Macromolecules **1998,** *31,* 3537−3541

New Bilaterally Linked Mesogens in Main-Chain Polymers with Exhibition of Biaxial Fluctuation in Nematic Phase

Tat-Hung Tong,[†] **Andrew Primak,**[‡] **Satyen Kumar,**[‡] **and Liang-Chy Chien***[,†]

Liquid Crystal Institute, Department of Chemical Physics, and Department of Physics and NSF ALCOM Center, Kent State University, Kent, Ohio 44242

Received December 5, 1997; Revised Manuscript Received February 19, 1998

ABSTRACT: The synthesis of a new series of liquid crystalline polyesters with bilaterally linked mesogens is described. The investigation of their mesomorphic behaviors by differential scanning calorimetry, X-ray diffraction, and polarization microscopy is presented. These new polymers exhibit only the nematic phase. X-ray diffraction studies reveal the existence of biaxial fluctuation in the nematic phase in two homologues of the series.

Introduction

Most commonly encountered polymeric liquid crystals (PLCs) have mesogens linked at their ends to the polymer backbone by flexible spacers. PLCs with mesogens linked bilaterally by flexible spacers have been less studied, and only a few examples of main-chain PLC with mesogen linked bilaterally to the main chain have been reported.[1−3] This type of PLC may exhibit interesting biaxial phase properties because bilateral attachment of spacers onto the mesogens will lead to a restriction of their rotational motions along the long molecular axis. As a result, the existence of additional orientational ordering with respect to the short axes is highly likely.

Biaxial nematic phases are of great experimental and theoretical interest. In the biaxial nematic state, orientational ordering of molecules exists along the long molecular axis and also along the short axes. The biaxial nematic phase has been identified in side-chain PLCs with side-on fixed mesogens.[4−6] The existance of orientational ordering of molecules along both long and short molecules has been realized in rigid-rod polymers with flexible side chains.[7,8] Krone and Ringsdorf[2] reported that main-chain polymers composed of bilaterally linked three-ring mesogenic cores showed mainly the monotropic nematic phase, and rapid crystallization during cooling precluded the exhibition of the biaxial nematic phase in these polymers. By extending the mesogenic unit to a four-ring core, the mesomorphic stability of bilaterally linked mesogens should be enhanced and realization of the biaxial nematic phase might be possible. Krone and Ringsdorf[2] demonstrated that PLC with bilaterally linked mesogens composed of a four-ring core indeed showed a wide enantiotropic nematic phase. In their case, however, the presence of cis/trans isomers in the azo groups on the mesogenic core may have introduced additional perturbation on the molecular packing order, and biaxial phase behavior could not be detected.

We believe that by incorporating a four-ring core with ester linkages instead of azo groups in bilaterally linked mesogens, the advantage of high mesomorphic stability can be retained without complication from the presence of isomers and realization of the biaxial nematic phase may still be possible. On this basis, we have synthesized and characterized a new series of liquid crystalline polyester with bilaterally linked mesogens.

Experimental Section

The starting materials were purchased from Aldrich Chemical Company, Inc., and were used without further purification. Column chromatography was performed on silica gel (Aldrich Chemical, 70−230 mesh, 60 Å). The ^{1}H NMR (200 MHz) spectra were recorded on a Varian Gemini-200 spectrometer. The IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. Elemental analyses were performed by Oneida Research Service, Inc., Whitesboro, NY. Differential scanning calorimetry (DSC) of the polymers was performed on a Perkin-Elmer DSC7 system equipped with TAC 7/DX thermal analysis controller. The experiments were conducted under nitrogen atmosphere; the scanning rates were 10 °C/min in all cases. Thermogravimetric analyses (TGA) were performed on a TA Instruments TGA 2950 system under nitrogen atmosphere with a heating rate of 20 °C/min. The anisotropic textures of the mesogenic compounds were analyzed with a Nikon OPTIPHOT2-POL polarizing microscope equipped with Mettler FP52 hot stage and a Mettler FP5 heating controller. Gel permeation chromatography (GPC) was performed on a Waters 510 HPLC instrument with a Waters 410 differential refractometer. The experiments were done using tetrahydrofuran (THF) as solvent (1 mL/min, 35 °C), with polystyrenes as standards. The X-ray diffraction patterns were recorded from a Siemens X-1000 system with an area detector using graphite monochromator to select CuK$_\alpha$ radiation. An in situ magnetic field of ~3 kG was applied to orient the nematic director. Actual sample alignment depended on the competition between the applied field and surface effects.

