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New Polydiene Side-Chain Liquid Crystalline Polymers. Synthesis and Microstructure

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ABSTRACT: Novel side-chain liquid crystalline polymers were synthesized based on the molecular design of the chemical structures of main-chain, spacer, and mesogenic groups. The main-chain structure is polydiene by the radical polymerization of diene derivatives with a mesogenic group. Spacer groups are not only oligomethylene but also those containing a siloxane or ether linkage. The stereochemistry of the main chain, elucidated by ^{1}H NMR, ^{13}C NMR, DEPT, and NOESY spectroscopies, is principally (*E*)-1,4 (cis concerning the carbon–carbon main chain). The polymers take the smectic liquid crystalline state with cyanobiphenyl, fluorobiphenyl, or alkoxybiphenyl as a mesogen. The transition temperatures of polymers with a spacer having a siloxane linkage are lower than those with hexamethylene as a spacer. Cooling the polymer with 4-(hexyloxy)biphenyl as a mesogen and siloxane linkage in the spacer seems to result in the change of the phase which is evidenced by the change in the optical polarization micrograph.

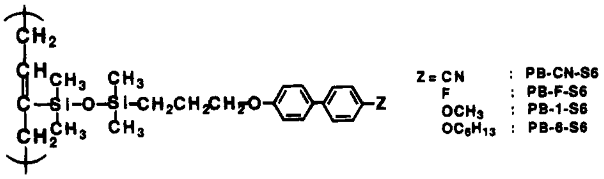
Introduction

Much attention has been paid recently to side-chain liquid crystalline polymers not only because of scientific interests but also because of their potential applications for electronic devices. Extensive researches have been carried out for both basic research and development to combine the properties of polymers and the electrooptic property of the low molecular mass mesogen. Polysiloxanes, polyacrylates, and polymethacrylates are usually used as main-chain components. There are only limited numbers of examples in which other main-chain structures like polyolefin, poly(vinyl ether), polyphosphazene, or polyisocyanate are used.[1-19] The temperature range and the mesophase structure of side-chain liquid crystalline polymers very much depend on the chemical structure of the polymers, namely, the flexibility of both the main-chain and spacer groups the chemical structure of the mesogenic groups.

It is generally considered that the spacer groups are acting as flexible connecting groups between main-chain and mesogenic groups which make it easy for the mesogenic groups to aggregate and to be organized into a liquid crystalline state. This situation can be said to fit in the case of a polymethacrylate main chain, whose T_g is as high as 100 °C, with more flexible oligomethylenes as spacer groups. The oligomethylene groups are really acting as flexible connecting groups between main-chain and mesogenic groups. In the cases of polysiloxane main-chain polymers, the situation is a little different. Namely, the main chain itself is very flexible ($T_g < -100$ °C) and can be said to be even more flexible than the spacer groups. Nevertheless, in both cases, the importance of the flexibility of the main-chain and spacer groups can be clearly seen.

We have been interested in the effects of the chemical structure of the main chain, the length and the structure of the spacers, and the structure of the mesogenic group on the liquid crystalline phase exhibited by the side-chain liquid crystalline polymers. It can be seen that polysiloxane is used as a flexible main-chain component in side-chain liquid crystalline polymers; the siloxane linkage could be used as a flexible component in the spacer by taking advantage of its low rotational energy barrier. However, there are only a few examples where a 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 interferes with the aggregation of mesogenic groups to form a mesophase if the dimethyl-substituted silyl group is introduced close to the main chain of vinyl polymers.

By considering the chemical structures of main-chain, spacer, and mesogenic groups, we reported two new types of side-chain liquid crystalline polymers based on the molecular design of the chemical structure of the polymers. First, polyether and polydiene were selected as main chains because both polymers have low T_g and were considered to act as flexible main chains.[22-25] Second, the siloxane linkage was selected as a constituent of the spacer group. Although the siloxane linkage is usually considered not to be a good spacer in vinyl type liquid crystalline side-chain polymers because of its bulkiness in spite of its flexibility, it should act as a good spacer if the steric hindrance in the case of the vinyl polymers could be avoided. Substituted biphenyl mesogenic groups were attached, through spacers having disiloxane linkages which are directly attached to the main chain, at every four carbons in the polydiene main chain, not every other carbon as in the case of the vinyl polymers. Steric hindrance can be avoided by this molecular design.[25]



In order to study, specially, the effects of spacer groups on mesophase structure, polymers having not only an oligomethylene spacer containing disiloxane but also a hexamethylene spacer or an oligomethylene spacer containing an ether linkage were synthesized, and their thermal behavior was studied. In this paper, the synthesis and elucidation of the microstructure of

