Synthesis of Chiral and Smectic C Phase Polymers

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ABSTRACT: A new series of the shish-kebab-type chiral polymers were synthesized by polycondensation of 2,5-bis(4-alkoxylbenzoyloxy)hydroquinone and diacyl dichloride. By means of differential scanning calorimetry, polarizing optical microscopy, wide-angle X-ray scattering, and polarimetric analysis, we found that all the chiral polymers were optically active and formed a smectic C phase when being heated to above their melting temperatures.

Introduction

Liquid crystal materials with a chiral smectic C phase have received much attention in recent years because of their scientific and technical potentials in, for example, nonlinear optics, information storage, and display devices.[1−3] The first polymer having a chiral smectic C (S_C*) phase was reported in 1984 by Shibaev et al.[4] In comparison with low-molar-mass liquid crystals, polymeric materials have the disadvantage of having higher rotational viscosity and longer switching time when used for display devices. For S_C* phase molecules an explanation was given by Sekiya et al.[5] According to them, the switch of molecular orientation from one tilt direction to the other can be achieved without translocation of the gravity center for low-molar-mass molecules. On the other hand, this translocation would occur for polymers because the end of the mesogenic unit is bonding to the polymer backbone. Otherwise, motions of main-chain segments are implicated. Interested in this model, we came to the idea of studying the liquid crystalline polymers in which the bonding of the mesogenic units to the main-chain backbone is not at the end but at the gravity center of the mesogenic units. Thus, the reorientation of the tilt direction may be achieved without translocation of gravity center. Two such classes of polymers are possible: the side-group-type polymers with mesogenic units laterally attached to the main chain (the “side-on polymer”) and the shish-kebab-type polymers in which the mesogenic units are incorporated in the polymers as the “kebabs” with the main chain as the “shish” or “skewer” (the “shish kebab”).[6] These two classes of polymers are relatively new and are much less studied than are the conventional main-chain-type and side-group-type (“end-on”) polymers. However, the studies on the side-on polymers have reached the conclusion that these polymers predominantly form a nematic phase.[7−10] On the other hand, the shish-kebab polymers have received only little attention.[11−14] Therefore, we decided to study the shish-kebab-type chiral polymers (see Scheme 2). The preliminary results of the optical activities and the mesophase properties of these new polymers are reported in this paper.

Experimental Section

Measurements. The elemental analyses were carried out by using an MOD 1106 instrument. ^{1}H NMR spectra were recorded on an ARX 400 spectrometer with tetramethylsilane as internal standard and deuterated chloroform or dimethyl sulfoxide as solvent. IR spectra were recorded on a Shimadzu-435 spectrometer. A VG-ZAB-HS instrument was used for mass determination of intermediates and monomers. Molecular weights and polydispersity of the polymers were determined with a Waters 201 GPC instrument with polystyrene as standard. A TA Instrument MDSC was used to determine the phase transition temperatures which are to be reported as the peak values. The heating rate was 5 °C/min. A Rigaku TG-DTA-DSC thermal analyzer was used to determine the thermal decomposition temperature, at a heating rate of 20 °C/min under nitrogen atmosphere. WAXD measurements were performed on a Phillip PW-1700 automatic powder diffractometer with a nickel-filtered Cu Kα at 40 kV voltage and 30 mA electric current. The scanning rate was 5 deg/min, and the scanning scope was 1.5−40 deg. Phase transitions and liquid crystalline properties were also studied by using POM (polarizing optical microscopy) with a Leitz 12 Pol type polarizing microscope and a Leitz 350 heating stage. The optical activity was determined on a WZZ-1 automatic polarimeter at 20 °C and 589.0 nm.

Synthesis of the Monomers and Polymers. The reaction sequence is shown in Scheme 1. 2,5-Dihydroxyquinone (**1**) was prepared according to a literature procedure.[15] (*S*)-(−)-4-Methyl-1-hexanol (**2B**) and 5-methyl-1-hexanol (**2D**) were prepared according to the literature.[16,17] The other compounds used in the syntheses were commercial products and used without further purification.

