Synthesis of Liquid Crystalline Polyoxetanes Bearing Cyanobiphenyl Mesogen and Siloxane-Containing Substituent in the Repeating Unit

Yusuke KAWAKAMI,[†] Masahiro SUZUKI, Yasuhiro KATO, and Atsunori MORI

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology,
Asahidai 1-1, Tatsunokuchi, Ishikawa 923-12, Japan

(Received January 12, 1996)

ABSTRACT: Cyanobiphenyl mesogen-containing oxetanes functionalized by a second siloxane-containing substituent on the same carbon atom of the ring were synthesized. Polymers were obtained by cationic polymerization with $\text{BF}_3 \cdot \text{OEt}_2$ or $\text{Et}_3\text{O}^+\text{BF}_4^-$ as an initiator. The polymers showed smectic liquid crystalline phase. Introduction of siloxane linkage in the second substituent kept the glass transition temperatures of the polymer almost constant irrespective of the difference of the spacer length. The clearing temperature became higher with the increase in the length of the spacer group connecting the mesogenic group to the main chain. By these two effects on the transition temperatures, the temperature range of the liquid crystalline state became wider with the increase in the length of the spacer group.

KEY WORDS Oxetane / Cyanobiphenyl / Siloxane Linkage / Cationic Polymerization / Glass Transition Temperature / Liquid Crystalline Polymer / Smectic Phase /

Much attention has been paid recently to liquid crystalline polymers, especially to side-chain type, because of their potential application for electronic devices. Poly(siloxane)s, poly(acrylate)s, and poly(methacrylate)s are common main chain components of such liquid crystalline polymers.^{1–4} There are some new examples in which hetero-atom containing main chain like poly(phosphazene), poly(aziridine), polyether, or poly(isocyanate) are used.^{5–24}

We have been interested in the relationship between the structures of main chain, spacer, and mesogenic group and the liquid crystalline phase exhibited by the polymer, and reported examples of liquid crystalline poly(oxetane)s^{20–22} and polydienes.^{25–27} In the reports,^{25–27} we showed the effective role of the siloxane linkage as a constituent of the spacer. Effectiveness of the introduction of a siloxane linkage in the spacer in exhibiting well-organized liquid crystalline phase was also pointed out.^{28–30}

Meanwhile considerable interests have been paid to the effect of the introduction of a second monomer component into a liquid crystalline polymers by random copolymerization^{31–35} or block copolymerization.³⁶ However, by these methods, second component can be introduced only on the basis of the monomer reactivity ratio or as a microphase-separated segments, accordingly, it is difficult to introduce a second specific functional group at the specific position to the mesogenic group.

We were interested in the effects of siloxane linkage as the second substituents, and synthesized oxetane monomers having a siloxane-containing substituent along with the mesogenic group on the same carbon atom in the molecule in order to introduce these groups at the specific position to the mesogenic group in the polymer. In this article, we would like to report on the synthesis of the monomers, polymerization and the effect of the second component on the liquid crystalline behavior of the formed polymers.

EXPERIMENTAL

General

¹H and ¹³C NMR spectra were obtained on a Varian NMR spectrometer Model Gemini 300 (300 MHz for ¹H, 75 MHz for ¹³C). Chemical shifts (δ) are given in ppm from TMS as an internal standard in CDCl_3 . GPC analyses were carried out on a JASCO GPC Model HLC 880 equipped with Shodex gels KF801 (exclusion molecular weight, polystyrene 1.5×10^3) and KF804 (exclusion molecular weight, polystyrene 4×10^5), using tetrahydrofuran as an eluent at the flow rate of 1 mL min^{-1} .

DSC analyses of monomers and polymers were carried out on a SEIKO thermal analysis system Model SSC 5200 equipped with DSC 120 with the heating rate of 3°C min^{-1} . The transition temperature is given at the point where transition starts. 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 OPTI-PHOTO2-POL equipped with a Mettler thermal analysis system Model FP900 with FP82HT hot stage and FP 90 controller. Pictures were taken at a little lower temperature than the peak after annealing in cooling process from isotropic state at appropriate intervals.

Synthesis

The synthetic method of the monomers is quite similar to that already reported.²¹ The synthetic route is shown in Scheme 1. The names of the monomers are abbreviated by the combination of oxetane (OX), mesogen (CN: cyanobiphenyl), length of spacer (number of

[†] To whom correspondence should be addressed.

methylene unit m), and the second substituent. For an example, OX-CN- m ,S6 indicates the monomer with cyanobiphenyl connected through m methylenes and having 3-(pentamethyldisiloxan-1-yl)propoxymethyl as the second substituent. S8 indicates 3-(heptamethyltrisiloxan-3-yl)propoxymethyl substituent. 3H and 3 of OX-CN- m ,3H or OX-CN- m ,3 indicate allyloxymethyl and propoxymethyl group, respectively.