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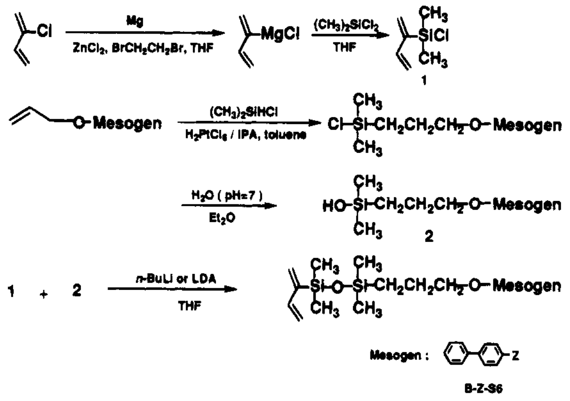
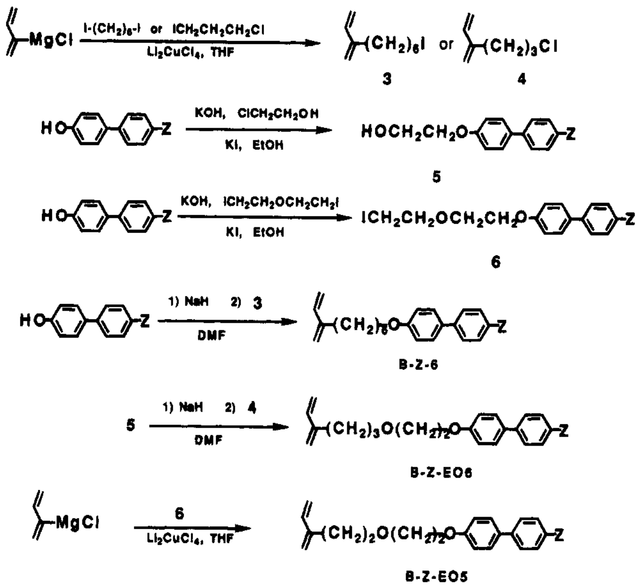
Scheme 1. Synthetic Route to Diene Monomers with a Disiloxane Linkage in the Spacer



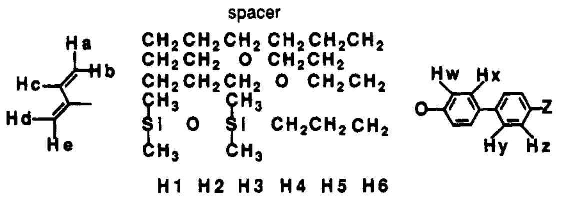
Scheme 2. Synthetic Routes to Diene Monomers with Various Types of Spacers



these new side-chain liquid crystalline polymers and observation of the mesophase by an optical polarization micrograph are described. An accurate investigation of the phase behavior of monomers and polymers will be made in the future.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were obtained on a Varian 200-MHz ^{1}H NMR (50 MHz for ^{13}C) spectrometer Model Gemini 200. Protons of diene, spacer, and biphenyl parts are designated as indicated below. Protons of the tail group (Z = OCH_3, OC_6H_{13}) are designated separately.



Chemical shifts are given in ppm from tetramethylsilane (TMS) in $CDCl_3$. A NOESY spectrum was obtained on a Varian 400-MHz ^{1}H NMR spectrometer Model Unity 400. The assignment of the ^{13}C signals of polymers was made based on a DEPT (distortionless enhancement by polarization transfer) spectrum.

GPC analysis was carried out on a Tosoh (TSK) GPC Model HLC 802 equipped with TSK gels G3000H (exclusion molecular weight, polystyrene 6 × 10^4) and G5000H (exclusion molecular weight, polystyrene 4 × 10^6), using chloroform as an eluent at a 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 a heating rate of 3 °C/min. The transition 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 a Mettler thermal analysis system Model FP800 with FP82 hot stage and FP 80 controller. Pictures were taken at a little lower temperature than the peak after annealing in the cooling process from the isotropic state at appropriate intervals.

Synthesis. The synthesis of the monomers is outlined in Schemes 1 and 2.

The abbreviated names of the monomers are given by the combination of B, which indicates butadiene, the abbreviated name of the mesogen [CN (Z = CN), F (Z = F), 1 (Z = OCH_3), and 6 (Z = OC_6H_{13})], and the abbreviated name of the spacer [S6 (spacer: $Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CH_2O$) and 6 (spacer: hexamethylene). Examples are B-6-S6 in which a (hexyloxy)-biphenyl mesogenic group is attached to the diene function through the spacer containing a disiloxane linkage and B-CN-6 with cyanobiphenyl attached through a hexamethylene spacer.

Typical procedures of the synthesis and characterization data are given.

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

4-Methoxy- or 4-(hexyloxy)-4′-hydroxybiphenyls were synthesized by alkylating 4,4′-dihydroxybiphenyl with dimethyl sulfate or bromohexane.

4-Methoxy-4-hydroxybiphenyl. 4,4′-Dihydroxybiphenyl (74.5 g, 400 mmol) was dissolved into a 10% aqueous sodium hydroxide solution (400 mL) under cooling. To this solution was added dropwise dimethyl sulfate (50.5 g, 400 mmol) during 3 h at 0 °C. Formed solid was separated by suction and heated in a 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 (DMSO-d_6): 2.49 (s, 1H O*H*), 3.76 (s, 3H, CH_3), 6.80 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hz*), 6.95 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hw*), 7.43, 7.45 (two d, 4H, *J* = 8.8 Hz, *Hx*, *Hy*).

4-(Hexyloxy)-4′-hydroxybiphenyl.[26] To a mixture of 4,4′-dihydroxybiphenyl (40.0 g, 210 mmol) and 1-bromohexane (8.0 g, 52 mmol) in ethanol (300 mL) was added dropwise an ethanol (100 mL) solution of potassium hydroxide (4.0 g, 71 mmol) during 2 h under refluxing conditions of the solvent. Stirring and heating were continued for 6 h after the completion of the addition. After the solvent and unreacted 1-bromohexane were removed under vacuum, the residual solid was dissolved into a 10% aqueous sodium hydroxide solution (300 mL). After the filtration, the solution was acidified with 20% hydrochloric acid, and formed solid was collected and purified by repeated recrystallization from ethanol. Mp: 157.5 °C. Yield: 83.3%. Chemical shifts (DMSO-d_6): 0.92 (t, 3H, *J* = 6.6 Hz, CH_3), 1.20−1.61 (m, 6H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.82 (m, 2H, OCH_2CH_2), 4.00 (t, 2H, *J* = 6.6 Hz, OCH_2), 6.91, 6.94 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hz*, *Hw*), 7.44, 7.46 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hx*, *Hy*).

