WM-360 instrument in CDCl$_3$ with tetramethylsilane as an internal standard. Average molecular weights were measured on a Hitachi Liquid Chromatograph 635 with a polystyrene standard using tetrahydrofuran as a mobile phase.

2-(10-Bromodecyl)-1,3-propanediol (3) ($n=10$). To a solution of 1,10-dibromodecane (25 g, 83 mmol) in absolute ethanol (100 ml), sodium diethyl malonate, prepared from sodium ethoxide (5.67g, 83.3 mmol) and diethyl malonate (13.3g, 83.3 mmol), was added dropwise for 2 h under reflux. After 20 h ethanol was distilled away, then 1 M hydrochloric acid (1 M=1 mol dm^{-3}) and ether were added to the residue. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether solution was washed with 5% aqueous sodium hydrogencarbonate and water, then dried over sodium sulfate. After evaporation of ether, the resultant residue was heated to 100°C at 0.1 mmHg (1mmHg=133.322 Pa) and unreacted substrates were distilled off. The residue was purified by column chromatography on silica gel using dichloromethane as an eluent, affording diethyl (10-bromodecyl)malonate as a pale yellow oil; yield 26.7g (65%); IR (neat) 1760, 1755 (C=O), and 1110 cm^{-1} (C–O); ^{1}H NMR δ=1.20—2.05 (24H, m, alkyl+$\mathrm{OCH_2C\underline{H}_3}$), 3.31 (1H, t, J=7 Hz, CH), 3.37 (2H, t, J=7 Hz, Br–CH$_2$), and 4.20 (4H, q, J=7 Hz, $\mathrm{OC\underline{H}_2CH_3}$).

To a solution of diethyl (10-bromodecyl) malonate (26.7g, 54.2 mmol) in methanol (500 ml), sodium borohydride (20.5 g, 542 mmol) was added with vigorously stirring at such a rate that the reaction mixture was continually refluxed. After all of sodium borohydride was added the mixture was refluxed for 30 min. Then water (100 ml) was added and the mixture was stirred for 1 h at room temperature. The inorganic salt was filtered off and the product was extracted with ether. The extract was washed with water and dried over sodium sulfate. After concentration the residue was purified by column chromatography on silica gel using dichloromethane, then ethyl acetate as eluents. Recrystallization from hexane gave 2-(10-bromodecyl)-1,3-propanediol as colorless needles; yield 12.8 g (80%); mp 33.0—34.0°C; IR (Nujol) 3345 (OH) and 1119 cm^{-1} (C–O); ^{1}H NMR δ=1.16—1.57 (18H, m, alkyl), 1.92 (1H, m, CH), 2.25 (2H, broad, OH), 3.40 (2H, t, J=7 Hz, Br–CH$_2$), 3.60 (2H, dd, J=11 and 11 Hz, CH$_2$O), and 3.97 (2H, dd, J=11 and 4Hz, CH$_2$O).

2-{4-[(*S*)-2-Methylbutoxy]phenyl}-5-(10-bromododecyl)-1,3,2-dioxaborinane (6a). A mixture of 4-

[(*S*)-2-methylbutoxy]phenylboronic acid (1.76 g, 10 mmol) and 2-(10-bromodecyl)-1,3-propanediol **3** (2.95 g, 10 mmol) in toluene (50 ml) was stirred under reflux for 2 h. During the reaction water formed was removed azeotropically using Dean-Stark apparatus. When the reaction was completed, toluene was distilled away, the resultant residue was purified by column chromatography on silica gel using dichloromethane as an eluent. Recrystallization from acetone gave pure product **6a** as colorless needles; yield 2.53 g (58%); IR (Nujol) 1600 (Ar), 1310 (B–O), and 1240 cm^{-1} (C–O); ^{1}H NMR $\delta=0.94$ (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 1.00 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.08—1.87 (21H, m, alkyl), 2.08 (1H, m, $C\underline{H}(CH_2O-)_2$), 3.40 (2H, t, $J=7$ Hz, Br–CH_2), 3.71—3.86 (4H, m, $CH_2OAr+CH(C\underline{H}_2O-)_2$, ax), 4.14 (2H, dd, $J_{gem}=11$ Hz and $J_{ax-eq}=5$ Hz, $C\underline{H}(CH_2O-)_2$, eq), 6.86 (2H, d, $J=9$ Hz, Ar), and 7.69 (2H, d, $J=9$ Hz, Ar).