Protons of oxetane and biphenyl rings are designated as indicated below.

The names of polymers are abbreviated by adding P to the abbreviated name of monomers. The assignment of the carbon signals of the polymers was made similarly to the reported results.²¹ Typical numbering of the carbon atoms is indicated below.

3,3-Bis(hydroxymethyl)oxetane. 3,3-Bis(hydroxymethyl)oxetane was prepared from pentaerythritol.³⁷ Yield 66%, bp 110–120°C (0.4 mmHg).

3-Allyloxymethyl-3-hydroxymethyloxetane. To a suspension of sodium hydride (6.0 g, 150 mmol) in dimethylformamide (DMF) (40 mL) was added a solution of 3,3-bis(hydroxymethyl)oxetane (16.5 g, 140 mmol) in DMF (20 mL) at room temperature. After stirring for 30 min, allyl bromide (8.5 g, 70 mmol) in DMF (20 mL) was added during 1 h, and the mixture was stirred overnight at room temperature. Dimethylformamide was removed under reduced pressure, diethyl ether (100 mL) was added, and the mixture was filtered. The filtrate was evaporated under reduced pressure to leave an oil. Purification by silica gel column chromatography afforded a colorless liquid. Yield 35%.

R_f = 0.35 (hexane : ethyl acetate = 1 : 1).

¹H chemical shifts: 2.38 (m, 1H, OH), 3.80 (s, 2H, CH₂OCH₂CH=CH₂), 3.96 (d, 2H, J = 6.0 Hz, CH₂OH), 4.03 (d with fine coupling, 2H, J = 6.0 Hz, CH₂CH=CH₂), 4.44, 4.51 (two d, 2H each, J = 6.0 Hz, Ha, Hb),

5.23 (d with fine coupling, 2H, J = 12.0 Hz, Hc), 5.28 (d with fine coupling, 2H, J = 18.0 Hz, Hd), 5.90 (m, 1H, CH=CH₂).

5.28 (d with fine coupling, 2H, J = 18.0 Hz, Hd), 5.90 (m, 1H, CH=CH₂).

3-Allyloxymethyl-3-[4-(bromobutoxy)methyl]oxetane. To a mixture of aq. 50 wt% NaOH (30 mL) and hexane (20 mL), and tetrabutylammonium bromide (0.32 g, 1.0 mmol) was added 3-allyloxymethyl-3-hydroxymethyloxetane (3.2 g, 20 mmol) and 1,4-dibromobutane (13.2 g, 61.2 mmol). After the mixture was stirred overnight at room temperature, the mixture was heated to reflux for 30 min. After cooling to room temperature, water (100 mL) was added to the mixture, and the mixture was allowed to separate. Aqueous layer was extracted with hexane (50 mL × 2), and the combined organic layer was dried over anhydrous magnesium sulfate. Removal of the solvent followed by distillation under reduced pressure afforded a colorless liquid. Yield 64%, bp 112°C (0.4 mmHg).

¹H chemical shifts: 1.66–2.05 (m, 4H, CH₂CH₂CH₂CH₂), 3.44 (t, 2H, J = 8.0 Hz, CH₂Br), 3.50 (t, 2H, J = 6.8 Hz, OCH₂CH₂), 3.63 (s, 2H, CH₂OCH₂CH₂), 3.67 (s, 2H, CH₂OCH₂CH=CH₂), 4.03 (d with fine coupling, 2H, J = 6.0 Hz, CH₂CH=CH₂), 4.48 (s, 4H, Ha, Hb), 5.23 (d with fine coupling, 2H, J = 12.0 Hz,

Hc), 5.28 (d with fine coupling, 2H, J = 18.0 Hz,

Hd), 5.90 (m, 1H, CH=CH₂).

Other 3-allyloxymethyl-3-[ω-(bromoalkoxy)methyl]oxetanes were similarly synthesized.

3-Allyloxymethyl-3-[5-(bromopentyloxy)methyl]oxetane. Yield 57%, bp 132°C (0.5 mmHg). ¹H chemical shifts: 1.66–2.05 (m, 6H, CH₂CH₂CH₂CH₂CH₂).

3-Allyloxymethyl-3-[6-(bromohexyloxy)methyl]oxetane. Yield 82%, bp 130°C (0.4 mmHg). ¹H chemical shifts: 1.35–1.92 (m, 8H, CH₂CH₂CH₂CH₂CH₂CH₂).