2-{(4-Cyanobiphenyl-4′-yl)oxy}ethanol. To a mixture of 4-cyano-4′-hydroxybiphenyl (5.0 g, 25 mmol), potassium iodide (0.4 g, 2.5 mmol), and sodium hydroxide (1.2 g, 30 mmol) in ethanol (300 mL) was added dropwise ethylene chlorohydrin

(2.0 g, 25 mmol) during 2 h under refluxing conditions of the solvent. After completion of the addition, stirring was continued under the same conditions for 24 h. After the solvent was removed under vacuum, chloroform (200 mL and 1 N hydrochloric acid (50 mL) were added, and the organic layer was separated. The chloroform solution was washed with water (200 mL) and dried over magnesium sulfate. The crude product obtained by evaporation of the solvent was purified by column chromatography. R_f 0.50 = (hexane:ether = 2:1). Mp: 121.2−122.2 °C. Yield: 45%. Chemical shifts: 2.10 (t, 1H, OH), 4.00 (t, 2H, J = 4.4 Hz, OCH_2), 4.15 (t, 2H, J = 4.4 Hz, HOCH_2), 7.03 (d, with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.54 (d, with fine coupling, 2H, J = 8.8 Hz, *Hx*), 7.62, 7.68 (two d, with fine coupling, 4H, J = 8.8 Hz, *Hy*, *Hz*).

Other hydroxyethylated biphenyls were similarly synthesized.

2-{(4-Fluorobiphenyl-4′-yl)oxy}ethanol. R_f = 0.50 (hexane:ether = 2:1). Mp: 128−128.5 °C. Yield: 21%. Chemical shifts: 2.10 (br s, 1H, OH), 4.00 (t, 2H, J = 4.4 Hz, OCH_2), 4.15 (t, 2H, J = 4.4 Hz, HOCH_2), 6.93 (d, with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.08 (t with fine coupling, 2H, J = 8.8 Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

2-{(4-Methoxybiphenyl-4′-yl)oxy}ethanol. R_f = 0.50 (hexane:ether = 2:1). Mp: 178−178.5 °C. Yield: 43%. Chemical shifts: 2.10 (br s, 1H, OH), 3.85 (s, 3H, OCH_3), 4.00 (t, 2H, J = 4.4 Hz, OCH_2), 4.15 (t, 2H, J = 4.4 Hz, HOCH_2), 6.91, 6.94 (two d with fine coupling, 4H, J = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d, with fine coupling, 4H, J = 8.8 Hz, *Hx*, *Hy*).

2-{(4-(Hexyloxy)biphenyl-4′-yl)oxy}ethanol. R_f = 0.50-(hexane:ether = 2:1). Mp: 164−164.7 °C. Yield: 17%. Chemical shifts: 0.93 (t, 3H, J = 6.6Hz, CH_3), 1.32−1.48 (m, 6H, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 1.79 (m, 2H, OCH$_2$CH_2), 2.10 (br s, 1H, OH), 4.00 (m, 4H, OCH_2), 4.15 (t, 2H, J = 4.2 Hz, HOCH_2), 6.91, 6.94 (two d with fine coupling, 4H, J = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d, with fine coupling, 4H, J = 8.8 Hz, *Hx*, *Hy*).

Bis(2-iodoethyl) Ether. To a mixture of diethylene glycol (13 g, 122 mmol), imidazole (18 g, 257 mmol), and triphenylphosphine (34 g, 260 mmol) in DMF (dimethylformamide) (150 mL) was added iodine (33 g, 260 mmol), and the reaction system was stirred for 0.5 h. After the solvent was removed, the reaction product was taken up into ether (100 mL). Formed solid on treatment with an aqueous sodium sulfite solution (100 mL) was separated by filtration. The organic layer was washed with water (300 mL) and dried over magnesium sulfate. The crude product was purified by distillation after evaporation of the solvent. Bp: 85.0 °C (0.5 mmHg). Yield: 78%. Chemical shifts: 3.27 (t, 4H, J = 6.4 Hz, ICH_2), 3.78 (t, 4H, J = 6.4Hz, OCH_2).

2-{(4-Cyanobiphenyl-4′-yl)oxy}ethyl 2-Iodoethyl Ether. To a mixture of bis(2-iodoethyl) ether (20 g, 61 mmol), 4-cyano-4′-hydroxybiphenyl (4.0 g, 20 mmol), and tetrabutylammonium bromide (0.33 g, 1.0 mmol) in DMF (200 mL) was added dropwise a 20% aqueous potassium carbonate solution (20 mL) during 1 h at room temperature. After the completion of the addition, stirring was contained for a further 2 h. After the solvent was removed, chloroform (50 mL) and water (20 mL) were added to the reaction mixture, and the organic layer was separated. The chloroform solution was washed with water (200 mL) and dried over magnesium sulfate. The crude product was purified by column chromatography after evaporation of the solvent. R_f = 0.40 (hexane:chloroform = 1:1). Mp: 78−79 °C. Yield: 69.0%. Chemical shifts: 3.29 (t, 2H, J = 6.4 Hz, ICH_2), 3.87 (two t, 2H each, J = 5.6 Hz, CH$_2$OCH_2CH_2O), 4.18 (t, 2H, J = 6.4 Hz, ICH$_2$CH_2O), 6.96 (d with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.50 (d with fine coupling, 2H, J = 8.8 Hz, *Hx*), 7.62, 7.68 (two d with fine coupling, 4H, J = 8.8 Hz, *Hy*, *Hz*).

