Synthesis of Liquid Crystalline Polymers with a Polyoxetane Main Chain

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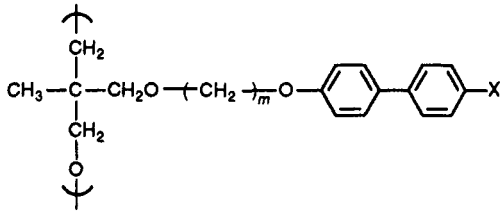
Received November 8, 1990; Revised Manuscript Received March 6, 1991

ABSTRACT: Oxetanes with different mesogenic and spacer groups were synthesized. Some of the polymers obtained by cationic polymerization with $BF_3 \cdot OEt_2$ as an initiator showed a smectic liquid crystalline phase. Not only cyano-substituted biphenyl but also fluorine-substituted biphenyl were found to be a good mesogenic group in these liquid crystalline polymers. Synthesis and polymerization of the monomers and thermal behavior of the polymers are reported.

Introduction

Much attention has been paid recently to liquid crystalline polymers, especially those with side chains, because of their potential application for electronic devices. Polysiloxanes, polyacrylates, and polymethacrylates are usually used as main-chain components of such liquid crystalline polymers.[1] There are only a few examples in which other main-chain structures like polyolefine, poly(vinyl ether), polyphosphazene, or polyisocyanate are used.[2-13] We have been interested in the effects of the structure of main chain, the length and the structure of the spacers, and the structure of mesogenic group on the liquid crystalline phase exhibited.[14] Meanwhile, studies to increase the types of main chains are also important.

In this article, we would like to report the first example of liquid crystalline polymers that have a polyoxetane main chain and a fluorine-substituted biphenyl mesogenic group.



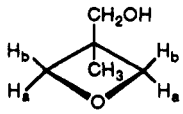
polyOX-*n*-*m*: X = $O(CH_2)_nH$
polyOX-CN-*m*: X = CN
polyOX-F-*m*: X = F

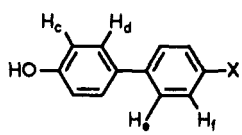
Experimental Section

Synthetic Route to Monomers. The synthesis of the monomers is outlined in Scheme I.

The names of the monomers are abbreviated as OX-*n*-*m*, OX-CN-*m*, or OX-F-*m* in the case of having alkoxy-, cyano-, or fluoro-substituted biphenyl mesogens, respectively, where *n* indicates the number of carbon atoms in the alkoxy group and *m* the number of carbon atoms of the methylene groups in the spacer.

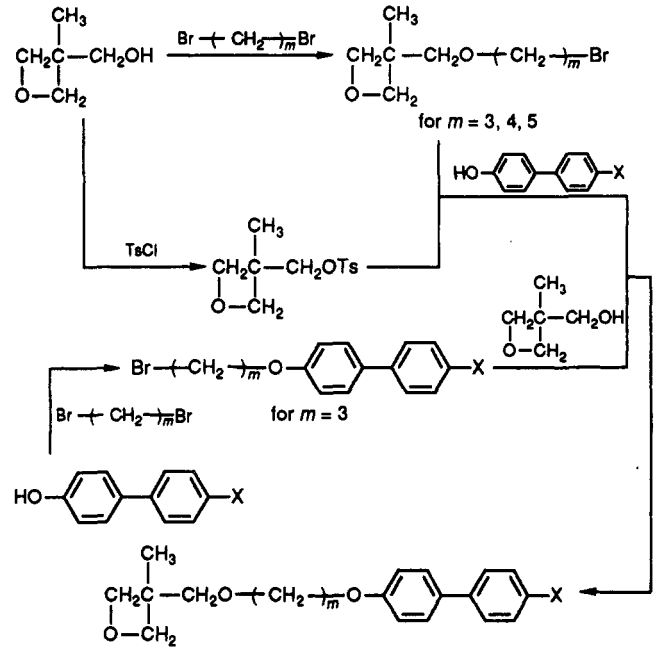
Analysis. ^1H and ^{13}C NMR spectra were obtained on a Varian 200-MHz ^1H NMR (50 MHz for ^{13}C) spectrometer, Model Gemini 200. Chemical shifts (δ) are given in parts per million from tetramethylsilane as an internal standard. Protons of oxetane and biphenyl rings are designated as indicated below.





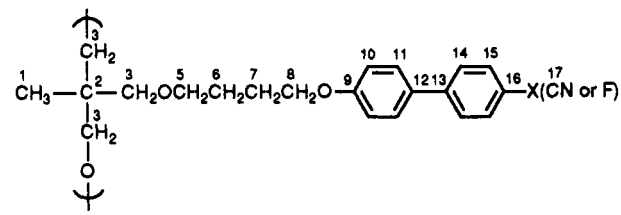
X = OR, CN, F

Scheme I
Synthesis of Monomers



monomer
OX-*n*-*m*: X = $O(CH_2)_nH$
OX-CN-*m*: X = CN
OX-F-*m*: X = F

The assignment of the carbon signals of polymers was made based on DEPT (distortionless enhancement by polarization transfer) spectra. The numbers of the carbon atoms are indicated below.



GPC analysis was carried out on a Tosoh (TSK) GPC Model HLC 802 equipped with TSK gel G3000H (exclusion molecular weight, polystyrene 6×10^4) and G5000H (exclusion molecular weight, polystyrene 4×10^6), using chloroform as eluent at the flow rate of 1 mL/min.

DSC analyses of monomers and polymers were carried out on a SEIKO thermal analysis system Model SSC 5500 equipped with DSC 100 with the heating rate of 3 °C/min. The transition

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temperature is given at the point where transition starts. For the samples that have multiple transitions, peak temperatures are given. The temperature was calibrated by the use of indium and tin metals as the standard (156.6 °C for indium and 231.9 °C for tin).

Optical polarization micrographs were taken on a Nikon optical polarization micrograph Model OPTIPHOTO-POL equipped with Mettler thermal analysis system Model FP800 with FP82 hot stage with FP 80 controller. In observing the texture of the samples, they were slowly cooled from isotropic state to a little lower temperature than the peak temperature and annealed at the constant temperature. Pictures were taken at appropriate intervals.

Synthesis of Monomers. Column chromatography was carried out on silica gel.

4-Cyano- or 4-Fluoro-4′-hydroxybiphenyl. Commercial 4-cyano-4′-hydroxybiphenyl (mp 192.4 °C) and 4-fluoro-4′-hydroxypbiphenyl (mp 168.8 °C) were purified by recrystallization.

4-Alkoxy-4′-hydroxybiphenyls were synthesized by alkylating 4,4′-dihydroxybiphenyl with dialkyl sulfate.