Synthesis of Compounds 3. Taking **3E** as example: In a flask 26.3 mL (0.14 mol) of *n*-decanol was dissolved in 50 mL of pyridine. Benzenesulfonyl chloride (27 mL, 0.21 mol) was added into the flask. The mixture was stirred at 4−6 °C for 5 h. Then 100 mL of water and 20 mL of hydrochloric acid were added into the flask. The organic layer was isolated and washed successively with water, sodium carbonate, dilute sulfuric acid, dilute hydrochloric acid, and water. The product was dried over sodium sulfate and distilled under vacuum to yield 40.1 g (97.4%) of *n*-decyl benzenesulfonylate. The product was mixed with 27.09 g (0.20 mol) of 4-hydroxylbenzoic acid, 27.0 g (0.40 mol) of KOH, 90 mL of alcohol, and 90 mL of water. The mixture was refluxed for 36 h and then cooled to room temperature. Hydrochloric acid was added to the above until its pH equals 1−2. A white precipitate was formed. The raw product was purified through recrystallization from ethanol to give **3E** (29.4 g, yield 78.8%). The other compounds of **3** (**3A**,

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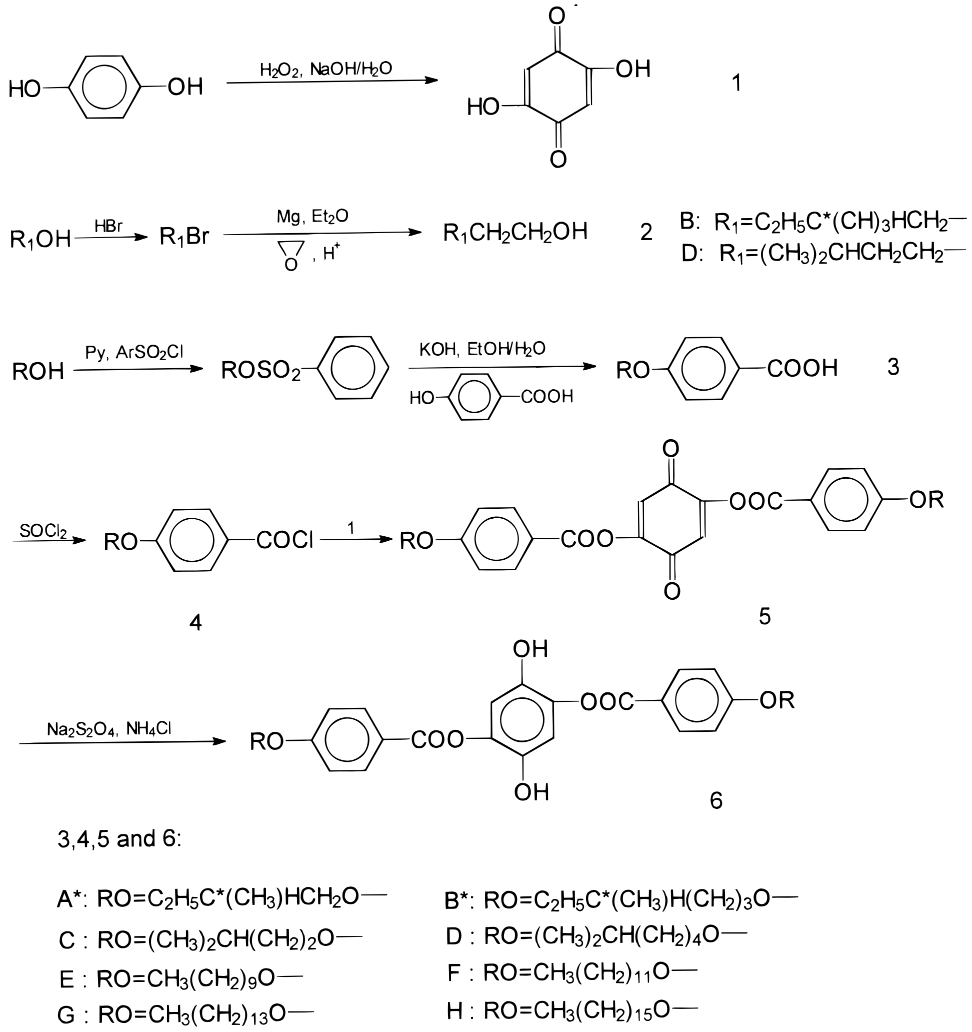
Scheme 1. Synthesis of Monomer 6