Other iodoethyl ethers having mesogenic groups were synthesized similarly.

2-{(4-Fluorobiphenyl-4′-yl)oxy}ethyl 2-Iodoethyl Ether. R_f = 0.35 (hexane:chloroform = 2:1). Mp: 82.5−83.0 °C. Yield: 61%. Chemical shifts: 6.93 (d with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.08 (t with fine coupling, 2H, J = 8.8 Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

2-{(4-Methoxybiphenyl-4′-yl)oxy}ethyl 2-Iodoethyl Ether. R_f = 0.35(hexane:ether = 1:4). Mp: 131.7−132.4 °C. Yield: 45%. Chemical shifts: 3.84 (s, 3H, OCH_3), 6.97 (dd, 4H, J_1 = 3.8 Hz, J_2 = 8.6 Hz, *Hw*, *Hz*), 7.47 (d, 4H, J = 9.0 Hz, *Hx*, *Hy*).

2-{(4-(Hexyloxy)biphenyl-4′-yl)oxy}ethyl 2-Iodoethyl Ether. R_f = 0.40 (hexane:chloroform = 3:2). Mp: 122.5−123.1 °C. Yield: 79%. Chemical shifts: 0.92 (t, 3H, J = 6.6 Hz, CH_3), 1.21−1.62 (m, 6H, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 1.82 (m, 2H, OCH$_2$CH_2), 4.00 (t, 2H, J = 6.6 Hz, OCH_2).

Methylene protons of the [(iodoethyl)oxy]ethyl groups of these compounds appeared at the corresponding positions with the cyano-substituted derivative.

4-Cyano-4′-(allyloxy)biphenyl. To a DMF (5 mL) solution of hexane-washed sodium hydride (0.45 g, 11 mmol) was added 4-cyano-4′-hydroxybiphenyl (2.0 g, 10 mmol) as a DMF (25 mL) solution during 0.5 h. After completion of the addition, stirring was continued for a further 1 h. To this reaction system was added allyl bromide (1.2 g, 10 mmol), and the reaction mixture was allowed to react for a further 4 h at room temperature. Chloroform (50 mL) was added, the solution was washed with water (50 mL), 1 N hydrochloric acid (50 mL), water (50 mL), and a saturated sodium chloride solution (50 mL), successively, and the chloroform solution was dried over sodium sulfate. Evaporation of the solvent gave the crude product, which was purified by recrystallization from ethanol. Mp: 82−82.5 °C. Yield: 87%. Chemical shifts: 4.55 (d with fine coupling, 2H, J = 5.2 Hz, CH$_2$=CHCH_2), 5.30 (dd, 1H, J_1 = 1.4 Hz, J_2 = 10.4 Hz, CH_2=CHCH$_2$, cis), 5.42 (dd, 1H, J_1 = 1.4 Hz, J_2 = 17.4 Hz, CH_2=CHCH$_2$, trans), 6.06 (m, 1H CH$_2$=CHCH$_2$), 6.96 (d with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.50 (d with fine coupling, 2H, J = 8.8 Hz, *Hx*), 7.62, 7.68 (two d with fine coupling, 4H, J = 8.8 Hz, *Hy*, *Hz*).

Other allyl ethers of mesogenic derivatives were similarly synthesized.

4-Fluoro-4′-(allyloxy)biphenyl. Mp: 94.0−94.3 °C. Yield: 82%. Chemical shifts: 6.93 (d with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.08 (d with fine coupling, 2H, J = 8.8 Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

4-Methoxy-4′-(allyloxy)biphenyl. Mp: 95.1−95.9 °C. Yield: 76%. Chemical shifts: 3.82 (s, 3H, OCH_3), 6.91, 6.94 (two d with fine coupling, 2H each, J = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, J = 8.8 Hz, *Hx*, *Hy*).

4-(Hexyloxy)-4′-(allyloxy)biphenyl. Mp: 131.0−131.8 °C. Yield: 96%. Chemical shifts: 1.15 (t, 3H, J = 6.6 Hz, CH_3), 1.30−1.71 (m, 6H, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 2.34 (m, 2H, OCH$_2$CH_2), 3.97 (t, 2H, J = 6.6 Hz, OCH_2), 6.91, 6.94 (two d with fine coupling, 2H each, J = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, J = 8.8 Hz, *Hx*, *Hy*).

Allyl protons of these compounds appeared at corresponding positions with cyano derivatives. The allyl derivatives were converted into (dimethylchlorosilyl)propyl derivatives by hydrosilylation reaction with dimethylchlorosilane and further converted into silanol.