Synthesis. The synthesis of monomer **7** is shown in Scheme 1. Compound **3** was obtained via Pd-catalyzed cross-coupling reaction[9] of the arylboronic acid **2** with **1**. Deprotection of the methoxy group with BBr_3[10] yields **4**. Selective protection of the phenolic groups at 2 and 2′ positions in **4** to give **5** was achieved with 1-cyclohexenyloxytrimethylsilane, using trimethylsilyl triflate (TMSOTf)[11] as catalyst. Compound **6** was obtained by 1,3-dicyclohexylcarbodiimide (DCC) esterification of **5** and 4-hexyloxybenzoic acid with 4-dimethylaminopyridine (DMAP)[12] as catalyst. Deprotection of **6** under mild acidic condition yields monomer **7**. Monomer **7** was then polymerized with the aliphatic dicarboxylic acid chlorides having different spacer length (Scheme 1) to give the polymers **8a**−**f**.

[†] Liquid Crystal Institute and NSF ALCOM Center.

[‡] Department of Physics and NSF ALCOM Center.

[*] To whom correspondence should be addressed. E-mail: CHIEN@SCORPIO.KENT.EDU.

S0024-9297(97)01772-5 CCC: $15.00

Scheme 1

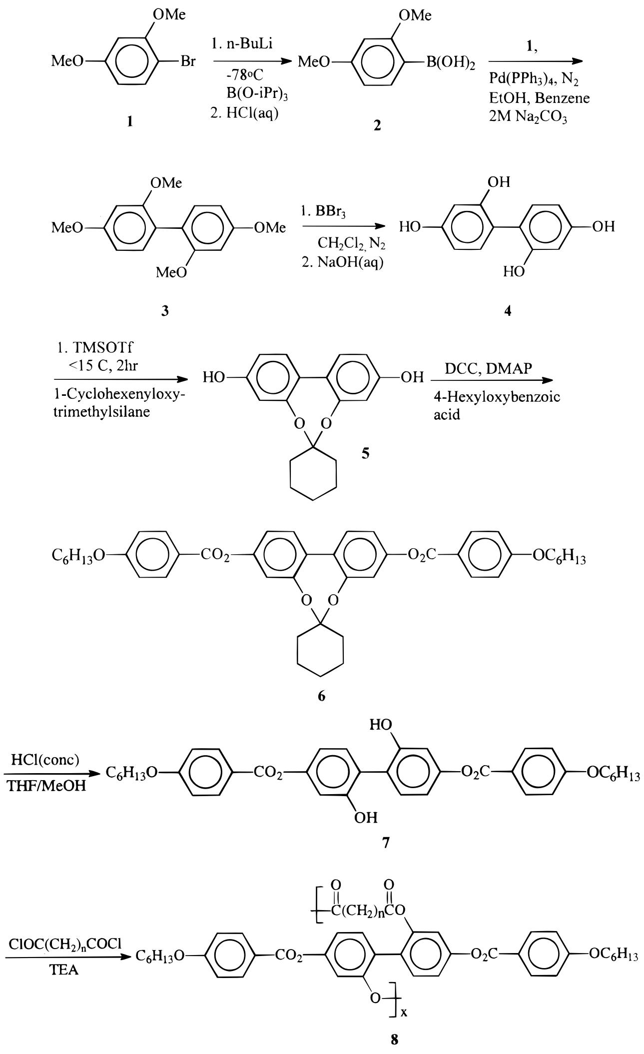

Table 1. Phase Transition Temperatures and Enthalpies (I−N) Obtained from DSC for 6, 7, and 8a−f

compound/ polymer	n	phase transition temperature (°C)[a]	ΔH_{NI} (cooling) (J g^{-1})
6	—	C 163 N 176 I	3.7
7	—	C 169 N 181 I[d]	—
8a	4	g 38 N 140 I	3.6
8b	5	g 38 r 84 C_1 123 C_2 130 N 141 I	3.9
8c	6	g 36 N 135 I	4.5
8d	7	g 29 N 127 I	3.9
8e	8	g 30 N 134 I	4.7
8f	10	g 22 r 47 C 130 (N 125) I	4.6

[a] C: crystal; N: nematic: I: isotropic; g: glass; d: decomposed; r: recrystallization.