3B, **3C**, **3D**, **3F**, **3G**, and **3H**) were prepared in a similar manner. Their yields were respectively 69.0%, 64.7%, 65.8%, 68.0%, 76.0%, 67.5%, and 76.3%.

Synthesis of Compounds 5. Taking **5E** as example. A mixture of 10.0 g (0.036 mol) of **3E** with an excess amount of thionyl chloride was heated to reflux for 1 h. The excess thionyl chloride was taken out with a rotary evaporator. The resulting acid chloride was washed with petroleum ether. THF (20 mL) and pyridine (2.6 mL) were added into the chloride to make a solution, into which 2,5-dihydroxybenzoquinone (2.3 g, 0.016 mol) dissolved in THF was added slowly. The solution was stirred for 3 h. The solvent was taken out with a rotary evaporator, and the raw product was recrystallized from acetone to give a light yellow product **5E** in 78% yield. The compounds **5A**, **5B**, **5C**, **5D**, **5F**, **5G**, and **5H** were prepared in a similar manner. Their yields were respectively 72%, 84%, 75%, 77%, 72%, 68%, and 89%.

Synthesis of Monomers 6. Taking **6E** as example: In a flask placed in an ice/water bath 3.0 g (0.0045 mol) of **5E** was dissolved in 50 mL of THF. With stirring, a solution of 11 g of NH_4Cl and 11 g of sodium hydrosulfite in 66 mL of deionized water was added dropwise into the flask. A white product was formed. The product was collected, washed with water, dried, and recrystallized from acetone to give **6E** (yield 97%, melting point T_m 170 °C, isotropization temperature T_i 173 °C). Similarly, the other monomers were synthesized with following results (yield; T_m, T_i of the mesophase if any, both in °C): **6A** (96%; 185), **6B** (96%; 152), **6C** (98%; 182), **6D** (99%; 162), **6F** (98%; 165, 167), **6G** (96%; 159, 163), and **6H** (97%; 157, 160). The chemical structures of all the monomers were characterized and proved by elemental analysis, ^{1}H NMR, IR, and mass spectroscopy.

Polymerization. The polymers were synthesized according to the reactions shown by Scheme 2. Thus, to a solution of monomer **6** (1 mmol) in 1 mL of pyridine and 5 mL of 1,1,2,2-tetrachloroethane (TCE) a solution of an equimolar amount of a diacyl dichloride in 5 mL of TCE was slowly added dropwise at 0 °C. The mixture was then allowed to react at room temperature for 74 h. The polymer was isolated by precipitation from THF/methanol solution and purified by washing with methanol.

Results and Discussion

Liquid Crystalline Property of the Polymers. All the polymers were white powders and soluble in THF at room temperature. They were characterized by using GPC, MDSC, WAXD, and POM. Their molecular weights from GPC and phase transition temperatures from MDSC were collected in Table 1. The number-averaged molecular weight (M_n) ranged from 5300 to 6500, and the weight-averaged (M_w) ranged from 11 000 to 14 000. The rather low molecular weights can be interpreted by the low nucleophilicity of the phenolic hydroxyl group. Because of the low degree of polymerization (DP ~ 7−8) the end groups should also affect the phase property. Nevertheless, all the polymers showed a reasonably broad temperature range of mesophase ($T_i - T_m \sim 40-78$ °C, Table 1), and both T_m and T_i of the polymers were found to decrease when the length of RO− was increased (in the polymers ⟨P6*R⟩) and when the flexible spacer unit became longer (in the