[3-{(4-Cyanobiphenyl-4′-yl)oxy}propyl]dimethylsilanol. To a toluene solution (15 mL) containing 4-(allyloxy)-4′-cyanobiphenyl (2.05 g, 8.7 mmol) were added catallytic amounts of chloroplatinic acid hexahydrate in IPA (isopropyl alcohol; 100 μL) and dimethylchlorosilane (8 g, 84 mmol), and the mixture was allowed to react for 12 h at 40−50 °C. Removal of excess dimethylchlorosilane under reduced pressure gave the product in quantitative yield. The product was hydrolyzed without isolation by pouring into an aqueous buffer solution kept at pH 7 and allowing to react for 1 h at 0 °C as an ether solution. The ether solution was concentrated at 0 °C to obtain a solid product, which was used for the following reaction without isolation. Chemical shifts: 0.16 (s, 6H, *H1*, *H3*), 0.75 (m, 2H, *H4*), 1.87 (m, 2H, *H5*), 3.97 (t, 2H, J = 6.6 Hz, *H6*), 6.96 (d with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.50 (d with fine coupling, 2H, J = 8.8 Hz, *Hx*), 7.62, 7.68 (two d with fine coupling, 2H each, J = 8.8 Hz, *Hy*, *Hz*).

Other silanols were similarly synthesized.

[3-{(4-Fluorobiphenyl-4′-yl)oxy}propyl]dimethylsilanol. Chemical shifts: 6.93 (d with fine coupling, 2H, J = 8.8 Hz, *Hw*), 7.08 (d with fine coupling, 2H, J = 8.8 Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

[3-{(4-Methoxybiphenyl-4′-yl)oxy}propyl]dimethylsilanol. Chemical shifts: 3.82 (s, 3H, OCH_3), 6.91, 6.93 (two d with fine coupling, 4H, $J = 8.8$ Hz, *Hw*, *Hz*), 7.46 (two d with fine coupling, 2H each, $J = 8.6$ Hz, *Hx*, *Hy*).

[3-{(4-(Hexyloxy)biphenyl-4′-yl)oxy}propyl]dimethylsilanol. Chemical shifts: 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 1.22–1.39 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.39–1.59 (m, 2H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 3.92 (t, 2H, $J = 6.8$ Hz, OCH_2), 6.91, 6.94 (two d with fine coupling, 2H each, $J = 8.8$ Hz, *Hw*, *Hz*), 7.44 (d with fine coupling, 4H, $J = 8.8$ Hz, *Hx*, *Hy*).

H1, H3, H4, H5, and H6 protons of these compounds were observed at corresponding positions with cyanobiphenyl-substituted silanol.

2-(1,3-Butadienyl)magnesium chloride.[27-29] In a flask under a nitrogen atmosphere were charged thoroughly dried magnesium turnings (4.0 g, 150 mmol), 1,2-dibromoethane (1 mL), and THF (tetrahydrofuran) (2 mL). The contents were heated under magnetic stirring to activate the magnesium surface, 1–3 mol % of zinc chloride was added, and the magnesium was covered with THF (50 mL). To this reaction system were added dropwise chloroprene (9 g, 100 mmol) and 1,2-dibromoethane (4 g, 20 mmol) as a THF (50 mL) solution during 40 min. After completion of the addition, stirring was continued for 30 min under refluxing conditions of the solvent. During this procedure, the color of the reaction system turned into grayish black. Although the supernatant solution was used without further purification, the extent of the Grignard formation was proved to be almost quantitative by titration.

2-(6-Iodohexyl)-1,3-butadiene (3). To a mixture of 1,6-diiodohexane (5.0 g, 15 mmol) and Li_2CuCl_4 (1–3 mol % 1,6-diiodohexane) in dry THF (20 mL) was added dropwise a THF solution (20 mL) of 2-(1,3-butadienyl)magnesium chloride (5 mmol) with stirring under a nitrogen atmosphere. Stirring was continued for 5 h at room temperature after completion of the addition, the solvent was removed under vacuum, and hexane (50 mL) and water (20 mL) were added to the residual solid. The organic layer was separated and dried over magnesium sulfate. The crude prouct obtained by the evaporation of the solvent was purified by column chromatography. $R_f = 0.39$ (hexane), liquid. Yield: 51.4%. Chemical shifts: 1.25–1.70 (m, 6H, *H2*, *H3*, *H4*), 1.83 (m 2H, *H5*), 2.21 (t, 2H, $J = 7.4$ Hz, *H1*), 3.19 (t, 2H, $J = 7.4$ Hz, *H6*), 5.00 (dd, 2H, $J_1 = 0.8$ Hz, $J_2 = 8.0$ Hz, *Hd*, *He*), 5.05 (dd, 1H, $J_1 = 0.8$ Hz, $J_2 = 10.0$ Hz, *Ha*), 5.25 (dd, 1H, $J_1 = 0.8$ Hz, $J_2 = 17.6$ Hz, *Hb*), 6.37 (dd, 1H, $J_1 = 10.0$ Hz, $J_2 = 17.6$ Hz, *Hc*).

2-(3-Chloropropyl)-1,3-butadiene (4). To a solution of 3-chloro-1-iodopropane (27 g, 214 mmol), THF (100 mL), and Li_2CuCl_4 (1–3 mol % 3-chloro-1-iodopropane) was added dropwise 2-(1,3-butadienyl)magnesium chloride (75 mmol) for 1 h at room temperature. After completion of the addition, stirring was continued for 3 h. After the solvent was removed, hexane (100 mL), water (50 mL), and 1 N hydrochloric acid (20 mL) were added and the organic layer was separated. The hexane solution was washed with water (200 mL) and dried over magnesium sulfate. Evaporation of the solvent gave the crude product which was purified by distillation. Bp: 153–153.5 °C. Yield: 55%. Chemical shifts: 2.26 (m, 2H, CH_2), 3.34 (t, 2H, $J = 6.4$ Hz, $C{=}CCH_2$), 3.65 (t, 2H, $J = 6.4$ Hz, CH_2Cl), 5.02 (two s, 2H, *Hd*, *He*), 5.10 (dd 1H, $J_1 = 0.8$ Hz, $J_2 = 10.0$ Hz, *Ha*), 5.23 (dd, 1H, $J_1 = 0.8$ Hz, $J_2 = 10.0$ Hz, *Hb*), 6.40 (dd, 1H, $J_1 = 10.0$ Hz, $J_2 = 17.6$ Hz, *Hc*).