2,4-Dimethoxyphenylboronic Acid (2). 1-Bromo-2,4-dimethoxybenzene (10 mL, 69 mmol) was dissolved in anhydrous THF (120 mL) and cooled to −78 °C. *n*-Butyllithium (10 mL, 10 M in hexanes, 100 mmol) was added in a dropwise manner under nitrogen. The resulting solution was stirred at −78 °C for 1 h. A solution of pre-cooled triisopropyl borate (33 mL, 140 mmol) in anhydrous THF (120 mL) was added in a dropwise manner to the stirred solution. The mixture was allowed to warm to room temperature and stirred under nitrogen overnight. Hydrochloric acid (10%, 80 mL) was added to the mixture, and the resulting solution was stirred for 3 h. The solution was extracted with diethyl ether (2 × 200 mL). The combined organic extracts were washed with brine (200 mL) and dried with anhydrous Na_2SO_4. The mixture was filtered and evaporated under reduced pressure. The residue was washed with a small amount of hexanes. The resulting solid was purified by filtering through a short silica gel column with ethyl acetate as eluent: yield, 8.8 g (69%); mp, 125−128 °C. ^1H NMR ($CDCl_3$): δ [ppm] = 3.82 (s, 3H), 3.89 (s, 3H), 5.69 (sbr, 2H), 6.46 (d, 1H, J = 2.18 Hz), 6.56 (dd, 1H, J = 8.25, 2.18 Hz), 7.77 (d, 1H, J = 8.25 Hz).

2,2′4,4′-Tetramethoxybiphenyl (3). Compound **1** (3.7 mL, 26 mmol) and tetrakistriphenylphosphine palladium (0.98 g, 0.85 mmol) were stirred in a mixture of benzene (200 mL) and 2 M Na_2CO_3 (200 mL) at room temperature. A solution of **1** (5.5 g, 30 mmol) in absolute ethanol (100 mL) was added under dry nitrogen. The resulting mixture was heated under reflux overnight. The solution was cooled to room temperature, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic extract was washed with brine (100 mL) and dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was recrystallized from ethanol to give a white solid: yield 5.5 g (78%); mp, 90−92 °C. ^1H NMR ($CDCl_3$): δ [ppm] = 3.75 (s, 3H), 3.84 (s, 3H), 6.51−6.57 (m, 2H), and 7.15 (d, 1H, J = 3.0 Hz).

2,2′,4,4′-Tetrahydroxybiphenyl (4). A solution of **3** (5.4 g, 20 mmol) in anhydrous CH_2Cl_2 (100 mL) was cooled to 0 °C in an ice bath. Boron tribromide (89 mL, 1.0 M in CH_2Cl_2, 89 mmol) was added in a dropwise manner under dry nitrogen. The resulting solution was allowed to warm to room temperature with stirring for 24 h. The resulting mixture was cooled in an ice bath, and 10% NaOH (50 mL) was added slowly. The mixture was allowed to stir for 3 h. Concentrated HCl(aq) was added in a dropwise manner until the solution became acidic. The mixture was then extracted with ethyl acetate (3 × 150 mL). The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by filtration through a short column of silica gel with ethyl acetate as eluent to give a white solid: yield, 3.9 g (90%); mp, 222−224 °C. ^1H NMR (acetone-d_6): δ [ppm] = 2.91 (sbr, 4H), 6.43−6.49 (m, 4H), and 7.03 (d, 2H, J = 8.4 Hz).