4-Methoxy-4′-hydroxybiphenyl. 4,4′-Dihydroxybiphenyl (74.48 g, 0.40 mol) was dissolved into 10% aqueous sodium hydroxide solution (400 mL) under cooling. To this solution, dimethyl sulfate (50.45 g, 0.40 mol) was added dropwise during 3 h at 0 °C. Formed solid was separated by suction and heated with 10% sodium hydroxide solution (500 mL). Finally, the mixture was boiled for a short period of time. Formed solid upon cooling was collected by filtration and again dissolved in boiling water (2000 mL). The solution was filtered while hot, and the filtrate was acidified with 20% hydrochloric acid at 70 °C. Formed solid on cooling was collected and purified by repeated recrystallization from ethanol: mp 183 °C, yield 56.4%. Chemical shifts: 3.82 (s, 3 H, CH_3), 6.86 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 6.93 (d with fine coupling, 2 H, J = 8.8 Hz, H_f), 7.40 (d with fine coupling 2 H, J = 8.8 Hz, H_d), 7.45 (d with fine coupling, 2 H, J = 8.8 Hz, H_e).

4-Ethoxy-4′-hydroxybiphenyl: mp 166 °C, yield 66.8%. Chemical shifts: 1.41 (t, 3 H, J = 6.9 Hz, CH_3), 4.05 (q, 2 H, J = 6.9 Hz, CH_3CH_2).

4-Propoxy-4′-hydroxybiphenyl: mp 134 °C, yield 21.4%. Chemical shifts: 1.02 (t, 3 H, J = 7.6 Hz, CH_3), 1.80 (m, 2 H, J = 7.2 Hz, CH_3CH_2), 3.93 (t, 2 H, J = 7.2 Hz, $CH_3CH_2CH_2$).

4-Butoxy-4′-hydroxybiphenyl: mp 168 °C, yield 45.8%. Chemical shifts: 0.96 (t, 3 H, J = 7.4 Hz, CH_3), 1.49 (m, 2 H, J = 7.2 Hz, CH_3CH_2), 1.77 (m, 2 H, J = 7.2 Hz, $CH_3CH_2CH_2$), 3.97 (t, 2 H, J = 7.2 Hz, $CH_3CH_2CH_2CH_2$).

Other protons of these compounds appeared at the corresponding positions with 4-methoxy-4′-hydroxybiphenyl.

3-(Hydroxymethyl)-3-methyloxetane was synthesized from 2-(hydroxymethyl)-2-methyl-1,3-propanediol,[15] yield 67.1%.

3-(Hydroxymethyl)-3-methyloxetane was tosylated with tosyl chloride or alkylated with α,ω-dibromoalkane.

3-[(Tosyloxy)methyl]-3-methyloxetane. To the aqueous solution (16 mL of water) of 3-(hydroxymethyl)-3-methyloxetane (1.82 g, 17.8 mmol) and sodium hydroxide (4.0 g, 0.10 mol) was added dropwise tosyl chloride (4.75 g, 24.9 mmol) in tetrahydrofuran (THF, 16 mL), and the mixture reacted for 2 h at room temperature. After THF was removed under reduced pressure, the product was isolated by extraction with ether three times (50 mL). The crude product was purified by column chromatography (eluent hexane:ether = 1:4, R_f = 0.6 for ether): mp 56.9 °C, yield 84%. Chemical shifts: 1.28 (s, 3 H, CH_3), 2.44 (s, 3 H, $C_6H_4CH_3$), 4.09 (s, 2 H, OCH_2), 4.31 (d, 1 H, J = 1.2 Hz, H_a), 4.35 (d, 1 H, J = 1, 2 Hz, H_b), 7.35, 7.79 (two d, J = 8.6 Hz, aromatic protons).

3-[(4-Bromobutoxy)methyl]-3-methyloxetane (m = 4). A two-phase system composed of dibromobutane (10.04 g, 46.5 mmol) in hexane (15 mL) and 3-(hydroxymethyl)-3-methyloxetane (1.55 g, 15.2 mmol), sodium hydroxide (10.0 g, 0.25 mol), and tetrabutylammonium bromide in water (20 mL) was stirred over night at room temperature and heated to reflux under stirring for 0.5 h. After the reaction system was cooled to room temperature, water (30 mL) was added, and the organic layer was extracted three times with hexane (30 mL each). Product was isolated by evaporating the solvent after drying the solution with magnesium sulfate. The crude product was purified by distillation: bp 66–70 °C (0.22 mmHg), yield 80.2%. Chemical shifts: 1.28 (s, 3 H, CH_3), 1.71, 1.94 (m, quint, 2 H each, $CH_2CH_2CH_2CH_2$), 3.43 (t, 2 H, J = 6.6 Hz, CH_2Br), 3.45 (s, 2 H, $C(CH_3)CH_2$), 3.48 (t, 2 H, J = 6.6 Hz, $CH_2OCH_2CH_2$), 4.33 (d, 2 H, J = 5.8 Hz, H_a), 4.48 (d, 2 H, J = 5.8 Hz, H_b).

3-[(3-Bromopropoxy)methyl]-3-methyloxetane (m = 3): bp 90–100 °C (0.8 mmHg), yield 44.3%. Chemical shifts: 2.09 (quintet, 2 H, J = 5.8 Hz, $CH_2CH_2CH_2$), 3.47 (s, 2 H, $C(CH_3)CH_2$) 3.43–3.55 (m, 4 H, $BrCH_2$, $CH_2OCH_2CH_2$).

3-[[(5-Bromopentyl)oxy]methyl]-3-methyloxetane (m = 5): bp 80–85 °C (0.15 mmHg), yield 73.2%. Chemical shifts: 1.56, 1.88 (m, 4 H; quint, 2 H; $CH_2CH_2CH_2CH_2CH_2$), 3.40 (t, 2 H, J = 6.6 Hz, CH_2Br), 3.45 (s, 2 H, $C(CH_3)CH_2$), 3.45 (t, 2 H, J = 6.6 Hz, $CH_2OCH_2CH_2$).

Methyl, H_a, and H_b protons of the oxetane ring of these compounds appeared at the corresponding positions with 3-[(4-bromobutoxy)methyl]-3-methyloxetane.

Monomers with three methylene spacers were synthesized by first attaching the spacer to the mesogenic group in order to make the product separation easy.

4-Cyano-4′-(3-bromopropoxy)biphenyl. 4-Cyano-4′-hydroxybiphenyl (1.35 g, 0.90 mmol) was converted into its sodium salt by reaction with sodium hydride in dimethylformamide (DMF) (20 mL). This solution was added dropwise into 1,3-dibromopropane (10.63 g, 52.6 mmol) in DMF (7 mL) at room temperature during 10 min and further reacted for 16 h at room temperature with stirring. After solvent and excess dibromopropane were removed under vacuum, chloroform (60 mL) and water (10 mL) were added to the residual solid, and the organic layer was separated. The chloroform layer was washed with water (100 mL) and dried over magnesium sulfate. Evaporation of the solvent gave crude product. The crude product was recrystallized from ethanol (10 mL): mp 100.1 °C, yield 67.3%. Chemical shifts: 2.33 (quintet, 2 H, J = 6.4 Hz, $CH_2CH_2CH_2$), 3.61 (t, 2 H, J = 6.4 Hz, $BrCH_2$), 4.15 (t, 2 H, J = 6.4 Hz, OCH_2), 6.99 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.50 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.61, 7.68 (two d with fine coupling, 4 H, J = 7.8 Hz, H_e, H_f).