2-(3-Dimethylchlorosilyl)-1,3-butadiene (1). To a THF solution (100 mL) of dichlorodimethylsilane (25 mL, 214 mmol) was added dropwise 2-(1,3-butadienyl)magnesium chloride (75 mmol) during 2 h at room temperature, and the reaction system was stirred for a further 12 h under a nitrogen atmosphere. After the solvent and excess dimethyldichlorosilane were removed under reduced pressure, dry pentane was added to the reaction mixture, and formed salt was removed by filtration. The product was isolated by distillation after the removal of the solvent. Bp: 34–37 °C (25 mmHg). Yield: 44%. Chemical shifts: 0.56 (s, 6H, CH_3), 5.16 (d, 1H, $J = 11.0$ Hz, *Ha*), 5.40 (d, 1H, $J = 18.0$ Hz, *Hb*), 5.64 (d, 1H, $J = 2.6$ Hz, *He*), 6.45 (dd, 1H, $J_1 = 11.0$ Hz, $J_2 = 18.0$ Hz, *Hc*).

2-[6-{(4-Cyanobiphenyl-4′-yl)oxy}hexyl]-1,3-butadiene (B-CN-6). 4-Cyano-4′-hydroxybiphenyl (0.3 g, 1.5 mmol) was converted into its sodium salt by reaction with NaH (60%) (0.07 g, 1.7 mmol) in DMF (5 mL). In this solution, 2-(6-iodohexyl)-1,3-butadiene (0.4 g, 1.5 mmol) was added dropwise at room temperature for 5 min and further reacted for 6 h at room temperature under stirring. After the solvent was removed under vacuum, diethyl ether (50 mL) and water (20 mL) were added to the residual solid, and the organic layer was separated. The ether solution was washed with water (100 mL) and dried over magnesium sulfate. Evaporation of the solvent gave a crude product which was purified by column chromatography. $R_f = 0.45$ (hexane:chloroform = 1:1). Yield: 77%. Chemical shifts: 1.30–1.71 (m, 6H, *H2*, *H3*, *H4*), 1.85 (m, 2H, *H5*), 2.25 (t, 2H, $J = 6.6$ Hz, *H1*), 4.05 (t, 2H, $J = 6.6$ Hz, *H6*), 5.02 (s, 2H, *Hd*, *He*), 5.10 (dd, 1H, $J_1 = 0.8$ Hz, $J_2 = 10.0$ Hz, *Ha*), 5.23 (dd, 1H, $J_1 = 0.8$ Hz, $J_2 = 10.0$ Hz, *Hb*), 6.40 (dd, 1H, $J_1 = 10.0$ Hz, $J_2 = 17.6$ Hz, *Hc*), 6.96 (d with fine coupling, 2H, $J = 8.8$ Hz, *Hw*), 7.50 (d with fine coupling, 2H, $J = 8.8$ Hz, *Hx*), 7.62, 7.68 (two d with fine coupling, 4H, $J = 8.8$ Hz, *Hy*, *Hz*).

Other monomers with hexamethylene as a spacer were similarly synthesized.

2-[6-{(4-Fluorobiphenyl-4′-yl)oxy}hexyl]-1,3-butadiene (B-F-6). $R_f = 0.49$ (hexane:ether = 12:1). Yield: 80.0%. Chemical shifts: 6.93 (d with fine coupling, 2H, $J = 8.8$ Hz, *Hw*), 7.08 (t with fine coupling, 2H, $J = 8.8$ Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

2-[6-{(4-Methoxybiphenyl-4′-yl)oxy}hexyl]-1,3-butadiene (B-1-6). $R_f = 0.40$ (hexane:ether = 12:1). Yield: 43.0%. Chemical shifts: 3.82 (s, 3H, OCH_3), 6.91, 6.94 (two d with fine coupling, 2H each, $J = 8.8$ Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, $J = 8.8$ Hz, *Hx*, *Hy*).

Protons of diene and the spacer group of these compounds appeared at the corresponding positions with B-CN-6.

2-[6-{(4-(Hexyloxy)biphenyl-4′-yl)oxy}hexyl]-1,3-butadiene (B-6-6). $R_f = 0.45$(hexane:ether = 13:1). Yield: 64.6%. Chemical shifts: 0.92 (t, 3H, $J = 6.6$ Hz, CH_3), 1.30–1.71 (m, 12H, *H2*, *H3*, *H4*, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.85 (m, 4H, *H5*, OCH_2CH_2), 2.25 (t, 2H, $J = 6.6$ Hz, *H1*), 3.97 (two t, 2H each, $J = 6.4$ Hz, *H6*, OCH_2), 6.96 (d with fine coupling, 4H, $J = 8.6$ Hz, *Hw*, *Hz*), 7.44 (d with fine coupling, 4H, $J = 8.8$ Hz, *Hx*, *Hy*).