3-Allyloxymethyl-3-[7-(bromoheptyloxy)methyl]oxetane. Yield 74%, bp 135°C (0.2 mmHg). ¹H chemical shifts: 1.32–1.92 (m, 10H, CH₂CH₂CH₂CH₂CH₂CH₂CH₂).

Other protons of these compounds appeared at the corresponding positions with 3-allyloxymethyl-3-[4-(bromobutoxy)methyl]oxetane.

3-Allyloxymethyl-3-[4-(4-cyanobiphenyl-4'-yloxy)butoxy]methyl]oxetane (OX-CN-4,3H). 3-Allyloxymethyl-3-[4-(bromobutoxy)methyl]oxetane (2.93 g, 10.0 mmol) in DMF (10 mL) was added dropwise to the sodium salt of 4-cyano-4'-hydroxybiphenyl (1.95 g, 10 mmol) prepared by the reaction with sodium hydride (0.53 g, 14.3 mmol) in DMF (30 mL). After stirring the reaction system overnight at room temperature, DMF was removed, chloroform (70 mL) and water (50 mL) were added. The mixture was shaken well and allowed to separate. The organic layer was washed with saturated aqueous NaHCO₃ (50 mL) and dried over anhydrous magnesium sulfate. A crude oil obtained by the removal of the solvent was subjected to silica gel column chromatography to give the product as a colorless liquid. Yield 58%.

R_f = 0.20 (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.72–2.00 (m, 4H, CH₂CH₂CH₂CH₂),

CH₂), 3.51 (t, 2H, $J=6.8$ Hz, CCH₂OCH₂CH₂), 3.63 (s, 2H, CH₂OCH₂CH₂), 3.66 (s, 2H, CH₂OCH₂CH=CH₂), 4.03 (d with fine coupling, 2H, $J=6.0$ Hz, CH₂CH=CH₂), 4.06 (t, 2H, $J=6.0$ Hz, CH₂-biphenyl), 4.49 (s, 4H, $J=6.0$ Hz, Ha, Hb), 5.20 (d with fine coupling, 2H,

$J=12.0$ Hz, , 5.28 (d with fine coupling, 2H,

$J=18.0$ Hz, , 5.90 (m, 1H, CH=CH₂), 6.99 (d, 2H, $J=8.8$ Hz, Hc), 7.54 (d, 2H, $J=8.8$ Hz, Hd), 7.66 (two d, 4H, $J=7.8$ Hz, He, Hf).

Other OX-CN-*m*,3H's were similarly synthesized.

3-Allyloxymethyl-3-{[5-(4-cyanobiphenyl-4'-yloxy)-pentyloxy]methyl}oxetane (OX-CN-5,3H). Yield 81%, colorless liquid.

$R_f=0.20$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.50—1.92 (m, 6H, CH₂CH₂CH₂-CH₂CH₂).

3-Allyloxymethyl-3-{[6-(4-cyanobiphenyl-4'-yloxy)-hexyloxy]methyl}oxetane (OX-CN-6,3H). Yield 78%, colorless liquid.

$R_f=0.20$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.42—1.92 (m, 8H, CH₂CH₂CH₂-CH₂CH₂CH₂).

3-Allyloxymethyl-3-{[7-(4-cyanobiphenyl-4'-yloxy)-heptyloxy]methyl}oxetane (OX-CN-7,3H). Yield 60%, colorless liquid.

$R_f=0.20$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.36—1.90 (m, 10H, CH₂CH₂-CH₂CH₂CH₂CH₂CH₂).

Other protons of these compounds appeared at the corresponding positions with OX-CN-4,3H.

4-Cyano-4'-(3-bromopropoxy)biphenyl. Yield 39%, mp 102.4°C.²¹

3-Allyloxymethyl-3-{[3-(4-cyanobiphenyl-4'-yloxy)-propyloxy]methyl}oxetane (OX-CN-3,3H). Yield 37%.

$R_f=0.20$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 2.08 (m, 2H, CH₂CH₂CH₂), 3.69 (t, 2H, $J=6.8$ Hz, CCH₂OCH₂CH₂).

Other protons of these compounds appeared at the corresponding positions with OX-CN-4,3H.

Monomers with siloxanyl groups in a second substituent were synthesized by hydrosilylation reaction of OX-CN-*m*,3H with pentamethyldisiloxane or 1,1,1,3,5,5,5-heptamethyltrisiloxane in the presence of platinum catalyst.