4-Methoxy-4′-(3-bromopropoxy)biphenyl: mp 103.0 °C, yield 66.0%. Chemical shifts: 2.32 (quintet, 2 H, J = 6.4 Hz, $CH_2CH_2CH_2$), 3.61 (t, 2 H, J = 6.4 Hz, $BrCH_2$), 3.82 (s, 3 H, CH_3), 4.12 (t, 2 H, J = 6.4 Hz, OCH_2), 6.94, 6.95 (two d with fine coupling, 4 H, J = 8.8 Hz, H_c, H_f), 7.45, 7.46 (two d with fine coupling, 4 H, J = 8.8 Hz, H_d, H_e).

4-Ethoxy-4′-(3-bromopropoxy)biphenyl: mp 118.6 °C, yield 61.0%. Chemical shifts: 1.41 (t, 3 H, J = 7.0 Hz, CH_3CH_2), 4.05 (q, 2 H, J = 7.0 Hz, CH_3CH_2).

4-Propoxy-4′-(3-bromopropoxy)biphenyl: mp 129.7 °C, yield 33.8%. Chemical shifts: 1.03 (t, 3 H, J = 7.4 Hz, CH_3CH_2), 1.81 (sextet, 2 H, J_1 = 7.4 Hz, J_2 = 6.6 Hz, CH_3CH_2), 3.94 (t, 2 H, J = 6.6 Hz, $CH_3CH_2CH_2$).

4-Butoxy-4′-(3-bromopropoxy)biphenyl: mp 125.6 °C, yield 45.3%. Chemical shifts: 0.96 (t, 3 H, J = 7.4 Hz, CH_3CH_2), 1.48 (m, 2 H, CH_3CH_2), 1.77 (m, 2 H, $CH_3CH_2CH_2$), 3.97 (t, 2 H, J = 6.6 Hz, $CH_3CH_2CH_2CH_2$).

Other protons of these compounds appeared at the corresponding positions with 4-methoxy-4′-(3-bromopropoxy)biphenyl.

4-Fluoro-4′-(3-bromopropoxy)biphenyl. The product was separated and purified by column chromatography (eluent, chloroform; R_f = 0.67): liquid, yield 73%. Chemical shifts: 2.32 (quintet, 2 H, J = 6.0 Hz, $CH_2CH_2CH_2$), 3.61 (t, 2 H, J = 6.0 Hz, $BrCH_2$), 4.13 (t, 2 H, J = 6.0 Hz, OCH_2), 6.95 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.08 (t with fine coupling, J = 8.8 Hz, H_f), 7.45 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.47 (q with fine coupling, 2 H, J_1 = 8.8 Hz, J_2 = 5.4 Hz, H_e).

The tosylate or bromides were converted into monomers by the formation of ether linkage.

3-[[(4-Cyanobiphenyl-4′-yl)oxy]methyl]-3-methyloxetane (OX-CN-0). 3-[(Tosyloxy)methyl]-3-methyloxetane (1.37

g, 5.33 mmol) in dimethyl sulfoxide (DMSO) (10 mL) was added dropwise into the solution of 4-hydroxy-4′-cyanobiphenyl (0.95 g, 4.87 mmol) and potassium *tert*-butoxide (0.83 g, 7.40 mmol) in DMSO (30 mL) during 10 min. The reaction mixture was stirred for 24 h at room temperature. After 1 day, the solvent was removed under reduced pressure and the remaining crude product was resolved in chloroform (50 mL). The reaction system was neutralized with dilute hydrochloric acid and extracted three times with chloroform (30 mL each). The combined organic layer was washed with water (20 mL) and dried over magnesium sulfate. Product was isolated by column chromatography (eluent ether: hexane = 1:1; R_f = 0.2) after the removal of the solvent. Chemical shifts: 1.44 (s, 3 H, CH_3), 4.06 (s, 2 H, $C(CH_3)CH_2$), 4.46 (d, 2 H, J = 5.8 Hz, H_a), 4.62 (d, 2 H, J = 5.8 Hz, H_b), 7.02 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.53 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.62, 7.69 (two d with fine coupling, 4 H, J = 7.8 Hz, H_e, H_f).

3-[[(4-Fluorobiphenyl-4′-yl)oxy]methyl]-3-methyloxetane (OX-F-0). The product was separated and purified by column chromatography (eluent hexane:ether:chloroform = 2:1:1; R_f = 0.18). Chemical shifts: 6.98 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.08 (t with fine coupling, 2 H, J = 8.8 Hz, H_f), 7.46 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.48 (q with fine coupling, 2 H, J_1 = 8.8 Hz, J_2 = 5.4 Hz, H_e). Other protons of this monomer appeared at the corresponding positions with OX-CN-0.

Monomers with three methylene spacer were synthesized through the formation of ether linkage between 3-(hydroxymethyl)-3-methyloxetane and 4-substituted-4′-(3-bromopropoxy)-biphenyl.

3-{[3-[(4-Methoxybiphenyl-4′-yl)oxy]propoxy]methyl}-3-methyloxetane (OX-1-3). To an aqueous solution of 50% sodium hydroxide (1.2 g, 15 mmol) and tetrabutylammonium bromide (0.014.5 g, 0.045 mmol), were added 4-methoxy-4′-(3-bromopropoxy)biphenyl (0.30 g, 0.93 mmol) and 3-(hydroxymethyl)-3-methyloxetane (0.97 g, 9.57 mmol) dropwise as a THF (3 mL) solution during 10 min. The reaction system was allowed to react for a further 2 h under the refluxing condition of the system. After 2 h, the reaction system was cooled to room temperature. After the removal of THF, the water layer was extracted three times with chloroform (40 mL each), and the combined organic solution was washed with 5% hydrochloric acid (30 mL) followed by water (30 mL). The product was isolated by column chromatography (eluent hexane:ether:chloroform = 2:1:1; R_f = 0.2) after drying and evaporating the solvent. Chemical shifts: 1.28 (s, 3 H, CH_3), 2.06 (quintet, 2 H, J = 6.2 Hz, $CH_2CH_2CH_2$), 3.49 (s, 2 H, $C(CH_3)CH_2$), 3.65 (t, 2 H, J = 6.0 Hz, $CH_2OCH_2CH_2$), 3.82 (s, 3 H, OCH_3), 4.08 (t, 2 H, J = 6.0 Hz, OCH_2), 4.33 (d, 2 H, J = 5.8 Hz, H_a), 4.50 (d, 2 H, J = 5.8 Hz, H_b), 6.94 (overlapped d with fine coupling, 4 H, J = 8.8 Hz, H_c, H_f), 7.44, 7.46 (two d with fine coupling, 2 H, J = 8.8 Hz, H_d, H_e).