Diene protons of this compound appeared at the corresponding positions with B-CN-6.

2-[2-{2-[(4-Cyanobiphenyl-4′-yl)oxy]ethoxy}ethyl]-1,3-butadiene (B-CN-EO5). To a mixture of 2-{(4-cyanobiphenyl-4′-yl)oxy}ethyl 2-iodoethyl ether (3.5 g, 8.9 mmol), THF (50 mL), and Li_2CuCl_4 (1–3 mol % 2-{(4-cyanobiphenyl-4′-yl)oxy}ethyl 2-iodoethyl ether) was added dropwise a THF solution of 2-(1,3-butadienyl)magnesium chloride (15 mmol) during 1 h at room temperature. After completion of the addition, stirring was continued for 2 h at 60 °C. After the solvent was removed, ether (50 mL) and water (30 mL) were added and the organic layer was separated. The ether solution was washed with water (200 mL) and dried over magnesium sulfate. The crude product obtained by evaporation of the solvent was purified by column chromatography. $R_f = 0.5$ ($CHCl_3$), liquid. Yield: 36%. Chemical shifts: 2.57 (t, 2H, $J = 5.0$ Hz, *H1*), 3.71 (t, 2H, $J = 5.0$ Hz, *H4*), 3.85 (t, 2H, $J = 5.0$ Hz, *H5*), 4.18 (t, 2H, $J = 5.0$ Hz, *H2*), 5.08 (m, 3H, *Ha*, *Hd*, *He*), 5.28 (d, 1H, $J = 17.6$ Hz, *Hb*), 6.40 (dd, 1H, $J_1 = 11.0$ Hz, $J_2 = 17.6$ Hz, *Hc*), 6.96 (d, with fine coupling, 2H, $J = 8.8$ Hz, *Hw*), 7.50 (d, with fine coupling, 2H, $J = 8.8$ Hz, *Hx*), 7.62, 7.68 (two d, with fine coupling, 4H, $J = 8.8$ Hz, *Hy*, *Hz*).

Other monomers having spacers were similarly synthesized.

2-[2-{2-[(4-Fluorobiphenyl-4′-yl)oxy]ethoxy}ethyl]-1,3-butadiene (B-F-EO5). Recrystallization (methanol). Yield: 60%. Chemical shifts: 6.93 (d with fine coupling, 2H, $J = 8.8$ Hz, *Hw*), 7.08 (t with fine coupling, 2H, $J = 8.8$ Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

2-[2-{2-[(Methoxybiphenyl-4′-yl)oxy]ethoxy}ethyl]-1,3-butadiene (B-1-EO5). $R_f = 0.42$ (hexane:ether = 3:1). Yield: 75%. Chemical shifts: 3.84 (s, 3H, OCH_3), 6.91, 6.94 (two d with fine coupling, 2H each, $J = 8.8$ Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, $J = 8.8$ Hz, *Hx*, *Hy*).

2-[2-{2-[(4-(Hexyloxy)biphenyl-4′-yl)oxy]ethoxy}ethyl]-1,3-butadiene (B-6-EO5). R_f = 0.50 (hexane:ether = 2:1). Yield: 75%. Chemical shifts: 0.91 (t, 3H, *J* = 6.6 Hz, CH_3), 1.2−1.6 (m, 6H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.82 (m, 2H, OCH_2CH_2), 3.99 (t, 2H, *J* = 6.6 Hz, OCH_2), 6.91, 6.94 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hx*, *Hy*).

Diene and spacer protons of these compounds appeared at the corresponding positions with B-CN-EO5.

2-[3-{2-[(4-Cyanobiphenyl-4′-yl)oxy]ethoxy}propyl]-1,3-butadiene (B-CN-EO6). 2-{(4-Cyanobiphenyl-4′-yl)oxy}-ethanol (2.0 g, 10 mmol) was converted into its sodium salt by reaction with sodium hydride (60%) (0.45 g, 11 mmol) in DMF (5 mL) for 2 h at 80 °C. To this solution, when cooled down to room temperature was added dropwise 2-(3-chloropropyl)-1,3-butadiene (1.2 g, 10 mmol) at room temperature with stirring for 10 min, and the mixture was further reacted for 4 h at 80 °C. Chloroform (50 mL) and water (20 mL) were added to the solution, and the organic layer was separated. The chloroform solution was washed with water (200 mL) and dried over magnesium sulfate. The crude product obtained by evaporation of the solvent was purified by column chromatography. R_f = 0.50 (hexane:ether = 2:1), liquid. Yield: 44%. Chemical shifts: 1.75 (m, 2H, *H2*), 2.24 (t, 2H, *J* = 7.4 Hz, *H1*), 3.51 (t, 2H, *J* = 4.2 Hz, *H3*), 3.74 (t, 2H, *J* = 4.2 Hz, *H5*), 4.10 (t, 2H, *J* = 4.2Hz, *H6*), 4.96 (s, 2H, *Hd*, *He*), 5.02 (dd, 1H, J_1 = 0.6 Hz, J_2 = 10.0 Hz, *Ha*), 5.20 (dd, 1H, J_1 = 0.6 Hz, J_2 = 17.6 Hz, *Hb*), 6.32 (dd, 1H, J_1 = 10.0 Hz, J_2 = 17.6 Hz, *Hc*), 6.96 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hw*), 7.50 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hx*), 7.62, 7.68 (two d with fine coupling, 4H, *J* = 8.8 Hz, *Hy*, *Hz*).