3-{[3-Pentamethyldisiloxanyl]propoxy}methyl-3-{[3-(4-cyanobiphenyl-4'-yloxy)propoxy]-methyl}oxetane (OX-CN-3,S6). To a solution of OX-CN-3,3H (0.87 g, 2.1 mmol) in toluene (2.0 mL) was added a 0.02 mL of 0.1 M solution of H₂PtCl₆·H₂O in 2-propanol. After stirred for 10 min, pentamethyldisiloxane (0.59 g, 4.0 mmol) was added. The reaction was continued until the complete consumption of OX-CN-3,3H was confirmed by thin layer chromatography (about 1 h). Removal of the solvent under reduced pressure left a crude oil, which was purified by column chromatography on silica gel to give a light yellow liquid. Yield 57%.

$R_f=0.32$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 0.06 (s, 6H, CH₂SiMe₂OSiMe₃), 0.08 (s, 9H, CH₂SiMe₂OSiMe₃), 0.51 (m, 2H, CH₂CH₂-SiMe₂O), 1.58 (m, 2H, CH₂CH₂CH₂SiMe₂O), 2.19 (m,

2H, CH₂CH₂CH₂-biphenyl), 3.39 (t, 2H, $J=8.1$ Hz, OCH₂CH₂CH₂SiMe₂O), 3.62 (s, 2H, CCH₂OCH₂-CH₂CH₂-biphenyl), 3.65 (s, 2H, CCH₂OCH₂CH₂CH₂-SiMe₂O), 3.69 (t, 2H, $J=6.8$ Hz, OCH₂CH₂CH₂-biphenyl), 4.06 (t, 2H, $J=6.0$ Hz, CH₂O-biphenyl), 4.46, 4.49 (two d, 2H each, $J=6.0$ Hz, Ha, Hb), 6.99 (d, 2H, $J=8.8$ Hz, Hc), 7.54 (d, 2H, $J=8.8$ Hz, Hd), 7.68 (two d, 4H, $J=7.8$ Hz, He, Hf).

3-{[3-Pentamethyldisiloxanyl]propoxy}methyl-3-{[4-(4-cyanobiphenyl-4'-yloxy)butoxy]methyl}oxetane (OX-CN-4,S6). Yield 61%, white liquid.

$R_f=0.32$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.54—1.90 (m, 6H, CH₂CH₂CH₂-CH₂O and CH₂CH₂CH₂SiMe₂O), 3.50 (t, 2H, $J=6.8$ Hz, OCH₂CH₂CH₂CH₂).

3-{[3-Pentamethyldisiloxanyl]propoxy}methyl-3-{[5-(4-cyanobiphenyl-4'-yloxy)pentyloxy]methyl}oxetane (OX-CN-5,S6). Yield 58%, colorless liquid.

$R_f=0.32$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.52—1.92 (m, 8H, CH₂CH₂CH₂-CH₂CH₂O and CH₂CH₂CH₂SiMe₂O), 3.51 (t, 2H, $J=6.8$ Hz, OCH₂CH₂CH₂CH₂).

In case of synthesis of OX-CN-6,S6, OX-CN-7,S6, and OX-CN-5,S8, platinum-1,3-(divinyl)tetramethyldisiloxane complex in xylene (7.7 mmol l⁻¹) was used as the catalyst.³⁸

3-{[3-Pentamethyldisiloxanyl]propoxy}methyl-3-{[6-(4-cyanobiphenyl-4'-yloxy)hexyloxy]methyl}oxetane (OX-CN-6,S6). Yield 62%, light yellow liquid.

$R_f=0.32$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.42—1.90 (m, 10H, CH₂CH₂-CH₂CH₂CH₂CH₂O and CH₂CH₂CH₂SiMe₂O), 3.50 (t, 2H, $J=6.8$ Hz, OCH₂CH₂CH₂CH₂).

3-{[3-Pentamethyldisiloxanyl]propoxy}methyl-3-{[7-(4-cyanobiphenyl-4'-yloxy)heptyloxy]methyl}oxetane (OX-CN-7,S6). Yield 47%, light yellow liquid.

$R_f=0.32$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 1.47—1.90 (m, 12H, CH₂CH₂-CH₂CH₂CH₂CH₂CH₂O and CH₂CH₂CH₂SiMe₂O), 3.48 (t, 2H, $J=6.8$ Hz, OCH₂CH₂CH₂CH₂).

Other protons of these monomers appeared at the corresponding positions with OX-CN-3,S6.