2-(4-Carboxylphenyl)-5-(10-bromodecyl)-1,3,2-dioxaborinane (5). 4-Carboxyphenylboronic acid (2.49 g, 15 mmol) was reacted with 2-(10-bromodecyl)-1,3-propanediol **3** (4.43 g, 15 mmol) in toluene (80 ml) under reflux for 2 h. During the reaction water formed was removed azeotropically. Then the reaction mixture was cooled to room temperature and the crystals separated were collected by filtration. Colorless needles; yield 4.8 g (75%); IR (Nujol) 3400—2500 (OH) and 1690 cm^{-1} (C=O). This carboxylic acid showed mesomorphic properties. The phase sequence (temperatures in °C) is as follows: K·154·N·175·I.

2-{4-[(*S*)-2-Methylbutoxycarbonyl]phenyl}-5-(10-bromodecyl)-1,3,2-dioxaborinane (6c). Carboxylic acid **5** (1.92 g, 4.5 mmol) and (*S*)-2-methyl-1-butanol (0.42 g, 4.8 mmol) in benzene (50 ml) were heated under reflux for 5 h in the presence of sulfric acid (0.5 ml). Benzene was removed by evaporation and the resultant residue was purified by column chromatography on silica gel using dichloromethane as an eluent. Recrystallization from hexane gave pure **6c** as colorless needles; yield 1.54 g (69%); IR (Nujol) 1725 (C=O) and 1250 cm^{-1} (C–O); ^{1}H NMR $\delta=0.96$ (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 1.00 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.25—1.87 (21H, m, alkyl), 2.10 (1H, m, $C\underline{H}(CH_2O-)_2$), 3.41 (2H, t, $J=7$ Hz, Br–CH_2), 3.77 (2H, dd, $J_{gem}=10$ and $J_{ax-ax}=10$ Hz, $CH(C\underline{H}_2O-)_2$, ax), 4.10—4.23 (4H, m, $CO_2CH_2+CH(C\underline{H}_2O-)_2$, eq), 7.83 (2H, d, $J=8$ Hz, Ar), and 7.99 (2H, d, $J=8$ Hz, Ar).

2-[4-[4-[(*S*)-2-Methylbutoxycarbonyl]phenoxycarbonyl]phenyl]-5-(10-bromodecyl)-1,3,2-dioxaborinane (6f). Carboxylic acid **5** (1.92 g, 4.5 mmol) was treated with thionyl chloride (0.56 g, 4.7 mmol) in the presence of *N*,*N*-dimethylformamide (0.2 ml) in 1,2-dichloroethane (15 ml) under reflux for 1 h. Removal of the solvent under reduced pressure afforded the acyl chloride, which was used for the next reaction, esterification, without further purification. To a solution of (*S*)-2-methylbutyl 4-hydroxybenzoate (1.12 g, 5.4 mmol) in pyridine (8 ml), a solution of the acyl chloride in tetrahydrofuran (15 ml) was added dropwise at 0°C, and then stirred at room temperature for 20 h. The solvent was evaporated and the product was extracted with ether. The extract was washed with water and dried over sodium sulfate. After concentration, the residue was purified by column chromatography on silica gel using hexane-dichloromethane (1 : 4) as an eluent. Recrystallization from hexane gave the product as colorless needles; yield 1.44 g (52%); IR (Nujol) 1750, 1730 (C=O), and 1250 cm^{-1} (C–O); ^{1}H NMR $\delta=0.97$ (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 1.02 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.30—1.90 (21H, m, alkyl), 2.10 (1H, m, $C\underline{H}(CH_2O-)_2$), 3.41 (2H, t, $J=7$ Hz, Br–CH_2), 3.80 (2H, dd, $J_{gem}=11$ and $J_{ax-ax}=11$ Hz, $CH(C\underline{H}_2O-)_2$, ax), 4.12—4.25 (4H, m, $CO_2CH_2+CH(CH_2O-)_2$, eq), 7.31 (2H, d, $J=9$ Hz, Ar), 7.91 (2H, d, $J=9$ Hz, Ar), 8.12 (2H, d, $J=9$ Hz, Ar), and 8.15 (2H, d, $J=9$ Hz, Ar).