2,2′-Cyclohexylidenedioxy-4,4′-dihydroxybiphenyl (5). Compound **4** (6.7 g, 31 mmol) was suspended in anhydrous diethyl ether (85 mL) and was cooled to −20 °C. Cyclohexenyloxytrimethylsilane (10 mL, 51 mmol) was added followed by trimethylsilyl triflate (1.9 mL, 12 mmol). The resulting mixture was stirred at −20 °C under dry nitrogen for 2.5 h. The solution was then washed with 0.1 M $NaHCO_3$ (2 × 50 mL). The organic layer was separated and dried with anhydrous Na_2SO_4, and solvent was evaporated under reduced pressure. The residue was purified by column chromatography (eluent: ethyl acetate/hexane, 1/2): yield, 5.3 g (57%); mp, 155 °C dec. ^1H NMR ($CDCl_3$): δ [ppm] = 1.52−1.66 (m, 2H), 1.70−1.77 (m, 4H), 1.90−1.95 (m, 4H), 4.96 (sbr, 2H), 6.63 (d, 2H, J = 2.6 Hz), 6.71 (dd, 2H, J = 8.2, 2.6 Hz), and 7.28 (d, 2H, 8.2 Hz).

2,2′-Cyclohexylidenedioxy-4,4′-bis(4″-hexyloxybenzoyloxy)biphenyl (6). Compound **5** (4.0 g, 13 mmol) was dissolved in anhydrous 1,2-dimethoxyethane (DME) (20 mL), followed by the addition of DCC (5.8 g, 28 mmol). 4-Hexyloxybenzoic acid (6.2 g, 28 mmol) was added in small portions to the solution. DMAP (0.36 g, 3.0 mmol) was added, and the resulting mixture was stirred at room temperature overnight. The solvent was then evaporated under reduced pressure. CH_2Cl_2 (50 mL) was added to the residue, and the resulting suspension was filtered. The residue was washed with several portions of CH_2Cl_2. The solvent in the filtrate was then evaporated under reduced pressure, and the residue was recrystallized from ethyl acetate to give white crystals: yield, 7.1 g (75%). Transition temperatures are listed in Table 1. ^1H NMR ($CDCl_3$): δ [ppm] = 0.91 (t, 6H, J = 6.7 Hz), 1.31−1.60 (m, 14H), 1.70−1.86 (m, 8H), 1.95−1.98 (m, 4H), 4.05 (t, 4H, J = 6.5 Hz), 6.98 (d, 4H, J = 8.8 Hz), 7.04 (d, 2H, J = 2.3 Hz), 7.16 (dd, 2H, J = 8.5, 2.3 Hz), 7.53 (d, 2H, 8.5 Hz), and 8.16 (d, 4H, J = 8.8 Hz). Calcd for $C_{44}H_{50}O_8$: C, 74.76; H 7.13. Found: C, 74.30; H, 7.17.

Table 2. Molecular Weights and Polydispersities Measured by GPC and TGA Data for Polymer 8a–f

polymer	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n	temp at 5% weight loss (°C)	temp at 10% weight loss (°C)
8a	6800	4900	1.38	354	377
8b	17200	9900	1.73	379	397
8c	17100	8700	1.96	377	394
8d	24300	12300	1.98	388	407
8e	21400	12500	1.71	376	404
8f	12400	6500	1.90	363	399

2,2′-Dihydroxy-4,4′-bis(4″-hexyloxybenzoyloxy)biphenyl (7). Compound **6** was heated under reflux in a solution of concentrated HCl (19 mL), methanol (190 mL), and THF (150 mL) for 2 h. The resulting solution was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue was diluted with water (400 mL) and filtered. The residue was recrystallized from a mixture of ethanol and ethyl acetate to give white crystals: yield: 4.7 g (75%). Transition temperatures are listed in Table 1. ^{1}H NMR (CDCl$_3$): δ [ppm] = 0.91 (t, 6H, 6.7 Hz), 1.30–1.51 (m, 12H), 1.75–1.85 (m, 4H), 4.04 (t, 4H, J = 6.5 Hz), 6.65 (sbr, 2H), 6.85–6.89 (m, 4H), 6.97 (d, 4H, J = 8.9 Hz), 7.24–7.29 (m, 2H), and 8.15 (d, 4H, J = 8.9 Hz). Calcd for $C_{38}H_{42}O_8$: C, 72.82; H, 6.75. Found: C, 72.52; H, 6.83.

