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Notes

Side-Chain Liquid Crystalline Polydiene

Yusuke Kawakami*

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology, Hokuriku Asahidai 15, Tatsunokuchi, Ishikawa 923-12, Japan

Kozo Toida and Yasuhiro Ito

Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan

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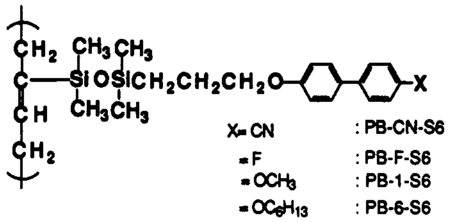
Much attention has been paid recently to side-chain liquid crystalline polymers for both research and development.[1,2] Finkelmann started a systematic research on side-chain liquid crystalline polymers.[3,4] It has been recognized that the structure of main-chain, mesogenic, and tail groups, the structure and length of spacer, and the spacing of the mesogenic groups along the main chain are the principal factors for determining the liquid crystalline phase. Although there have been extensive reports on the effects of the length of the methylene groups as spacer on the liquid crystalline phase,[3] relatively few studies have pointed out the importance of the chemical structure of the main chain and the structure and spacing of the mesogenic group along the main chain.

Polysiloxanes, polyacrylates, and polymethacrylates are usually used as main-chain components and alkoxy- or cyano-substituted biphenyls as mesogenic groups.[1] Liquid crystalline polymers having a polyolefin, poly(vinyl ether), polyphosphazene, or polyisocyanate main chain were recently reported.[5-16] We reported a novel side-chain smectic liquid crystalline polyoxetane with cyano- or fluoro-substituted biphenyl as the mesogenic group and pointed out the importance of the flexibility of the main chain and the structure of the mesogen on the liquid crystalline structure.[17-19]

It can be seen that polysiloxane is used as a flexible main-chain component in side-chain liquid crystalline polymers, and thus the siloxane linkage might be used as a flexible component in the spacer by taking advantage of its low rotational energy barrier. However, there are only few examples where siloxane linkage is used as a spacer component.[20,21] In these studies, the siloxane linkage is used in the middle of the alkylene spacer group. This seems to be because the steric requirement of the dimethyl-substituted siloxane linkage interfers with the aggregation of the mesogenic group to form a mesophase, if it is introduced close to the main chain of vinyl polymers.

In this note, we would like to report on another example of novel side-chain liquid crystalline polymers with a polydiene main chain and siloxane linkage directly attached to the main chain as a flexible component of the spacer, whose structure is shown in the following figure, in order to show the importance of the flexibility of the main chain and spacer and spacing of the mesogenic group along the main chain for a side-chain liquid crystalline polymer to exhibit a well-organized mesophase structure.



Monomers were synthesized according to Scheme I.

A 3-(dimethylchlorosilyl)propyl group was first introduced into the mesogenic group by a hydrosilylation reaction, and the polymerizable diene function was connected to the mesogenic group by the formation of a disiloxane linkage to give the monomer structure. The products were isolated by column chromatography. Although details of the synthesis will be published elsewhere, characterization data of several monomers are given.

2-[3-{3-[(4-Cyanobiphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]butadiene (B-CN-S6)]. R_f = 0.22 (eluent; hexane:ether = 12:1). Yield: 54%. Mp: 35.3 °C. Chemical shifts: 0.09 (s, 6 H, $CH_3SiC{=}CH_2$), 0.22 (s, 6 H, CH_3SiO), 0.64 (m, 2 H, $SiCH_2$), 1.82 (m, 2 H, $SiCH_2CH_2CH_2O$), 3.94 (t, 2 H, J = 6.8 Hz, $SiCH_2CH_2CH_2O$), 5.08 (d, 1 H, J = 10.6 Hz, H_4), 5.31 (d, 1 H, J = 17.8 Hz, H_5), 5.48, 5.71 (two d, 1 H each, J = 3.2 Hz, H_1, H_2), 6.43 (dd, 1 H, J_1 = 10.6 Hz, J_2 = 17.8 Hz, H_3), 6.96 (d with fine coupling, 2 H, J = 8.8 Hz, H_6), 7.50 (d with fine coupling, 2 H, J = 8.8 Hz, H_7), 7.62, 7.68 (two d with fine coupling, 4 H, J = 8.6 Hz, H_8, H_9).

2-[3-{3-[(4-Fluorobiphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]butadiene (B-F-S6). R_f = 0.39 (eluent; hexane:ether = 13:1). Yield: 20%. Liquid. Chemical shifts: 6.93 (d with fine coupling, 2 H, J = 8.8 Hz, H_6), 7.08 (t, 2 H, J = 8.8 Hz, H_9), 7.46 (m, 2 H, H_7, H_8).