3-{[3-[(4-Ethoxybiphenyl-4′-yl)oxy]propoxy]methyl}-3-methyloxetane (OX-2-3). Chemical shifts: 1.41 (t, 3 H, J = 6.9 Hz, CH_3CH_2), 4.05 (q, 2 H, J = 6.9 Hz, CH_3CH_2).

3-{[3-[(4-Propoxybiphenyl-4′-yl)oxy]propoxy]methyl}-3-methyloxetane (OX-3-3). Chemical shifts: 1.03 (t, 3 H, J = 6.9 Hz, CH_3CH_2), 1.80 (sextet, 2 H, J_1 = 6.6 Hz, J_2 = 7.4 Hz, CH_3CH_2), 3.93 (t, 2 H, J = 6.9 Hz, $CH_3CH_2CH_2$).

3-{[3-[(4-Butoxybiphenyl-4′-yl)oxy]propoxy]methyl}-3-methyloxetane (OX-4-3). Chemical shifts: 0.96 (t, 3 H, J = 6.9 Hz, CH_3CH_2), 1.48 (m, 2 H, CH_3CH_2), 1.77 (m, 2 H, $CH_3CH_2CH_2$), 3.97 (t, 2 H, J = 6.9 Hz, $CH_3CH_2CH_2CH_2$).

Other protons of these monomers appeared at the corresponding positions with OX-1-3.

3-{[3-[(4-Cyanobiphenyl-4′-yl)oxy]propoxy]methyl}-3-methyloxetane (OX-CN-3). R_f = 0.18; eluent hexane:ether: chloroform = 2:1:1. Chemical shifts: 1.28 (s, 3 H, CH_3), 2.08 (quintet, 2 H, J = 6.0 Hz, $CH_2CH_2CH_2$), 3.48 (s, 2 H, $C(CH_3)CH_2$), 3.65 (t, 2 H, J = 6.0 Hz, $CH_2OCH_2CH_2$), 4.11 (t, 2 H, J = 6.0 Hz, OCH_2), 4.33 (d, 2 H, J = 5.8 Hz, H_a), 4.50 (d, 2 H, J = 5.8 Hz, H_b), 6.98 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.51 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.61, 7.68 (two d with fine coupling, 4 H, J = 7.8 Hz, H_e, H_f).

3-{[3-[(4-Fluorobiphenyl-4′-yl)oxy]propoxy]methyl}-3-methyloxetane (OX-F-3). R_f = 0.18; eluent hexane:ether: chloroform = 2:1:1). Chemical shifts: 4.09 (t, 2 H, J = 6.0 Hz, OCH_2), 6.94 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.08 (t with fine coupling, 2 H, J = 8.8 Hz, H_f), 7.44 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.47 (q with fine coupling, 2 H, J_1 = 8.8 Hz, J_2 = 5.4 Hz, H_e). Other protons of this monomer appeared at the corresponding positions with OX-CN-3.

Monomers with four and five methylene spacer were synthesized through the formation of an ether linkage between 3-[(4-bromobutoxy)methyl]-3-methyloxetane or 3-[[(5-bromopentyl)-oxy]methyl]-3-methyloxetane and 4-substituted-4′-hydroxybiphenyl.

3-{[4-[(4-Methoxybiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane (OX-1-4). To sodium hydride (0.030 g, 1.2 mmol) dispersed in DMF (5 mL), was added 4-methoxy-4′-hydroxybiphenyl (0.20 g, 0.93 mmol) portionwise. The reaction system was stirred for 30 min at room temperature and for a further 10 min at 60 °C. To this solution, 3-[(4-bromobutoxy)-methyl]-3-methyloxetane (0.30 g, 1.3 mmol) in DMF (5 mL) was added dropwise during 10 min, and the reaction system was stirred for 3 h at room temperature. After 3 h, DMF was removed under vacuum, and chloroform (50 mL) and water (30 mL) were added to the residual solid. The chloroform layer was separated and washed with aqueous sodium carbonate (30 mL). The product was isolated by column chromatography after drying and evaporating the solvent (eluent hexane:ether:chloroform = 2:1:1; R_f = 0.3). Chemical shifts: 1.29 (s, 3 H, CH_3), 1.82 (m, 4 H, $CH_2CH_2CH_2CH_2$), 3.47 (s, 2 H, $C(CH_3)CH_2$), 3.54 (t, 2 H, J = 6.0 Hz, $CH_2OCH_2CH_2$), 3.82 (s, 3 H, OCH_3), 4.00 (t, 2 H, J = 6.0 Hz, OCH_2), 4.34 (d, 2 H, J = 5.8 Hz, H_a), 4.50 (d, 2 H, J = 5.8 Hz, H_b), 6.92, 6.93 (two d with fine coupling, 4 H, J = 8.8 Hz, H_c, H_f), 7.44, 7.46 (two d with fine coupling, 2 H, J = 8.8 Hz, H_d, H_e).

3-{[4-[(4-Ethoxybiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane (OX-2-4). Chemical shifts: 1.41 (t, 3 H, J = 6.9 Hz, CH_3CH_2), 4.05 (q, 2 H, J = 6.0 Hz, CH_3CH_2).

3-{[4-[(4-Propoxybiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane (OX-3-4). Chemical shifts: 1.03 (t, 3 H, J = 6.9 Hz, CH_3CH_2), 1.82 (m, 6 H, CH_3CH_2, $CH_2CH_2CH_2CH_2$), 3.93 (t, 2 H, J = 6.9 Hz, $CH_3CH_2CH_2$).

3-{[4-[(4-Butoxybiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane (OX-4-4). Chemical shifts: 0.96 (t, 3 H, J = 7.2 Hz, CH_3CH_2), 1.48 (sextet, 2 H, J = 7.2 Hz, CH_3CH_2), 1.78 (m, 6 H, $CH_3CH_2CH_2$, $CH_2CH_2CH_2CH_2$), 3.97 (t, 2 H, J = 6.9 Hz, $CH_3CH_2CH_2CH_2$), 4.00 (t, 2 H, J = 6.0 Hz, OCH_2).

Other protons of these monomers appeared at the corresponding position with OX-1-4.

3-{[4-[(4-Cyanobiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane (OX-CN-4). R_f = 0.18; eluent hexane:ether: chloroform = 2:1:1). Chemical shifts: 1.29 (s, 3 H, CH_3), 1.80 (m, 4 H, $CH_2CH_2CH_2CH_2$), 3.47 (s, 2 H, $C(CH_3)CH_2$), 3.54 (t, 2 H, J = 6.0 Hz, $CH_2OCH_2CH_2$), 4.03 (t, 2 H, J = 6.0 Hz, OCH_2), 4.34 (d, 2 H, J = 5.8 Hz, H_a), 4.50 (d, 2 H, J = 5.8 Hz, H_b), 6.97 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.51 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.61, 7.68 (two d with fine coupling, 4 H, J = 7.8 Hz, H_e, H_f).