Polymerization of Monomer 7 with Alkanedioyl Chloride (8e). As an example, the polymerization of **7** with sebacoyl chloride is described below: Compound **7** and sebacoyl chloride (0.34 mL, 1.6 mmol) were mixed in anhydrous CH_2Cl_2 (10 mL). Triethylamine (0.46 mL, 3.5 mmol) was added in a dropwise manner to the mixture, and the resulting mixture was stirred at room temperature for 3 days. The polymer was then precipitated from methanol (200 mL). The precipitate obtained was redissolved in small amount of ethyl acetate and reprecipitated three times from methanol to yield 0.75 g (59%) of **8e**. Transition temperatures are listed in Table 1. ^{1}H NMR (CDCl$_3$): δ [ppm] = 0.90 (t, 6H, J = 6.4 Hz), 1.18–1.57 (m, 24H), 1.76–1.83 (m, 4H), 2.26 (t, 4H, J = 6.9 Hz), 3.99 (t, 4H, J = 6.4 Hz), 6.94 (d, 4H, J = 8.8 Hz), 7.08 (d, 2H, J = 2.2 Hz), 7.14 (dd, 2H, J = 8.3, 2.2 Hz), 7.30 (d, 2H, J = 8.3 Hz), and 8.10 (d, 4H, J = 8.8 Hz).

Results

Intermediate **6**, monomer **7**, and polymers **8a**–**f** are all nematogenic as revealed by investigation with polarization microscopy. No zigzag lines or other anomalies that have been described for biaxial nematics could be observed. The phase transition behaviors studied by DSC and the relative molecular weights measured by GPC for polymers **8a**–**f** are summarized in Table 1. The transition enthalpies of ~3.6–4.7 J/g also point to the nematic phase. The TGA results of the polymers are summarized in Table 2. The DSC traces of polymers **8a**–**f** are shown in Figure 1. Typical nematic droplets were observed for polymers **8a**–**f** at the clearing points under the polarizing microscope (Figure 2a), which on further cooling were fused to form the marbled texture. The Schlieren texture was obtained only with a very thin sample (Figure 2b). The exhibition of nematic phase in polymers **8b**–**e** has been verified by X-ray diffraction. In addition, it was found that the small-angle X-ray reflections for **8b** and **8e** split into four diffuse lobes for the magnetically aligned samples (Figure 3). The results indicate the existence of biaxial fluctuation in the nematic phase for these two homologues, in which short-range smectic C-like arrangement of mesogens is present in the nematic phase. Clear indication of biaxiality in the other homologues of the series was not observed because of the difficulties encountered in aligning the samples. For **8a**, only an isotropic pattern was observed, and crystallization during annealing of sample for **8f** precluded the verification of nematic phase by X-ray diffraction in this sample.