3-{[(1,1,1,3,5,5,5-Heptamethyldisiloxan-3-yl)propoxy]methyl}-3-{[5-(4-cyanobiphenyl-4'-yloxy)pentyloxy]methyl}oxetane (OX-CN-5,S8). OX-CN-5,S8 was synthesized using 1,1,1,3,5,5,5-heptamethyltrisiloxane in the same manner as described above to yield OX-CN-5,S6. Yield 71%, light yellow liquid.

$R_f=0.38$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

¹H chemical shifts: 0.10 (s, 21H, CH₂SiMe(OSiMe₃)₂), 0.45 (m, 2H, CH₂CH₂CH₂SiMe), 1.52—1.90 (m, 8H, CH₂CH₂CH₂CH₂CH₂O and CH₂CH₂CH₂SiMe₂O), 3.44 (t, 2H, $J=6.8$ Hz, OCH₂CH₂CH₂CH₂).

Other protons of this monomer appeared at the corresponding positions with OX-CN-5,S6.

3-Propoxymethyl-3-{[5-(4-cyanobiphenyl-4'-yloxy)-pentyloxy]methyl}oxetane (OX-CN-5,3). A solution of OX-CN-5,3H (0.63 g, 1.5 mmol) in ethyl acetate (15 mL) was stirred in the presence of palladium carbon (75 mg) under hydrogen atmosphere overnight at room temperature. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane : chloroform : ether = 2 : 1 : 1 as eluent). Yield 85%, color-

less liquid.

$R_f = 0.25$ (hexane : chloroform : diethyl ether = 2 : 1 : 1).

^1H chemical shifts: 0.92 (t, 3H, $J = 7.2$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 1.50–1.90 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ and $\text{OCH}_2\text{CH}_2\text{CH}_3$), 3.42 (t, 2H, $J = 6.6$ Hz, $\text{OCH}_2\text{CH}_2\text{CH}_3$).

Other protons of this monomer appeared at the corresponding positions with OX-CN-5,3H.

Polymerization

Dichloromethane was dried over calcium hydride and was distilled just prior to use. Monomers (0.85 mmol) were dissolved in 3 mL of dichloromethane and dried over calcium hydride for half a day. After calcium hydride was filtered off, the filtrate was evaporated and dried *in vacuo* at 60°C for more than 1 day. Polymerizations were carried out in dichloromethane for 24–48 h at 0°C. Boron trifluoride ether complex (1.0 mol L^{-1}) or triethyloxonium tetrafluoroborate (1.0 mol L^{-1}) was used as an initiator. Polymers were recovered by pouring in methanol and purified by repeated reprecipitation from dichloromethane into methanol. In the GPC chromatogram of polymers before purification, a low molecular weight fraction was sometimes observed. Cyclic oligomers may have been produced.^{39,40} Such an oligomer fraction was removed by reprecipitation. The absence of monomer in polymer was checked by GPC.

Typical ^{13}C NMR data are given for polyOX-CN-5, S6.

Poly[3-{[3-Pentamethyldisiloxanyl]propoxy}methyl-3-{[5-(4-cyanobiphenyl-4'-yloxy)pentyl]oxy}methyl]oxetane (POX-CN-5, S6). ^1H chemical shifts: 0.00–0.15 (t, 15H, $\text{CH}_2\text{SiMe}_2\text{OSiMe}_3$), 0.47 (t, 2H, $\text{CH}_2\text{CH}_2\text{SiMe}_2\text{O}$), 1.45–1.85 (br, 8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ and $\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{O}$), 3.25–3.45 (br, 12H, $\text{CCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, and $\text{CH}_2\text{CCH}_2\text{O}$ (main chain)), 4.02 (br, 2H, $\text{CH}_2\text{O-biphenyl}$), 6.90 (br d, 2H, $J = 8.8$ Hz, *Hc*), 7.44 (br d, 2H, $J = 8.8$ Hz, *Hd*), 7.60 (br two d, 4H, $J = 7.8$ Hz, *He*, *Hf*). ^{13}C chemical shifts: 0.37 (C23), 2.03 (C22), 14.43 (C21), 22.82 (C6), 23.59 (C20), 29.15 (C5), 29.59 (C7), 45.89 (C2), 67.93 (C1), 70.04, 70.65, 71.34 (C3, C4, C18, C19), 74.40 (C8), 110.20 (C16), 115.01 (C10), 118.90 (C17), 126.95 (C14), 128.25 (C11), 131.31 (C12), 132.53 (C15), 145.03 (C13), 159.68 (C9).

RESULTS AND DISCUSSION

Synthesis

Monoallylation of 3,3-bis(hydroxymethyl)oxetane was possible by using excess 3,3-bis(hydroxymethyl)oxetane to allyl bromide in moderate (35%) yield. Hydrosilylation reaction of 3-allyloxymethyl-3-hydroxymethyloxetane gave the corresponding monomers OX-CN-*m*, S6 and OX-CN-*m*, S8 ($m = 4$ –7) in moderate to good yield.