Scheme 2. Synthesis of the Polymers ⟨PnR*⟩ and ⟨P6*R⟩

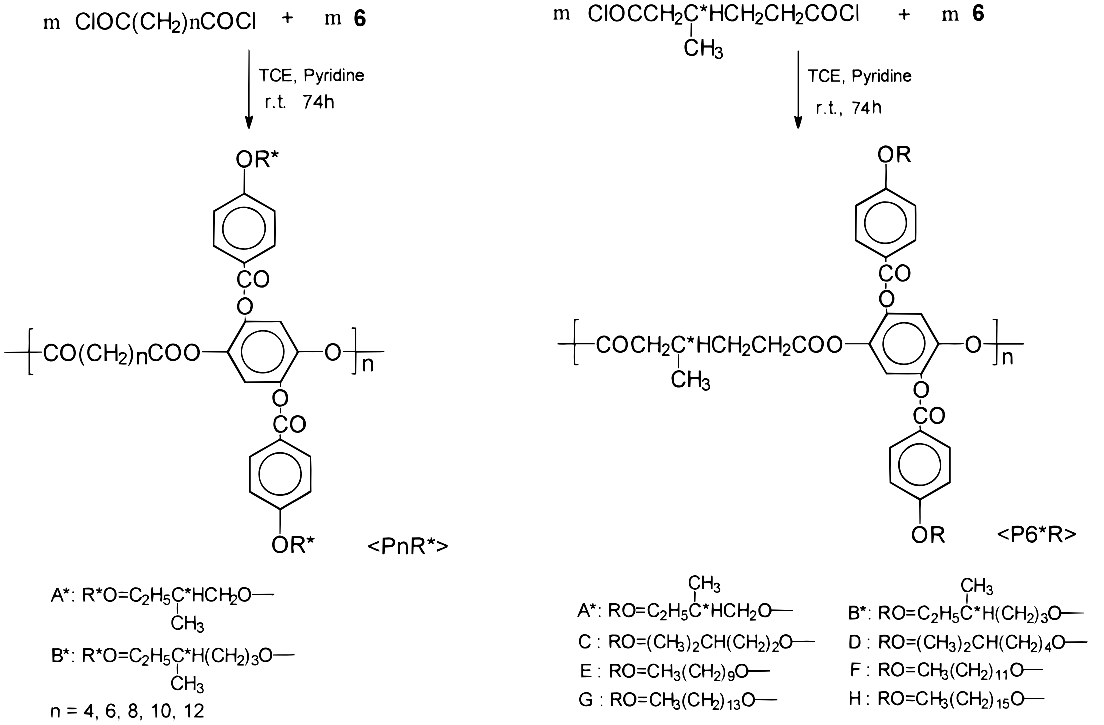


Table 1. Molecular Weight and Phase Transition Temperatures of the Polymers

	mol wt[a]		transition temp (°C)[b]		transition enthalpy (J/g)	
polymers	$\bar{M}_n$	$\bar{M}_w$	T_m	T_i	ΔH_m	ΔH_i
P4A*	5300	11 000	87	165	6.4	6.7
P6A*	5400	11 000	81	154	5.3	5.6
P8A*	5600	12 000	73	133	6.8	6.6
P10A*	5600	11 000	70	125	4.7	5.0
P12A*	5500	11 000	65	117	6.1	5.8
P4B*	5600	11 000	77	152	4.8	4.0
P6B*	5700	12 000	71	143	4.3	4.5
P8B*	5600	12 000	68	135	3.8	4.2
P10B*	5800	12 000	61	113	4.1	3.9
P12B*	6000	12 000	55	102	3.9	3.7
P6*A*	5400	11 000	78	135	3.7	4.3
P6*B*	5600	12 000	75	128	3.9	4.2
P6*C	5500	11 000	72	137	4.2	6.3
P6*D	5600	12 000	68	134	5.8	4.7
P6*E	6100	12 000	62	122	2.7	3.4
P6*F	6000	13 000	57	110	3.0	2.9
P6*G	6300	14 000	50	97	3.1	3.6
P6*H	6500	14 000	41	81	3.3	3.8

[a] Determined by using GPC. [b] Determined by using MDSC and proved by using POM.

polymers ⟨PnR*⟩). In Table 1 are also shown phase transition enthalpies of melting (ΔH_m) and isotropization (ΔH_i) in J/g.