2-(4-Substituted Phenyl)-5-[ω-(acryloyloxy)alkyl]-1,3,2-dioxaborinane (8); Representative Procedure.[12] A mixture of 2-[4-[4-[(*S*)-2-methylbutoxycarbonyl]phenoxycarbonyl]phenyl]-5-(10-bromodecyl)-1,3,2-dioxaborinane **6f** (1.23 g, 2 mmol), acrylic acid (0.22 g, 3 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (0.46 g, 3 mmol) in dry benzene (10 ml) was stirred at 80°C for 2 h. After evaporation of banzene, the resultant residue was purified by column chromatography on silica gel using dichloromethane as an eluent. Recrystallization from hexane gave 2-[4-[4-[(*S*)-2-methylbutoxycarbonyl]phenoxycarbonyl]phenyl]-5-(10-acryloyldecyl)-1,3,2-dioxaborinane **8f** as colorless needles; yield 0.95 g (82%); IR (Nujol) 1750, 1740, 1725 (C=O), 1600 (Ar), and 1250 cm^{-1} (C–O); ^{1}H NMR $\delta=0.97$ (3H, t, $J=8$ Hz, $CH_2C\underline{H}_3$), 1.02 (3H, d, $J=7$ Hz, $CHC\underline{H}_3$), 1.26—1.79 (21H, m, alkyl), 2.10 (1H, m, $C\underline{H}(CH_2O-)_2$), 3.80 (2H, dd, $J_{gem}=10$ and $J_{ax-ax}=10$ Hz, $CH(C\underline{H}_2O-)_2$, ax), 4.12—4.23 (6H, m, $CO_2CH_2\times2+CH(CH_2O-)_2$,eq), 5.81 (1H, dd, $J_{1\text{-}2}=2$ and $J_{1\text{-}3}=11$ Hz, H^1), 6.14 (1H, dd, $J_{3\text{-}1}=11$ and $J_{3\text{-}2}=18$ Hz, H^3), 6.37 (1H, dd, $J_{2\text{-}1}=2$ and $J_{2\text{-}3}=18$ Hz, H^2),7.31 (2H, d, $J=8$ Hz, Ar), 7.91 (2H, d, $J=8$ Hz, Ar), 8.12 (2H, d, $J=8$ Hz, Ar) and 8.15 (2H, d, $J=8$ Hz, Ar); Anal. Calcd for $C_{35}H_{47}O_8B$: C, 69.31; H, 7.81%. Found: C, 69.36; H, 7.70%.

The other derivatives of **8** were similarly prepared starting from the corresponding **6**.

Synthesis of Polymer 2; Representative Procedure. A solution of monomer **8f** (728 mg, 1.2 mmol) and 2.2′-azobisisobutyronitrile (24 μmol, 2 mol%) in dry toluene (8 ml) was placed in a glass ampule. After degassed three times the ampule was sealed and heated at 60°C for 6 h. After cooling the ampule, the reaction mixture was poured into methanol (100 ml) with stirring. The polymer precipitated was separated by centrifugation and purified at least twice by reprecipitation from a concentrated benzene solution into methanol. Lyophilization from a benzene solution gave **2f** as a spongy polymer; yield 146 mg (20%); IR (Nujol) 1750—1720 (C=O), 1600 (Ar), and 1255 cm^{-1} (C–O); ^{1}H NMR $\delta=0.88$—0.98 (6H, m, CH_3), 1.01—1.87 (24H, m, alkyl), 2.08 (1H, m, $C\underline{H}(CH_2O-)_2$), 3.75 (2H, m, $CH(C\underline{H}_2O-)_2$, ax), 4.01—4.19 (6H, m, $CO_2CH_2\times2+CH(CH_2O-)_2$, eq), 7.27 (2H, m, Ar), 7.89 (2H, m, Ar), and 8.12 (4H, m, Ar). Anal. Calcd for $(C_{35}H_{47}O_8B)_n$: C, 69.31; H, 7.81%. Found: C, 68.53; H, 7.57%.