2-[3-{3-[(4-Methoxybiphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]butadiene (B-1-S6). R_f = 0.40 (eluent; hexane:ether = 12:1). Yield: 43%. Mp: 72.5 °C. Chemical shifts: 3.82 (s, 3 H, OCH_3), 6.91, 6.94 (two d with fine coupling, 2 H each, J = 8.8 Hz, H_6, H_9), 7.44, 7.46 (two d with fine coupling, 2 H each, J = 8.8 Hz, H_7, H_8). Other protons of these monomers appeared at reasonable and corresponding positions with B-CN-S6.

2-[3-{3-[((4-Hexyloxy)biphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]butadiene (B-6-S6). R_f = 0.22 (eluent; hexane:ether = 40:1). Yield: 62%. Mp: 41.5 °C. Chemical shifts: 0.88 (t, 3 H, CH_3), 1.22–1.39 (m, 4 H, $CH_2CH_2CH_3$), 1.39–1.59 (m, 2 H, $OCH_2CH_2CH_2CH_2$), 1.78 (m, 2 H each, $SiCH_2CH_2CH_2O$, OCH_2CH_2) 3.92, 3.96 (two t, 2 H each, J = 6.8 Hz, $SiCH_2CH_2CH_2O$, OCH_2), 7.44 (d with fine coupling, 4 H, J = 8.8 Hz, H_7, H_8). Other protons of this monomer appeared at reasonable and corresponding positions with B-CN-S6 and B-1-S6.

Polymers were obtained in bulk at 60 °C in vacuo by using 1.0 mol % AIBN as an initiator (reaction time 24 h). Formed polymers were recovered by precipitation into hexane from chloroform solution and purified by repeated reprecipitation. All the monomers gave rather poor to reasonable yield in the polymerization (PB-CN-S6, 56%; PB-F-S6, 21%; PB-1-S6, 42%; PB-6-S6, 40%). The

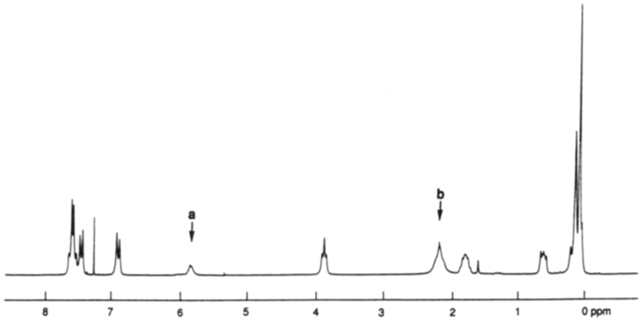
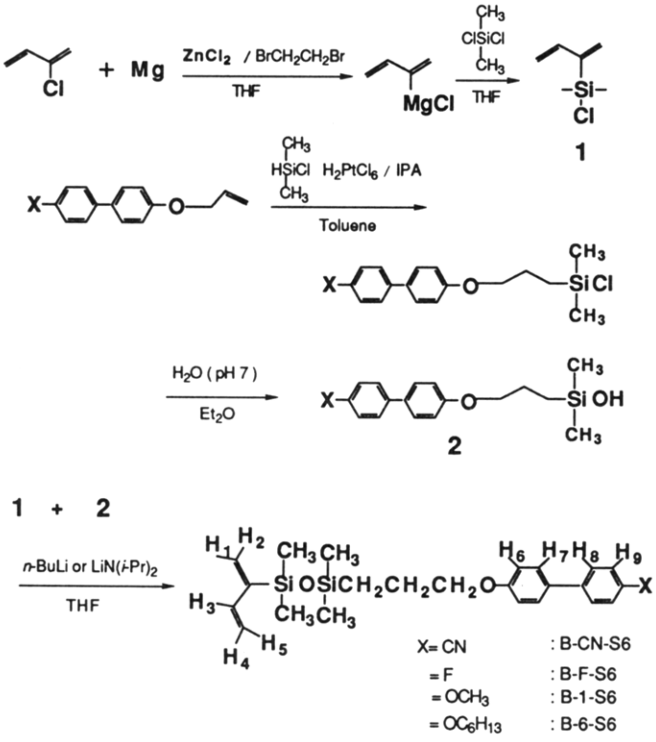


Figure 1. 200-MHz ^{1}H NMR spectrum of PB-CN-S6 taken in $CDCl_3$ at 23 °C.

Scheme I
Synthetic Route to Monomers



absence of monomer in the polymer was checked by thin-layer chromatography and GPC. The weight average molecular weight of polymers estimated by GPC using polystyrene standards ranges from 2.7×10^4 to 12.0×10^4 ($M_w/M_n \sim 1.4$). The names of polymers are abbreviated by the use of the combination of P and the abbreviated name of the monomer. For an example, poly(B-CN-S6) is abbreviated as PB-CN-S6.