The results obtained from POM were in a good agreement with those from DSC. By heating the polymer samples in POM, we observed first the melting and formation of a birefringent mesophase and then the transition of the liquid crystals into isotropic liquids. The smectic-type textures (focal conic defects and four-brush schlieren disclinations) were observed for the mesophases. Figure 1 gives one example of the focal−conic textures of the polymers.

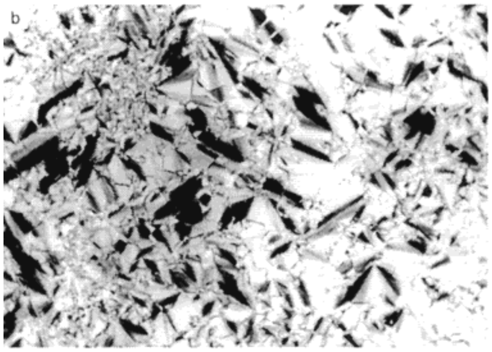


Figure 1. Focal−conic texture of P6*D taken at 95 °C.

In agreement with POM observations, the preliminary WAXD measurements also suggested that the mesophases of the polymers were smectic. Figure 2 presented the variable-temperature XRD powder patterns of the polymers using P6*G and P6B* as examples. The patterns recorded for the mesophase of the polymers had a scattering halo at wider angles but a diffraction peak at $2\theta \sim 4°$ which disappeared at T_i of the polymer. A layered structure was thus assumed for the mesophase. The results of the diffraction together with the determined spacing of the layers (d) and the calculated most-probable length by molecular simulation of the rodlike mesogenic moieties (L) were collected in Table 2. Because d is significantly shorter than L, the mesogenic rods must have been oriented with their long axis director inclined to and formed a tilt angle with the plane normal of the smectic layers. The tilt angle (α) was calculated according to the equation $\alpha = \cos^{-1}(d/L)$. In all the cases, the tilt angle is over 40°. This suggests that the polymers have the smectic C phase. Two XRD experiments were carried out at two different temperatures (with one close to T_m, the other close to T_i) for the smectic C phase of each polymer. The results (Table 2) showed that although the layer spacing determined at higher temperature was larger than the spacing determined at lower temperature, the tilt angle determined at higher temperature was still quite large.