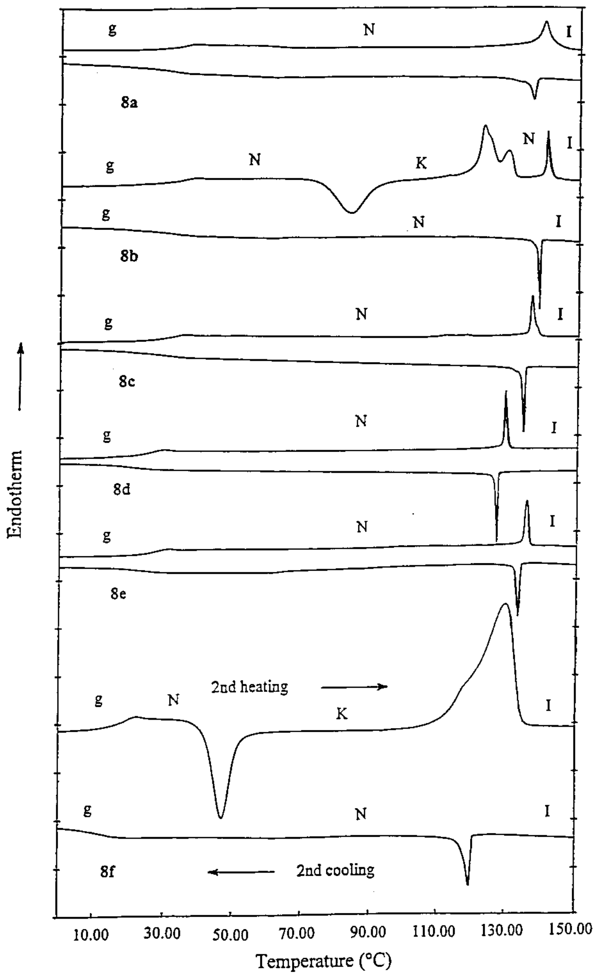

Figure 1. DSC traces (second heating and cooling) of polymers **8a**–**f**.

Discussion

Despite the apparent bulkiness of the lateral cyclohexylidene ketal, intermediate **6** exhibits an enantiotropic nematic phase. The perturbation imparted by the lateral substituent in **6** is compensated by the extended four-ring rigid mesogenic core. Monomer **7** also exhibits a nematic phase on heating from the crystalline state. However, at higher temperature (>181 °C), the mesophase gradually disappeared when investigated under polarizing microscope. This transition could not be detected by DSC. This observation is probably a result of transesterification, in which some of the 4″-hexyloxybenzoyloxy groups transesterified from the 4 and/or 4′ position of the biphenyl moiety to the 2 and/or 2′ position. This results in some molecules with a bent rigid core, and the liquid crystalline properties vanish because of the great perturbation induced by the presence of these bent shaped molecules.

The liquid crystalline polymers **8a**–**f** with n = 4, 5, 6, 7, and 8, respectively, exhibit enantiotropic nematic phases, but the liquid crystalline polymer with n = 10 exhibits monotropic nematic phase. This behavior is similar to other main-chain LCP with bilaterally linked mesogens reported by Krone and Ringsdorf.[2] The

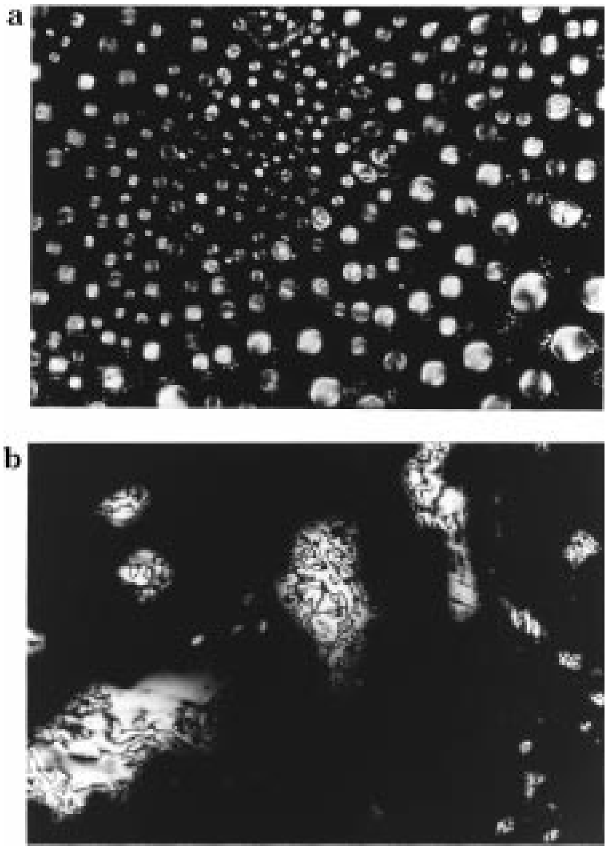

Figure 2. Microphotographs of polymer **8e**: (a) nematic droplets at the clearing point; (b) Schlieren texture at 130 °C.

exhibition of solely nematic phase in this series of LCP is due to the destabilization of smectic layers by the two lateral flexible spacers on the mesogen. In general, the differences among the clearing temperatures (T_{NI}) of different homologues in the series are small. However, with the exception of some anomalies, T_{NI} increases with the decrease in the length of the lateral spacer. This trend can be explained by the increasing perturbation imposed on the molecular packing as the length of the lateral chain increases. For the homologue with $n = 10$, the perturbation is probably too large and results in monotropic behavior. However, it has to be noted that a direct comparison of the transition temperatures should be taken with caution as they might be influenced by the molecular weight of the polymer obtained at the present range of molecular weight.[13] The low glass transition temperatures (T_g) of this series of polymer can be a result of their low molecular weight; however, the fact that the long terminal chains on the mesogens can also act as plasticizers to reduce T_g should not be ignored.