^{1}H NMR spectrum of PB-CN-S6 is shown in Figure 1. The area of the proton a, which is assigned to an olefin proton, is one-fourth of that of proton b which is assigned to methylene protons of the main chain. This fact excludes the possibility that polymers were formed through 3,4- or 1,2-opening of the diene functions. It is of interest to point out that the double bonds in the polymer main chain takes one predominant stereochemistry, presumably 1,4-*E* concerning the main chain as suggested by Nakahama.[22,23] This may be because the bulky mesogen-containing substituent tends to be incorporated at a trans position to the polymer main chain (*E* form) in the repeating monomer unit.

The transition temperature is given at the point where transition starts determined by DSC in heating process. The transition was enantiotropic. The polymers show the following transition temperatures: PB-CN-S6, 57.4 °C (smectic → isotropic; ΔH = 2.8 mJ/mg); PB-F-S6, 51.9, 73/4 °C (smectic → isotropic; ΔH = 6.1 mJ/mg); PB-1-S6, 116.3 °C (smectic → isotropic; ΔH = 16.9 mJ/mg) with a tail at lower temperature; PB-6-S6, 110.9 °C (smectic → isotropic; ΔH = 2.0 mJ/mg) with a shoulder at 107.5 °C (only in heating process). The transition temperatures of the polymers ranges from room temperature to around 115 °C. This might be an advantage when an application is considered.

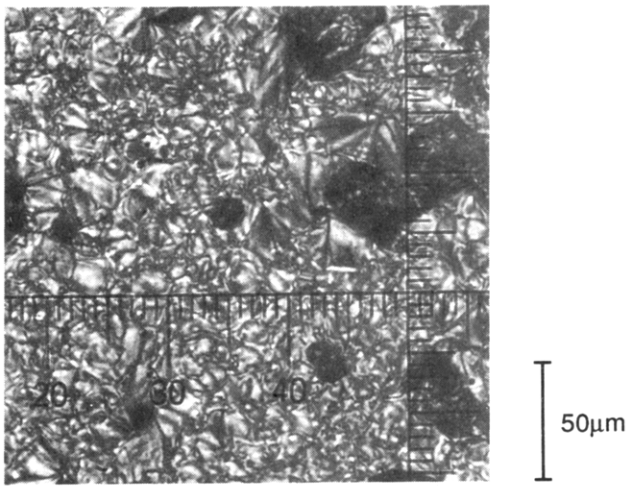


Figure 2. Optical polarization micrograph of PB-CN-S6 annealed at 57.3 °C for 15 h.

The monomers did not show any mesophase. An optical polarization micrograph of PB-CN-S6 is shown in Figure 2.

The polydiene with cyanobiphenyl as a mesogenic group linked through the siloxane linkage (PB-CN-S6) shows a well-organized smectic phase, which is in general agreement with other side-chain crystalline liquid polymers having a polar cyanobiphenyl mesogenic group.[1] The polymer with fluorobiphenyl (PB-F-S6) shows a similar smectic phase with a focal conic fan structure. It was already reported that polyoxetane with the same mesogenic group also showed a smectic phase.[17] The formed structures observed in the optical micrograph did not change even upon cooling to room temperature. The reason for the formation of the well-developed smectic structure of these polymers is considered not only because of the polar tail group but also because of the flexibility of the polydiene main chain, and the very mobile disiloxane in the spacer which also spaces the mosogenic groups apart from each other along the polymer main chain, compared with ordinary vinyl polymers. Although 4-cyanostyrene is reported to give a polymer of well-controlled structure,[24] the fluorine tail may be better when an anionic polymerization of the monomer is considered, avoiding unnecessary side reactions.

The polymer having hexyloxy as the tail group (PB-6-S6) also shows a smectic phase with a fan structure on annealing at the temperature slightly below the main transition temperature (108.5 °C). However, it turned into an unidentified fine structure on further cooling. Rearrangement of the mosogenic groups might be occurring. PB-1-S6 immediately formed a similar fine structure oncooling near the transition temperature. Details are now under investigation.

For comparison, the polymer with cyano-substituted mesogenic group connected to the main chain without siloxane linkage (poly[2-{6-[(4-cyanobiphenyl-4′-yl)oxy]hexyl}-1,3-butadiene]) was also prepared. This polymer has the transition temperature at 144.9 °C and formed a fan structure on cooling a little below the temperature.

Details of the syntheses of the monomers, of elucidation of the stereochemistry of the main chain, of the effects of the structure and length of the spacer and tail groups on the liquid crystalline phase will be reported soon.

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