Monomer with a three methylene spacer was synthesized by firstly attaching the spacer to the mesogenic group, then by forming the ether linkage, because the elimination from bromoalkyl function proceeded under the reaction condition.²¹ In synthesizing this compound, spacer was firstly introduced by the alkylation of 4-hydroxy-4'-cyanobiphenyl with excess 1,3-dibromopro-

pane in order to avoid disubstitution of the bromoalkyl group, followed by the reaction of the product with 3-allyloxymethyl-3-hydroxymethyloxetane in the presence of tetrabutylammonium bromide.

Since monomers are usually viscous oil, they were dried as dichloromethane solution. The results of the polymerization are summarized in Table I.

All monomers gave the polymers in rather low yield. This phenomenon is especially noticed in the polymerization of monomers having cyano group in the mesogen. The reason is not clear, but the cyano group might act as a weekly basic group to suppress the cationic polymerization. The use of higher concentration (2 mol%) of catalyst to try to increase the yield sometimes improve the situation. Furthermore, the difficulty to separate produced polymers and unreacted monomers also decreased the yield.

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

Thermal Analysis

Although thermal characterizations of the monomers by DSC were performed, none of the monomers exhibited any liquid crystallinity.

It is generally admitted that a polar cyano group on the mesogenic group gives a well-organized mesophase.¹⁾ Among the already reported polyoxetane main chain polymers, POX-CN-4, POX-CN-5 and POX-CN-6

Table I. Polymerization of monomers by $\text{BF}_3 \cdot \text{OEt}_2$ or $\text{Et}_3\text{O}^+\text{BF}_4^-$ in CH_2Cl_2 at 0°C^a

Monomer	Initiator	Yield	M_n^b	M_w	M_w/M_n
	mol%	%	$\times 10^4$	$\times 10^4$	
OX-CN-3, S6	$\text{BF}_3 \cdot \text{OEt}_2$ (1.00)	8	0.9	1.0	1.1
OX-CN-4, S6	(2.00)	10	1.9	2.3	1.3
OX-CN-5, S6	(2.00)	19	1.4	2.1	1.5
OX-CN-6, S6	$\text{Et}_3\text{O}^+\text{BF}_4^-$ (2.00)	29	1.4	2.0	1.4
OX-CN-7, S6	(2.00)	50	2.2	4.1	1.8
OX-CN-5, S8	(2.00)	45	2.7	3.8	1.4
OX-CN-5, 3	(2.00)	59	2.0	3.3	1.6
OX-CN-5 ^c	$\text{BF}_3 \cdot \text{OEt}_2$ (1.00)	34	1.3	2.3	1.8

^a Reaction time, 20–48 h; $[\text{M}] = 1.0 \text{ mol L}^{-1}$. ^b Estimated by GPC correlating to standard polystyrene. ^c Reference 21.

Table II. Thermal behavior of PolyOX's

Polymer	DSC (Heating) ^a		Texture under optical polarization microscopy
	T_g	T_i (ΔH_i)	
	°C	°C	
PolyOX-CN-3, S6	−3.4	—	—
PolyOX-CN-4, S6	−5.4	15.5 (4.1)	n.d.
PolyOX-CN-5, S6	−4.4	32.7 (5.8)	fan
PolyOX-CN-6, S6	−8.1	34.5 (5.9)	fan
PolyOX-CN-7, S6	−5.5	47.7 (5.8)	fan
PolyOX-CN-5, S8	15.3	41.3 (3.3)	fan
PolyOX-CN-5, 3	−5.5	36.6 (3.6)	fan
PolyOX-CN-5 ^b	16.0	95.8 (2.8)	fan

^a Values on second heating. Values in parentheses are transition enthalpy in mJ mg^{-1} unit. ^b Reference 21. n.d., liquid crystalline phase could not be determined.

showed well-developed smectic phases.

Results of thermal characterization by DSC analysis are shown in Table II.

Introduction of propoxymethyl group (ether linkage) as a second substituent of the polymer considerably lowered the glass transition and clearing temperatures (POX-CN-5,3). The effects of the additional introduction of disiloxane linkage together with ether linkage into the second substituent were not so significant in lowering the transition temperatures (POX-CN-5,S6). Relationship between the number of methylene group in the spacer (m) and transition temperature of POX-CN- m ,S6 is shown in Figure 1.