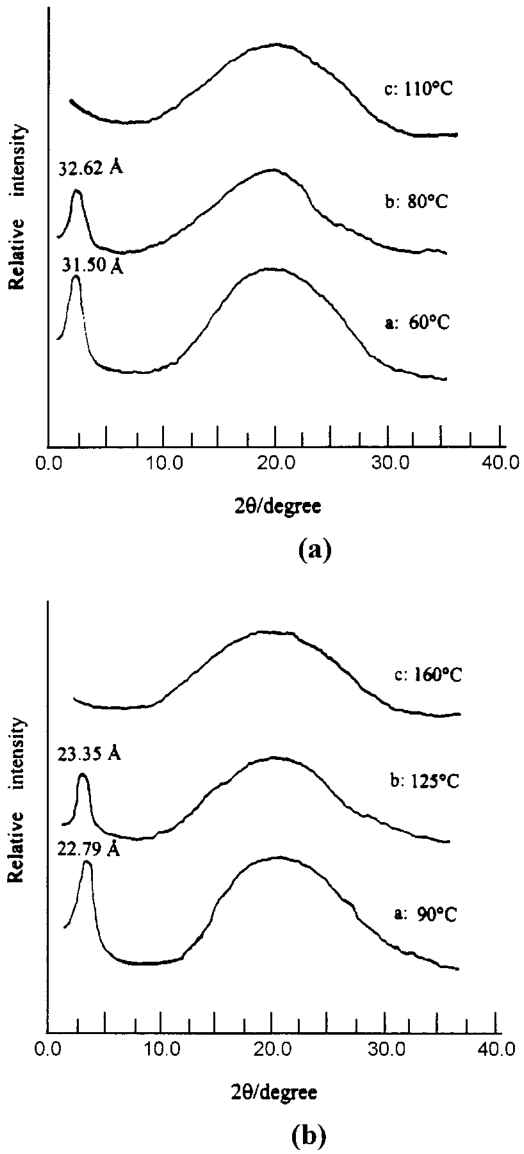


Figure 2. Powder X-ray diffraction patterns for polymers P6*G (a) and P6B* (b) at different temperature.

Optical Activity of the Chiral Intermediates and Polymers. The optical activity was determined for dilute solutions (~10^{-2} g/mL) with a WZZ-1 automatic polarimeter at 20 °C with a beam of 589.0 nm. The length of the sample cell was 200 mm. The results are collected in Table 3.

As shown in the table, all the chiral materials synthesized in this study are optically active. They were synthesized (Scheme 1) starting from (*S*)-(−)-2-methyl-1-butanol or (*S*)-(+)-4-methyl-1-haxanol. The former was a Fluka product which had a specific optical rotation of −6.3°, and the latter was synthesized according to the method of Pino and co-workers and gave a rotation of 7.81°.[16,17] In the next steps care was given to protect the chiral center by first activating the alcohol into its tosylate and by using mild reaction conditions. The resulting 4-[(*S*)-2-methylbutoxyl]benzoic acid and 4-[(*S*)-4-methylhexoxyl]benzoic acid were found to show respectively a specific optical rotation of 12.5 and 10.5 (deg dm^{-1} g^{-1} cm^3) and a molar rotation of 26.0 and 24.8 (10^{-2} deg dm^{-1} mol^{-1} cm^3). Although the chiral compounds and the chiral polymers all showed a significant optical activity, no optical purity was determined for them.

Table 2. Results of WAXD Measurements

polymers	*T* (°C)	2*θ* (deg)	*d* (Å)	*L* (Å)	α (deg)
P4A*	95	4.41	20.0	26.9	41.9
	135	4.32	20.4	26.9	40.6
P6A*	100	4.38	20.2	26.9	41.2
	140	4.30	20.5	26.9	40.3
P8A*	90	4.52	19.5	26.9	43.4
	125	4.45	19.8	26.9	42.5
P10A*	85	4.42	19.9	26.9	42.2
	110	4.32	20.4	26.9	40.6
P12A*	80	4.39	20.1	26.9	41.6
	100	4.31	20.5	26.9	40.3
P4B*	95	4.50	19.5	31.3	51.4
	130	4.32	20.4	31.3	49.3
P6B*	90	3.87	22.8	31.3	43.2
	126	3.78	23.3	31.3	41.8
P8B*	85	3.95	22.3	31.3	44.5
	120	3.86	22.8	31.3	43.2
P10B*				31.3	
P12B*	70	3.82	23.1	31.3	42.4
	95	3.72	23.7	31.3	40.7
P6*A*	95	4.48	19.7	26.9	42.8
	120	4.37	20.2	26.9	41.2
P6*B*	95	3.84	23.0	31.3	42.6
	110	3.74	23.6	31.3	41.0
P6*C	90	4.51	19.6	27.3	44.0
	120	4.41	20.0	27.3	42.8
P6*D				31.4	
P6*E				40.0	
P6*F	70	3.23	27.3	44.7	52.4
	90	2.75	32.0	44.7	44.3
P6*G	60	2.80	31.6	49.6	50.4
	80	2.71	32.6	49.6	48.9
P6*H	55	2.38	37.0	54.4	47.2
	75	2.20	40.1	54.4	42.7