We thank Materials and Electronic Devices Laboratory, Mitsubishi Electric Corp. for Ps measurements, and the Material Analysis Center, I.S.I.R., Osaka University, for spectral measurements and microanalyses. This work was partially supported by grant-in-aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture.

References

1) V. P. Shibaev and N. A. Plate, *Vysokomolek. Soedin., Ser. A*, **19**, 923 (1977); *Adv. Polym. Sci.*, **60/61**, 175 (1984); H. Finkelmann, "Polymer Liquid Crystals," ed by A. Ciferri, W. R. Kringbaum, and R. B. Mayer, Academic Press, New York (1982), p.35.

2) C. Pugh and V. Percec, *Polym. Bull.*, **16**, 521 (1986); H. Finkelmann, M. Happ, M. Portugal, and H. Ringsdorf, *Makromol. Chem.*, **179**, 2541 (1978); H. Fikelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 31 (1980).

3) M. V. Piskunov, S. G. Kostromin, L. B. Stroganov, V. P. Shibaev, and M. A. Plate, *Makromol. Chem., Rapid Commun.*, **3**, 443 (1982).

4) For example, H. Finkelmann, H. J. Kock, and G. Rehage, *Makromol. Chem., Rapid Commun.*, **2**, 317 (1981); V. V. Shilov, V. V. Tsukruk, and Y. S. Lipatov, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 41 (1984); G. Decobert, F. Soyer, and J. C. Dubois, *Polym. Bull.*, **14**, 179 (1985).

5) L. Strzelecki and L. Liebert, *Bull. Soc. Chim. Fr.*, **1973**, 597.

6) E. C. Hsu, S. B. Clough, and A. Blumstein, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 545 (1977).

7) A-M. Giround-Godquin and P. M. Maitlis, *Angew. Chem., Int. Ed. Engl.*, **30**, 375 (1991).

8) a) K. Seto, S. Takahashi, and T. Tahara, *J. Chem. Soc., Chem. Commun.*, **1985**, 122; b) H. Matsubara, K. Seto, T. Tahara, and S. Takahashi, *Bull. Chem. Soc. Jpn.*, **62**, 3896 (1989).

9) a) K. Seto, H. Matsubara, S. Takahashi, T. Tahara, M. Murakami, S. Miyake, T. Masumi, T. Ando, and A. Fukami, *J. Chem. Soc., Chem. Commun.*, **1988**, 56; b) H. Matsubara, K. Seto, H. Imazaki, and S. Takahashi, *J. Mater. Chem.*, **2**, 83 (1992).

10) H. Matsubara, K. Seto, H. Tabuchi, H. Imazaki, and S. Takahashi, *Chem. Lett.*, **1989**, 1519.

11) M. R. Brown and H. Rapoport, *J. Org. Chem.*, **28**, 3261 (1963).

12) N. Ono, T. Yamada, T. Saito, K. Tanaka, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **51**, 2401 (1978).

13) H. Matsubara, S. Takahashi, K. Seto, and H. Imazaki, *Mol. Cryst. Liq. Cryst.*, **180B**, 337 (1990).

14) V. P. Shibaev and N. A. Plate, *Pure Appl. Chem.*, **57**, 1589 (1985).

15) S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto, and K. Kawasaki, *Mol. Cryst. Liq. Cryst.*, **155**, 93 (1988).

16) K. Seto, Doctor's Thesis, Osaka City University, 1991.

17) B. Hahn and V. Percec, *Macromolecules*, **20**, 1961 (1987); **22**, 1588 (1989); *Mol. Cryst. Liq. Cryst.*, **157**, 125 (1988).

18) M. Murakami, S. Miyake, T. Masumi, T. Ando, A. Fukami, S. Takahashi, K. Seto, and T. Tahara, *Mol. Cryst. Liq. Cryst.*, **162B**, 149 (1988).

19) G. Scherowsky, U. Muller, J. Springer, W. Trapp, A. M. Levelut, and P. Davidson, *Liq. Cryst.*, **4**, 1297 (1989).