It can be seen that, as the length of alkylene spacer increases, the clearing temperature is elevated (POX-CN-4,S6 $\rightarrow$ POX-CN-7,S6) in keeping the glass transition temperature almost constant irrespective of the length of the spacer. As a result, temperature range of the liquid crystalline state of POX-CN- m ,S6 is increased.

The glass transition temperature of comb-shaped or side-chain liquid crystalline polymers usually decreases with the length of branch¹ or spacer.⁴¹ This change is not saturated even with the length of 12 carbon chain. The glass transition temperatures of the POX-CN- m ,S6 are kept almost constant by the presence of S6 sub-

Figure 1. Dependence of m on the transition temperatures of POX-CN- m ,S6. m , the number of methylene units in the spacer; ●, clearing temperature; ○, glass transition temperature.

stituent even when the length of the spacer (m) has been changed from 4 to 7 carbons. This suggests that the glass transition temperature of these polymers are mainly controlled by the presence of siloxane linkage in the side chain. Related to this, the glass transition temperature of side-chain liquid crystalline polymer with polysiloxane main chain does not change with the length of the spacer.⁴²

It is of interest to point out that the transition enthalpy is higher in the presence of siloxane linkage (4.1, 5.8, 5.9, and 5.8 mJ mg^{-1} for POX-CN-4,S6, POX-CN-5,S6, POX-CN-6,S6, and POX-CN-7,S6) than that by the introduction of propoxy group (3.6 mJ mg^{-1} for POX-CN-5,3). Organization of mesogenic groups are apparently made easier by the presence of linear siloxane linkage. Transition entropy calculated from these values decreased with the length of the spacer. Further detailed consideration is needed since the geometrical effects of the spacer by the change of the length (odd-even) are included.

Even the introduction of siloxane linkage did not lower the transition temperatures when it is introduced as a branched form (S8). It is already reported that the effect of lowering the glass transition temperature of polystyrene by the branched (*p*-oligodimethylsiloxane)-substituent is smaller than that by linear substituent.⁴³ Although direct comparison could not be made, the transition enthalpy seems smaller in case of branched substituent compared with the linear substituent (3.3 mJ mg^{-1} for POX-CN-S8).

POX-CN-3,S6 showed glass transition temperature at -3.4°C , however was found not to be liquid crystalline. POX-CN-4,S6 exhibited two transition temperatures at -5.4 and 15.5°C , assignable to glass transition and clearing temperatures. However, we could not yet observe the definite texture, presumably because of the low clearing point and narrow liquid crystalline temperature range. POX-CN-5,S6, POX-CN-6,S6, and POX-CN-7,S6 exhibited two transition temperatures, respectively. Optical polarization micrographs of POX-CN-5,S6, POX-CN-6,S6, and POX-CN-7,S6 are shown in Figure 2.

It took quite long time for POX-CN-5,S6 to form liquid crystalline phase. The reason is not clear, however,

Figure 2. Optical polarization micrographs of POX-CN m ,S6. a) $m=5$ annealed at 24.0°C for 1 month; b) $m=6$ annealed at 34.0°C for 12 h; c) $m=7$ annealed at 48.0°C for 24 h.

closeness of the transition temperature to room temperature might be one reason. All polymers showed basically fan texture, and are considered to take smectic phase. Even the presence of bulky but flexible siloxanyl group as the second substituent of these polymers can give rise to liquid crystalline state.

POX-CN-5,S8 also showed two transition temperatures, between which fan texture was observed by optical polarization microscope indicating smectic phase.

CONCLUSION

Introduction of siloxane containing substituent as a second substituent in the liquid crystalline polyoxetane main chain kept the glass transition temperature of the polymer almost constant irrespective of the spacer length. The mesomorphic temperature range was widen with the increase in the length of the methylene spacer.

Acknowledgment. Financial supports from a Grant-in-Aid for Scientific Research (07651078, 07555595, 07246219) from the Ministry of Education, Science, Sports, and Culture of Japan are gratefully acknowledged.