3-{[4-[(4-Fluorobiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane (OX-F-4). R_f = 0.18; eluent hexane:ether: chloroform = 2:1:1). Chemical shifts: 6.93 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.07 (t with fine coupling, 2 H, J = 8.8 Hz, H_f), 7.44 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.47 (q with fine coupling, 2 H, J_1 = 8.8 Hz, J_2 = 5.4 Hz, H_e). Other protons of this monomer appeared at the corresponding positions with OX-CN-4.

3-{[[5-[(4-Cyanobiphenyl-4′-yl)oxy]pentyl]oxy]methyl}-3-methyloxetane (OX-CN-5). Chemical shifts: 1.29 (s, 3 H, CH_3), 1.60, 1.82 (m, 4 H; quint, 2 H; $CH_2CH_2CH_2CH_2CH_2$), 3.46 (s, 2 H, $C(CH_3)CH_2$), 3.49 (t, 2 H, J = 6.0 Hz, $CH_2OCH_2CH_2$), 4.00 (t, 2 H, J = 6.0 Hz, OCH_2), 4.34 (d, 2 H, J = 5.8 Hz, H_a), 4.56 (d, 2 H, J = 5.8 Hz, H_b), 6.97 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.51 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.61, 7.68 (two d with fine coupling, 4 H, J = 7.8 Hz, H_e, H_f).

3-{[[5-[(4-Fluorobiphenyl-4′-yl)oxy]pentyl]oxy]methyl}-3-methyloxetane (OX-F-5). Chemical shifts: 1.58, 1.80 (m, 4 H; quint, 2 H; $CH_2CH_2CH_2CH_2CH_2$), 3.98 (t, 2 H, J = 6.0 Hz, OCH_2), 4.50 (d, 2 H, J = 5.8 Hz, H_b), 6.93 (d with fine coupling, 2 H, J = 8.8 Hz, H_c), 7.08 (t with fine coupling, 2 H, J = 8.8 Hz, H_f), 7.44 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.47 (q with

Table I
Synthesis of Monomers[a]

X	n	m	yield, %	transition, °C[c]
$O(CH_2)_nH$	1	3	37.7	65.6
	2	3	37.4	77.1
	3	3	35.7	81.4
	4	3	46.7	93.5
	1	4	40.4	71.4
	2	4	97.1	(54.0, 86.5) 79.0[e]
	3	4	82.8	(56.6, 90.3) 85.9[e]
	4	4	69.7	(55.0, 91.2)
CN		0	66.0	97.8
		3	31.7	d
		4	92.2	48.1
		5	67.8	49.4
F		0	88.2	77.7
		3	24.4	d
		4	65.3	42.7
		5	72.2	d

[a] X, n, and m indicate the substituent on the biphenyl ring, the number of carbon atoms in the alkoxy substituent, and the number of carbon atoms of the methylene groups in the spacer (see Scheme I). [d] Determined by DSC. Values in parentheses are temperatures at peak. [e] Second and repeated heating. [d] Liquid at room temperature.

fine coupling, 2 H, J_1 = 8.8 Hz, J_2 = 5.4 Hz, H_e). Other protons of this monomer appeared at the corresponding positions with OX-CN-5.

Polymerization. Dichloromethane was drived over calcium hydride and was distilled just prior to use. Freshly distilled boron trifluoride ether complex was used as an initiator. Polymerizations were carried out in dichloromethane at 0 °C. Crystalline monomers were dried under vacuum at 60 °C after purification by column chromatography. Liquid monomers, mainly monomers with three methylene spacers, were dried over calcium hydride as a dichloromethane solution. The supernatant solution was used.

Polymers were purified by repeated reprecipitation. The absence of monomer in polymer was checked by thin-layer chromatography and GPC.

Results and Discussion

In the synthesis of 3-[(ω-bromoalkoxy)methyl]-3-methyloxetane, an excess amount of dibromoalkane was used in order to avoid disubstitution of the bromoalkyl group by 3-(hydroxymethyl)-3-methyloxetane. Yield of the desired product tended to decrease by heating at higher temperature or by prolonged heating because of the elimination reaction. For instance, heating the reaction system to reflux for 1.5 h from the initial stage of the reaction reduced the yield of the product to 49 (m = 4) and 44% (m = 3).

Yield and melting points of monomers are tabulated in Table I.

Monomers without methylene spacer were synthesized by the reaction of 3-[(tosyloxy)methyl]-3-methyloxetane with the potassium salt of 4-functionalized-4′-hydroxybiphenyl in dimethyl sulfoxide. Monomers with four or five methylene group were synthesized by the coupling reaction of 3-[(4-bromobutoxy)- or 3-[(5-bromopentoxy)methyl]-3-methyloxetane with sodium salt of the biphenyl derivatives in dimethylformamide. Initial attachment of a spacer group to the oxetane ring sometimes makes the separation of the product difficult, specially in the case of the monomer with a three methylene spacer. Coupling of 4′-(3-bromopropyl)-4-alkoxy-, 4-cyano-, or 4-fluorobiphenyl with 3-(hydroxymethyl)-3-methyloxetane under phase transfer condition was employed. Reasonable yield was obtained.

Table II
Polymerization of Mesogenic Monomers[a] by Boron Trifluoride Ether Complex

monomer	concn, mol/L	BF_3OEt_2, mol %	yield, %	M_w[b] × 10^3	M_n × 10^3	M_w/M_n
OX-1-3	1.4	1.15	68.0	46.8	11.8	3.9
OX-2-3	1.1	1.80	83.3	15.5	6.8	2.3
OX-3-3	1.2	1.41	59.8	14.6	6.6	2.2
OX-4-3	0.89	1.14	70.0	24.4	11.0	2.2
OX-1-4	2.1	1.67	96.0	36.1	12.8	2.8
OX-2-4	0.93	1.01	59.3	22.6	9.5	2.4
OX-3-4	1.2	1.21	68.2	13.4	6.1	2.2
OX-4-4	1.1	0.97	57.2	15.0	7.5	2.0
OX-(1-4-*co*-2-4)	1.3	1.22	64.7	16.2	7.5	2.1
OX-(3-3-*co*-3-4)	1.4	1.56	83.7	20.8	9.3	2.2
OX-CN-0	1.0	1.00	43.0	16.6	10.7	1.6
OX-CN-3	0.76	1.00	48.9	39.3	16.6	2.4
OX-CN-4	2.7	1.20	38.4	85.2	38.5	2.2
OX-CN-5	1.0	1.00	33.9	23.0	13.0	1.8
OX-F-0	1.0	1.00	91.2	c	c	c
OX-F-3	0.43	0.91	92.0	16.7	8.3	2.0
OX-F-4	1.0	1.00	99.3	45.6	26.6	1.7
OX-F-5	1.0	1.00	88.2	29.4	13.3	2.2

[a] Solvent, CH_2Cl_2, temp, °C; time, 20–28 h. [b] Estimated by GPC, correlating to standard polystyrene. [c] Not soluble in ordinary solvent.