The degradation temperatures of the polymers in the series are very similar, with that for **8a** being slightly lower than those of the other homologues. The lower thermal stability of **8a** is probably due to the lower molecular weight of **8a** with respect to the others.

X-ray diffraction experiments revealed the presence of biaxial fluctuation in the nematic phase in two homologues (**8b** and **8e**) of the series. Upon cooling of these two polymer samples from the isotropic phase to the nematic phase in the presence of a magnetic field, the wide-angle scattering ring split into two diffuse crescents, as would be observed for an oriented nematic phase. However, the small angle reflection split into four symmetrically arranged spots, resembling the observations in some low molecular weight liquid crystals.[14-16] This type of pattern has not been reported before for bilaterally linked mesogens in main-chain polymers.[2] As previously mentioned, this pattern corresponds to the presence of smectic C-like biaxial fluctuation in the nematic phase. A similar X-ray diffraction pattern has been reported for cross-shaped mesogens in main-chain polymer,[17] although no explanation for the origin of the phenomenon was provided. It is well known that flexible lateral aliphatic chain tend to orient along the long molecular axis of the mesogenic core in the liquid crystalline phase.[18-20] In the present case, this orientation may result in a tilted arrangement of the mesogens on the macromolecules with respect to the nematic director, as depicted schematically in Figure

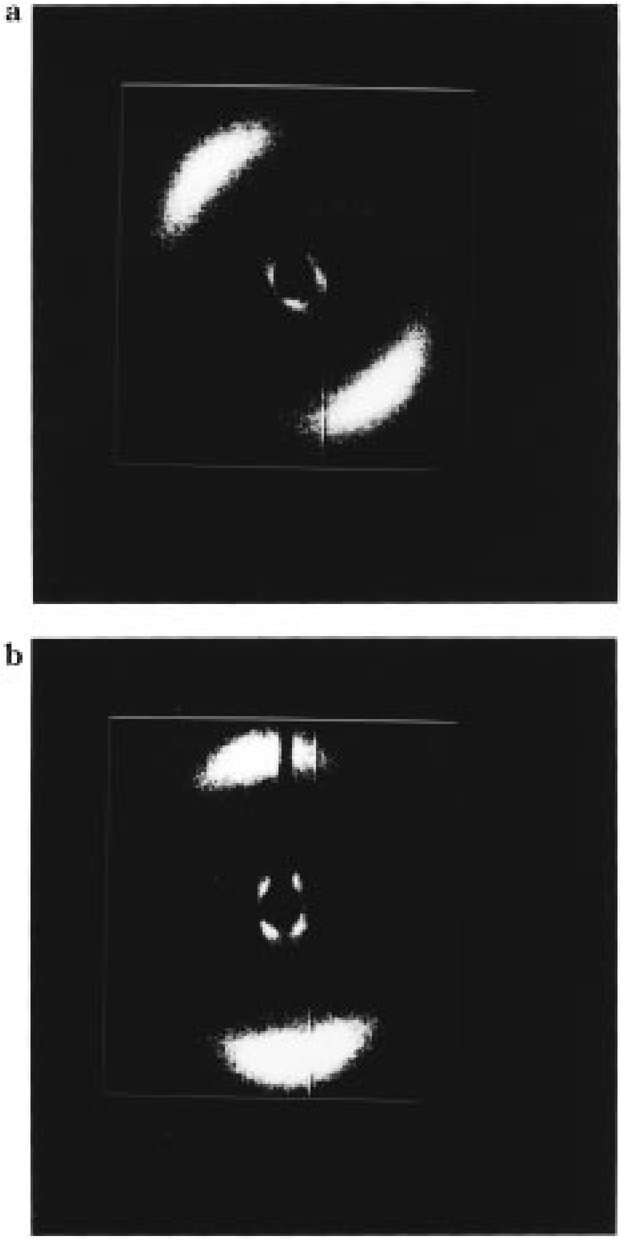

Figure 3. X-ray diffraction pattern of **8b** in (a) nematic phase at 135 °C (one reflection spot was blocked by the beamstopper) and (b) nematic phase at 80 °C, in the presence of a magnetic field. The estimated average tilt angle from the X-ray diffraction pattern for the biaxial fluctuation was 35°.