REFERENCES

1. N. A. Plate and V. P. Shibaev, Ed., "Comb-Shaped Polymers and Liquid Crystals," Plenum, New York, N.Y., 1987.
2. C. B. McArdle, Ed., "Side Chain Liquid Crystal Polymers," Chapman and Hall, New York, N.Y., 1989.
3. A. A. Collyer, Ed., "Liquid Crystal Polymers: From Structures to Applications," Elsevier, Barking, 1992.
4. N. A. Plate, Ed., "Liquid-Crystal Polymers," Plenum, New York, N.Y., 1993.
5. C. Kim and H. R. Allcock, *Macromolecules*, **20**, 1727 (1987).
6. R. E. Singler, R. A. Willingham, R. W. Lenz, and A. Furukawa, *Macromolecules*, **20**, 1728 (1987).
7. M. Kojima and J. H. Magill, *Polymer*, **30**, 579 (1989).
8. H. R. Allcock and C. Kim, *Macromolecules*, **23**, 3881 (1990).
9. K. Moriya, S. Yano, and M. Kajiwara, *Chem. Lett.*, 1039 (1990).
10. B. Durairaj, E. T. Samulski, and T. M. Shaw, *Macromolecules*, **23**, 1229 (1990).
11. F. Andruzzi, D. Lupinacci, and P. L. Magagnini, *Macromolecules*, **13**, 15 (1980).
12. V. Percec, *J. Polym. Sci.-Polym. Chem.*, **25**, 2269 (1987).
13. V. P. Shibaev, *Polym. Bull.*, **20**, 249 (1993).
14. E. Akiyama and Y. Nagase, *Makromol. Chem., Rapid Commun.*, **14**, 251 (1993).
15. E. Akiyama, Y. Nagase, and N. Koide, *Macromol. Chem. Phys.*, **196**, 3391 (1995).
16. D. Taton, A. L. Borgne, N. Spassky, and C. Noel, *Macromol. Chem. Phys.*, **196**, 2941 (1995).
17. S. Ujiie and K. Iimura, *Kobunshi Ronbunshu (in Japanese)*, **48**, 719 (1991).
18. S. Ujiie and K. Iimura, *Macromolecules*, **25**, 3174 (1992).
19. S. Ujiie and K. Iimura, *Polym. J.*, **25**, 347 (1993).
20. Y. Kawakami and K. Takahashi, *Polym. Bull.*, **25**, 521 (1991).
21. Y. Kawakami, K. Takahashi, and H. Hibino, *Macromolecules*, **24**, 4531 (1991).
22. Y. Kawakami, K. Takahashi, S. Nishiguchi, and K. Toida, *Polym. Int.*, **31**, 35 (1993).
23. M. Motoi, K. Noguchi, A. Arano, S. Kanoh, and A. Ueyama, *Bull. Chem. Soc. Jpn.*, **66**, 1778 (1993).
24. Y.-H. Lu and C.-S. Hsu, *Macromolecules*, **28**, 1673 (1995).
25. Y. Kawakami, K. Toida, and Y. Ito, *Macromolecules*, **26**, 1177 (1993).
26. Y. Kawakami and K. Toida, *Macromolecules*, **28**, 816 (1995).
27. Y. Kawakami, M. Ichitani, H. Kunisada, and Y. Yuki, *Polym. J.*, **28**, 513 (1996).
28. P. Robert, J.-J. Villenave, M. Fontanille, J.-M. Gilli, and O. Sixou, *Mol. Cryst. Liq. Cryst.*, **155**, 161 (1988).
29. M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H.-W. Schmidt, and P. Tschirner, *Pure Appl. Chem.*, **57**, 1009 (1985).
30. Y. Nagase and Y. Takamura, *Makromol. Chem.*, **193**, 1225 (1992).
31. C. T. Imrie, F. E. Karasz, and G. S. Attard, *Macromolecules*, **25**, 1278 (1992).
32. C. T. Imrie, F. E. Karasz, and G. S. Attard, *Macromolecules*, **27**, 1578 (1994).
33. S. Ujiie, Y. Tanaka, and K. Iimura, *Chem. Lett.*, 1037 (1991).
34. Y. Kosaka and T. Uryu, *Macromolecules*, **28**, 870 (1995).
35. P. Roche and Y. Zhao, *Macromolecules*, **28**, 2819 (1995).
36. M. Yamada, T. Iguchi, A. Hirano, S. Nakahama, and J. Watanabe, *Macromolecules*, **28**, 50 (1995).
37. A. Moradian and J. B. Cloke, *J. Am. Chem. Soc.*, **67**, 942 (1945).
38. G. Chandra, P. Y. Lo, P. B. Hitchcock, and M. F. Lappert, *Organometallics*, **6**, 191 (1987).
39. J. B. Rose, *J. Chem. Soc.*, **542** (1956).
40. J. B. Rose, *J. Chem. Soc.*, **546** (1956).
41. V. P. Shibaev, S. G. Kostromin, and N. A. Plate, *Eur. Polym. J.*, **18**, 651 (1982).
42. H. Ringsdorf and A. Schneller, *Br. Polym. J.*, **13**, 43 (1981).
43. Y. Kawakami and T. Sugisaka, *J. Membrane Sci.*, **50**, 189 (1990).