Monomers OX-2-4 and OX-4-4 showed two thermal transitions in DSC analysis and showed a mesophase under cross-polarized light; however, the phase could not be identified. Other monomers showed only one transition temperature and did not show a mesophase. Steric hindrance of the oxetane ring may make it difficult for the monomers with a short spacer to take a liquid crystalline state. Long spacer and alkoxy tail groups might be needed to take a liquid crystalline state.

The results of polymerization by BF_3·OEt_2 as an initiator are shown in Table II.

All monomers gave reasonable to good yields in the polymerization. Cyano-substituted monomers gave the polymers in rather low yield. The reason is not clear, but the cyano group might act as a weakly basic group to suppress cationic polymerization. Fluorine-substituted monomer can be easily polymerized under cationic conditions.

In the GPC chromatogram of polymers before purification, a low molecular weight fraction was sometimes observed. Cyclic oligomers may have been produced.[16,17] Such an oligomer fraction was removed by reprecipitation.

Polymers had the expected chemical structure formed by ring-opening polymerization of monomers as studied by ^{13}C NMR.

Typical examples are given for polyOX-CN-4, polyOX-F-4, and poly(OX-F-5).

Poly[3-{[4-[(4-cyanobiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane] (PolyOX-CN-4). Chemical shifts: ^1H NMR 0.88 (br s, 3 H, CH_3), 1.60–1.89 (m, 4 H, $CH_2CH_2CH_2CH_2$), 3.16 (br s, 4 H, CH_2CCH_2O main chain), 3.22 (br s, 2 H, $C(CH_3)CH_2$), 3.38 (m, 2 H, $CH_2OCH_2CH_2$), 3.92 (t, 2 H, J = 5.8 Hz, OCH_2), 6.88 (d, 2 H, J = 8.8 Hz, H_c), 7.42 (d, 2 H, J = 8.8 Hz, H_d), 7.52, 7.59 (two d, 4 H, J = 8.6 Hz, H_e, H_f); ^{13}C NMR 17.66 (C1), 26.37 (C6, C7), 41.50 (C2), 68.09 (C3), 71.26, 73.77 (C4, C5), 74.55 (C8), 110.47 (C16), 115.35 (C10), 119.34 (C17), 127.34 (C14), 128.67 (C11), 131.67 (C12), 132.95 (C15), 145.44 (C13), 160.13 (C9).

Poly[3-{[4-[(4-Fluorobiphenyl-4′-yl)oxy]butoxy]methyl}-3-methyloxetane] (PolyOX-F-4). Chemical shifts: ^1H NMR 6.84 (d, 2 H, J = 8.8 Hz, H_c), 7.00 (t, 2 H, J = 8.8 Hz, H_f), 7.34 (d with fine coupling, 2 H, J = 8.8 Hz, H_d), 7.38 (q with fine coupling, 2 H, J = 8.8 Hz, H_e);

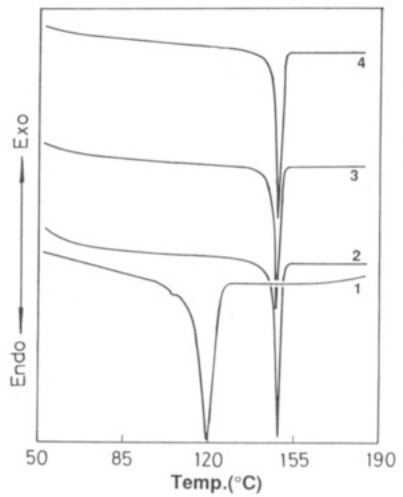

Figure 1. DSC curves of the polyOX-*n*-3 series having a three methylene spacer (m = 3). Numbers in the figure indicate the number of carbon atoms in the alkoxy group (n).

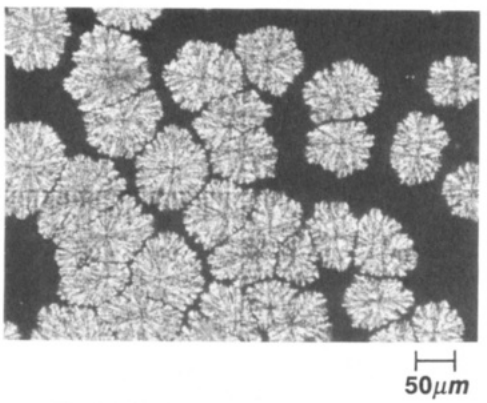

Figure 2. Optical polarization micrograph of polyOX-2-3 annealed at 142.0 °C for 20 min.

^{13}C NMR 115.10 (C10), 115.86 (d, J = 21.4 Hz, C15), 128.30 (C11), 128.47 (d, J = 8.2 Hz, C14), 132.96 (C12), 137.26 (C13), 159.05 (C9), 162.52 (d, J = 244.9 Hz, C16). Other signals appeared at quite similar positions to those of poly(OX-CN-4).

Poly[3-{[[5-[(4-fluorobiphenyl-4′-yl)oxy]pentyl]oxy]methyl}-3-methyloxetane] (PolyOX-F-5). Chemical shifts: ^{1}H NMR 1.37–1.83 (m, 6 H, $CH_2CH_2CH_2CH_2CH_2$), 3.33 (m, 2 H, $CH_2OCH_2CH_2$), 3.88 (t, 2 H, J = 5.8 Hz, OCH_2). Other signals appeared at quite similar positions to those of poly(OX-F-4).

In the ^{1}H NMR spectra of the polymers, a very weak signal assignable to ethoxy group was observed at 1.20 (t, J = 7.2 Hz) and 3.46 (q, J = 7.2 Hz) ppm. Initiation not only by a proton but also by an ethyl group may have occurred. Further study is needed to elucidate the real reaction mechanism.

Monomers with similar substituents on the biphenyl ring showed almost identical reactivity to each other in the polymerization. A copolymer having almost the same composition as the monomer feed was obtained in the copolymerization reaction of alkoxy-substituted biphenyl monomers.

Molecular weights and molecular weight distributions of polymers are reasonably high and narrow. The proper choice of an initiator may give better defined polymers.

A typical DSC curve and optical polarization micrographs of polyOX-2-3 are shown in Figures 1 and 2. Only one thermal transition was observed in the DSC. Although some organized phase was observed in the optical polarization micrograph below the transition temperature, no conclusion as to whether it was a mesophase or not be drawn. Similar behavior was observed for polyOX-1-3, polyOX-3-3, and polyOX-4-3 with three methylene spacers. PolyOX-1-4 showed only one transition like polyOX-*n*-3 having a three methylene spacer. Two or more thermal transitions were seen in the DSC for polyOX-2-4, polyOX-3-4, and polyOX-4-4 or for copolymers having four methylene spacers as typically shown in Figure 3. Thermal behavior of the polymers are tabulated in Table III.