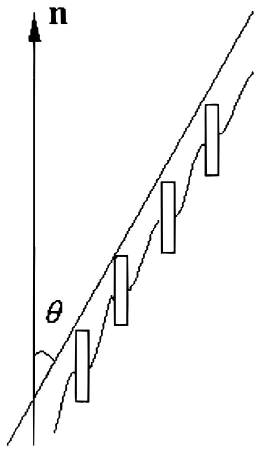

Figure 4. Schematic representation for the possible arrangement of mesogens exhibiting biaxial fluctuation in the nematic phase (*n*: nematic director; *θ*: tilt angle for the biaxial fluctuation).

4, and thus may explain the existence of this smectic C-like biaxial fluctuation.

Conoscopic investigation of the polymers has not been accomplished because of the difficulties encountered in obtaining a good homeotropic orientation.

Conclusions

A new series of main-chain PLCs with bilaterally linked mesogens has been synthesized. Although the existence of a biaxial nematic phase in these polymers could not be confirmed, the evidence for the existence of biaxial fluctuation in the nematic phase has been established in two homologues of the series.

Acknowledgment. The authors thank Professor A. C. Griffin at the University of Southern Mississippi for stimulating discussions and suggestions. Financial support by NSF ALCOM Center (Grant No. DMR 89-20147) is gratefully acknowledged.

References and Notes

(1) Berg, S.; Krone, V.; Ringsdorf, H.; Ebert, M.; Hirschmann, H.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 381.
(2) Krone, V.; Ringsdorf, H. *Liq. Cryst.* **1991**, *9*, 165.
(3) Noh, H.-G.; Shim, H. K.; Chang, J. H.; Jin, J. I. *Macromolecules* **1997**, *30*, 1521.
(4) Hessel, F.; Finkelmann, H. *Polym. Bull.* **1986**, *15*, 349.
(5) Hessel, F.; Herr, R.-P.; Finkelmann, H. *Makromol. Chem.* **1987**, *188*, 1597.
(6) Keller, P. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 171.
(7) Ebert, M.; Herrmann-Schönherr, O.; Wendorff, J. H.; Ringsdorf, H.; Tschirner, P. *Liq. Cryst.* **1990**, *7*, 63.
(8) Harkness, B. R.; Watanabe, J. *Macromolecules* **1991**, *24*, 6759.
(9) Miyaura, N.; Yanagi, T.; Suzucki, A. *Synth. Commun.* **1981**, *11*, 513.
(10) Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.
(11) Harada, T.; Ueda, S.; Yoshida, T.; Inoue, A.; Takeuchi, M.; Ogawa, N.; Oku, A. *J. Org. Chem.* **1994**, *59*, 7575.
(12) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475.
(13) Krone, V.; Ringsdorf, H. *Liq. Cryst.* **1991**, *9*, 207.
(14) De Vries, A. *Mol. Cryst. Liq. Cryst.* **1970**, *10*, 219.
(15) Azároff, L. V.; Schuman, C. A. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 309.
(16) Soto Bustamante, E. A.; Hasse, W. *Liq. Cryst.* **1997**, *23*, 603.
(17) Krone, V.; Ringsdorf, H. *Liq. Cryst.* **1991**, *9*, 195.
(18) Weissflog, W.; Demus, D. *Cryst. Res. Technol.* **1983**, *18*, K21.
(19) Weissflog, W.; Demus, D. *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *129*, 235.
(20) Berdaguè, P.; Perez, F.; Bayle, J. P.; Ho, M.-S.; Fung, B. M. *New J. Chem.* **1995**, *19*, 383.

MA971772R