Table 3. Optical Activity of the Chiral Intermediates and Polymers

compds or polymers	no. of chiral carbons in the compd[a]	solution concn (10^{-2} g/mL)	optical rotation (deg,°,+)	specific rotation (deg dm^{-1} g^{-1} cm^3)	molar rotation[b] (10^{-2} deg dm^{-1} mol^{-1} cm^3)
3A*	1	1.649	0.412	12.5	26.0
5A*	2	1.615	0.378	11.7	60.9
6A*	2	1.787	0.411	11.5	60.1
3B*	1	1.757	0.369	10.5	24.8
5B*	2	1.582	0.310	9.80	56.5
6B*	2	1.677	0.275	8.20	47.5
P4A*	2	1.635	0.275	8.41	53.1
P6A*	2	1.726	0.283	8.20	54.1
P8A*	2	1.722	0.276	8.01	55.1
P10A*	2	1.730	0.281	8.12	58.1
P12A*	2	1.642	0.266	8.10	60.3
P4B*	2	1.708	0.277	8.11	53.5
P6B*	2	1.777	0.285	8.02	55.2
P8B*	2	1.713	0.281	8.20	58.7
P10B*	2	1.743	0.275	7.89	58.7
P12B*	2	1.725	0.266	7.71	59.5
P6*A*	3	1.708	0.434	12.7	82.0
P6*B*	3	1.712	0.421	12.3	86.3
P6*C	1	1.722	0.138	4.00	25.8
P6*D	1	1.730	0.142	4.09	28.7
P6*E	1	1.732	0.135	3.91	30.7
P6*F	1	1.729	0.138	3.99	33.6
P6*G	1	1.731	0.128	3.69	33.1
P6*H	1	1.736	0.121	3.48	33.2

[a] Number of chiral center of each repeating unit for polymers.
[b] Molar rotations were calculated with the molecular weight for low-molar-mass molecules and that of the repeating momomeric unit for polymers.

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References and Notes

(1) Mcardle, C. B. *Side Chain Liquid Crystal Polymers*; Blackie and Son Ltd.: Glasgow, 1989.

(2) Suzuki, T.; Okawa, T.; Ohnuma, T. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 755.

(3) Chiellini, E.; Galli, G.; Coni, F. *Makromol. Chem. Macromol. Symp.* **1990**, *69*, 51.

(4) Shibaev, V. P.; Kozlovsky, M.; Beresnev, L. *Polym. Bull.* **1984**, *12*, 299.

(5) Sekiya, T.; Yuasa, K.; Uchda, S. *Liq. Cryst.* **1993**, *14*, 1255.

(6) Zhou, Q. F.; Li, H. M.; Feng, X. D. *Macromolecules* **1987**, *20*, 233.

(7) Hessl, F.; Finkemann, H. *Makromol. Chem.* **1987**, *188*, 1597.

(8) Keller, P.; Hardouin, R.; Mauzac, M.; Achard, M. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 71.

(9) Zhou, Q. F.; Wan, X. H.; Zhu, X. L.; Zhang, F.; Feng, X. D. *Mol. Cryst. Liq. Cryst.* **1993**, *231*, 107.

(10) Gray, G. W.; Hill, J. S.; Lacey, D. *Mol. Cryst. Liq. Cryst.* **1991**, *197*, 43.

(11) Berg, S.; Krone, V.; Ringsdrof, H. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 381.

(12) Zhou, Q. F.; Li, Z. F.; Zhang, Z. Y.; Pei, X. Y. *Macromolecules* **1989**, *22*, 3821.

(13) Li, Z. F.; Zhou, Q. F.; Zhang, Z. Y. *Polym. Biomater. Int. Symp.* **1990**, *3*, 9.

(14) Zhou, Q. F.; Xie, R.; Zhu, Y. T. *Makromol. Symp.* **1997**, *118*, 183.

(15) Reuben, G. J.; Shonle, H. A. *J. Am. Chem. Soc.* **1946**, *67*, 1034.

(16) Pino, P.; Lardicci, L.; Centoni, L. *Gazz. Chim. Ital.* **1961,** *91*, 428−440.

(17) Lardicci, L.; Pino, P. *Gazz. Chim. Ital.* **1961,** *91*, 441−457.

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