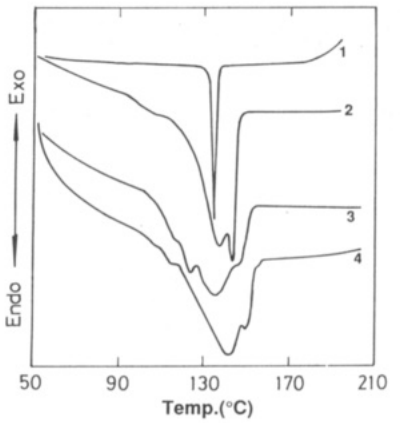

Figure 3. DSC curves of the polyOX-*n*-4 series having a four methylene spacer (m = 4). Numbers in the figure indicate the length of the alkoxy group (n).

Table III
Thermal Behavior of PolyOX's

polymer	DSC (heating)[a] T_g, °C	DSC (heating)[a] transition, °C	texture under optical polarization microscopy
polyOX-1-3	103	115	nd[b]
polyOX-2-3	c	147	nd
polyOX-3-3	c	149	nd
polyOX-4-3	c	148	nd
polyOX-1-4	c	139	nd
polyOX-2-4	c	(148, 154)	nd
polyOX-3-4	c	(120, 125, 136, 146)	nd
polyOX-4-4	108	(145, 151)	nd
polyOX-(1-4-*co*-2-4)	c	139	nd
polyOX-(3-3-*co*-3-4)	c	(139, 146)	nd
polyOX-CN-0	c	96	c
polyOX-CN-3	33	c	c
polyOX-CN-4	c	84	fan
polyOX-CN-5	16	96	fan
polyOX-F-0	c	150	c
polyOX-F-3	c	72	nd
polyOX-F-4	c	103	fan
polyOX-F-5	c	90	fan

[a] Values on second heating. Values in parentheses are temperatures at peak. [b] nd, phase could not be determined. [c] Did not show.

In contrast to polyOX-1-4, which showed quite a similar structure to the polyOX-*n*-3 series, which has three methylene spacer, polyOX-2-4 showed a smaller texture as shown in Figure 4; however, concrete phases could not be identified by the optical polarization micrograph.

It was found that polyoxetane acts as a possible main-chain component for a side-chain liquid crystalline polymer with alkoxy-functionalized biphenyl as the mesogenic group. However, a definite conclusion as to whether the polymers really show a liquid crystalline state or not could not be drawn. Further study is needed to find a suitable condition for obtaining the liquid crystalline state.

It is generally admitted that a polar cyano group on the mesogenic group gives a better organized phase than an alkoxy group.[1] In the polyoxetane main chain polymers,

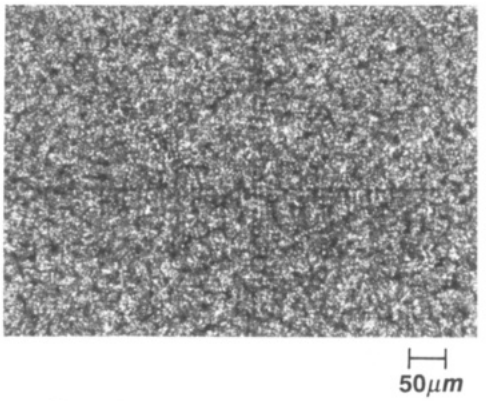

Figure 4. Optical polarization micrograph of polyOX-2-4 annealed at 149.9 °C for 30 min.

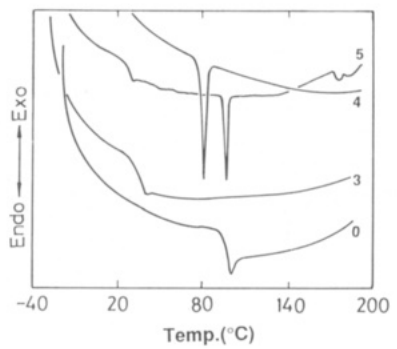

Figure 5. DSC curves of the polyOX-CN-*m* series. Numbers in the figure indicate the length of the methylene spacer (*m*).

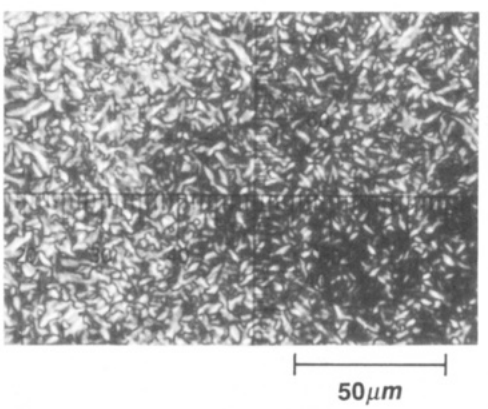

Figure 6. Optical polarization micrograph of polyOX-CN-4 annealed at 82.5 °C for 30 min.

polyOX-CN-0 and polyOX-CN-3 did not show any thermal transition other than the glass transition temperature in the DSC as shown in Figure 5. No liquid crystalline state was observed either, in the optical polarization micrograph. Contrary to this, polyOX-CN-4 and polyOX-CN-5 showed discrete transitions starting at 84 and 96 °C, respectively, and discrete mesophase structures in both the cooling and the heating processes. Typical change of the mesophase structure seen in optical polarization micrograph is shown in Figures 6–10. The batonett structure formed at 82.5 or 96.5 °C in about 30 min was changed into a well-developed fanlike focal conic structure under further annealing. A well-developed smectic phase was considered to be taken.

Compared with the fact that six methylene and ester functions are needed to form a nematic phase even for polyacrylate with cyanobiphenyl or alkoxybiphenyl mesogenic group,[1] a shorter spacer, namely, a four methylene and ether function, was enough for polyoxetane with

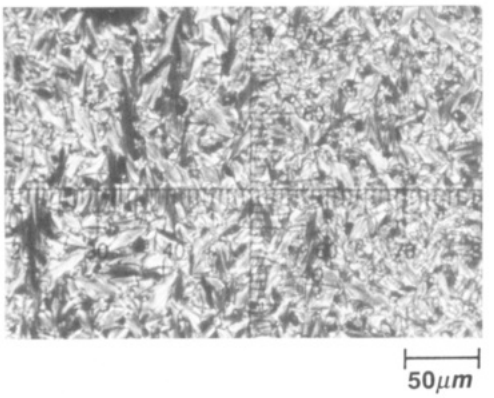

Figure 7. Optical polarization micrograph of polyOX-CN-4 annealed at 82.5 °C for 6.5 h.

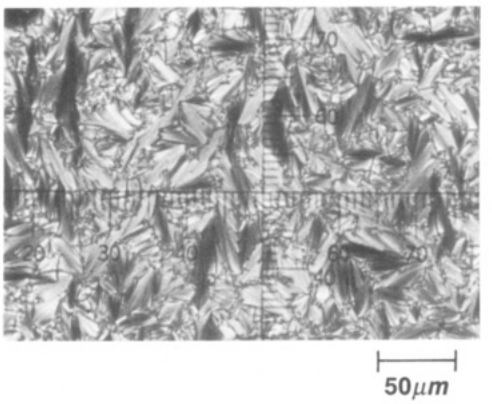

Figure 8. Optical polarization micrograph of polyOX-CN-4 annealed at 82.5 °C for 2 days.

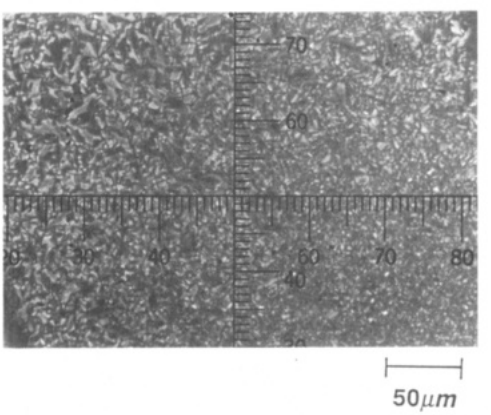

Figure 9. Optical polarization micrograph of polyOX-CN-5 annealed at 96.5 °C for 20 min.

cyano-substituted biphenyl as the mesogenic group to form a more ordered smectic phase. In such polymers, the main-chain polyether is considerably flexible compared with polymethacrylate or polyacrylate, which seems to make it easy to organize mesogenic groups. This is the first example in which polyoxetane was used as the main chain of a liquid crystalline polymer.

The structure of the mesogenic group is also one of the important factors in determining the mesophase structure. Polar and less bulky cyano-substituted biphenyl seems to be a good mesogenic group. The polar interaction between cyano-substituted biphenyls makes it easy for the mesogenic groups to organize. Apparently, alkoxy-substituted biphenyls are not good mesogenic groups for polyoxetane to take on well-ordered structure.

Related to this, fluoro-substituted biphenyl was of interest as a possible mesogenic group. The fluorine atom

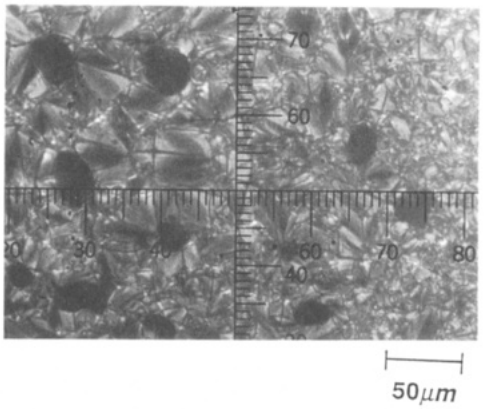

Figure 10. Optical polarization micrograph of polyOX-CN-5 annealed at 96.5 °C for 2 days.

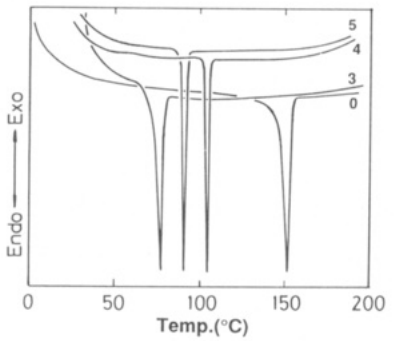

Figure 11. DSC curves of the polyOX-F-*m* series. Numbers in the figure indicate the length of the methylene spacer (*m*).

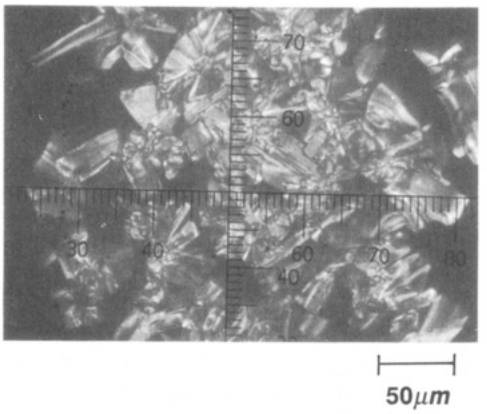

Figure 12. Optical polarization micrograph of polyOX-F-4 annealed at 102.2 °C for 2 days.

has a spherelike structure and might disturb the requirement for the shape of the biphenyl derivative as a mesogenic group. Thermal transitions of polyOX-F-*m*'s are shown in Figure 11. All the polymers showed only one transition.

PolyOX-F-3 showed a sanded structure. PolyOX-F-4 took on a discrete smectic fan architecture as shown in the optical polarization micrograph in Figure 12. PolyOX-F-5, which showed a batonnet structure in the early stage of annealing, also took on a well-developed structure as shown in Figure 13, after prolonged annealing. This is the first example in which the fluorine atom is used as a tail group for a biphenyl mesogen in a liquid crystalline polymer.

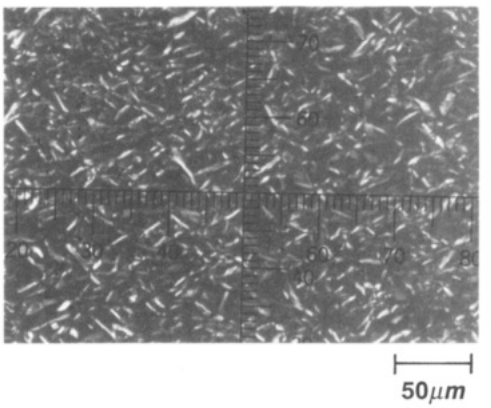

Figure 13. Optical polarization micrograph of polyOX-F-5 annealed at 89.2 °C for 2 days.

It will be interesting to study further the relationship between the flexibility of the polymer main chain and the phases exhibited in light of the primary structure of polymers. In polyoxetane, the flexible repeating ether unit $(CH_3)CCH_2OCH_2$ seems to function partly as a spacer. Such a flexible main chain makes it easy to organize the mesogenic groups, even with a shorter spacer compared with the ordinary length required for polymethacrylate or polyacrylate.

Conclusion

It was shown that polyoxetane can act as a main chain of liquid crystalline polymers by studying the relationship between chemical structure of polymers and the mesophase exhibited by the polymers. Polyoxetanes with cyanobiphenyl as a mesogenic group showed a smectic liquid crystalline phase. Fluorobiphenyl was found to be a novel and good mesogenic group for polyoxetane to take a smectic phase.

Acknowledgment. Financial support from a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control (02205057) and from a Grant-in-Aid for Developmental Scientific Research (63850184) is gratefully acknowledged.

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