2-[3-{2-[(4-Fluorobiphenyl-4′-yl)oxy]ethoxy}propyl]-1,3-butadiene (B-F-EO6). R_f = 0.50 (hexane:ether = 3:1). Yield: 37%. Chemical shifts: 6.93 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hw*), 7.08 (t with fine coupling, 2H, *J* = 8.8 Hz, *Hz*), 7.46 (m, 4H, *Hx*, *Hy*).

2-[3-{2-[(4-Methoxybiphenyl-4′-yl)oxy]ethoxy}propyl]-1,3-butadiene (B-1-EO6). R_f = 0.49 (hexane:ether = 2:3). Yield: 76%. Chemical shifts: 3.84 (s, 3H, OCH_3), 6.91, 6.94 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hx*, *Hy*).

2-[3-{2-[(4-(hexyloxy)biphenyl-4′-yl)oxy]ethoxy}propyl]-1,3-butadiene (B-6-EO6). R_f = 0.50 (hexane:ether = 3:2). Yield: 58%. Chemical shifts: 0.91 (t, 3H, *J* = 6.6 Hz, CH_3), 130−1.55 (m, 6H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.81 (m, 2H, OCH_2CH_2), 3.98 (t, 2H, *J* = 6.6 Hz, OCH_2), 6.95 (t with fine coupling, 4H, *J* = 6.6 Hz, *Hw*, *Hz*), 7.46 (d with fine coupling, 4H *J* = 8.8 Hz, *Hx*, *Hy*).

Diene and spacer protons of these compounds were observed at the corresponding positions with B-CN-EO6.

2-[3-{3-[(4-Cyanobiphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]-1,3-butadiene [B-CN-S6]. The silanols were reacted with the chlorosilyl group of 2-(3-dimethylchlorosilyl)-1,3-butadiene in the presence of *tert*-butyllithium or LDA (lithium diisopropyl amide). The product was isolated by column chromatography.

A typical procedure is as follows: LDA was prepared by mixing *n*-butyllithium with diisopropylamine at −78 °C, allowing the mixture to react for 40 min at 0 °C, and again cooling to −78 °C. To a THF solution (10 mL) of [3-{(4-cyanobiphenyl-4′-yl)oxy}propyl]dimethylsilanol (8.7 mmol equiv, directly used after the hydrolysis of the product of the hydrosilylation reaction) and 2-(3-dimethylchlorosilyl)-1,3-butadiene (1.24 g, 9 mmol) was added a THF solution (10 mL) of LDA (10 mmol), and the mixture was allowed to react for 12 h at room temperature. The product was isolated by column chromatography after evaporation of the solvent. R_f = 0.22 (hexane:ether = 12:1). Yield: 54%. Chemical shifts: 0.09 (s, 6H, *H3*), 0.22 (s, 6H, *H1*), 0.64 (m, 2H, *H4*), 1.82 (m, 2H, *H5*), 3.94 (t, 2H, *J* = 6.8 Hz, *H6*), 5.08 (d, 1H, *J* = 10.6 Hz, *Ha*), 5.31 (d, 1H, *J* = 17.8 Hz, *Hb*), 5.48, 5.71 (two d, 1H each, *J* = 3.2 Hz, *Hd*, *He*), 6.43 (dd, 1H, J_1 = 10.6 Hz, J_2 = 17.8 Hz, *Hc*), 6.96 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hw*), 7.50 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hx*), 7.62, 7.68 (two d with fine coupling, 4H, *J* = 8.6 Hz, *Hy*, *Hz*).

Other monomers with disiloxane as the spacer were similarly synthesized using *n*-butyllithium as a base.

2-[3-{3-{(4-Fluorobiphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]-1,3-butadiene [B-F-S6]. R_f = 0.39 (hexane:ether = 13:1), liquid. Yield: 20%. Chemical shifts: 6.93 (d with fine coupling, 2H, *J* = 8.8 Hz, *Hw*), 7.08 (t with fine coupling, 2H, *J* = 8.8 Hz, *Hx*), 7.46 (m, 4H, *J* = 8.6 Hz, *Hx*, *Hy*).

2-[3-{3-[(4-Methoxybiphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]-1,3-butadiene [B-1-S6]. R_f = 0.40 (hexane:ether = 12:1). Yield: 43%. Chemical shifts: 6.91, 6.94 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hw*, *Hz*), 7.44, 7.46 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hx*, *Hy*).

2-[3-{3-[(4-(Hexyloxy)biphenyl-4′-yl)oxy]propyl}tetramethyldisiloxanyl]-1,3-butadiene [B-6-S6]. R_f = 0.22 (hexane:ether = 40:1). Yield: 62%. Chemical shifts: 0.88 (t, 3H, CH_3), 1.22−1.39 (m, 4H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.39−1.59 (m, 2H, $OCH_2CH_2CH_2CH_2CH_2CH_3$), 1.78 (m, 2H, OCH_2CH_2), 3.92 (t, 2H, *J* = 6.8 Hz, OCH_2), 6.91, 6.94 (two d with fine coupling, 2H each, *J* = 8.8 Hz, *Hw*, *Hz*), 7.44 (d with fine coupling, 4H, *J* = 8.8 Hz, *Hx*, *Hy*).

Protons of diene and spacer of these compounds were observed at the corresponding positions with B-CN-S6.

Polymerization. Benzene and THF were dried over calcium hydride, or lithium aluminum hydride, just prior to use. Monomers were dried under vacuum at 60 °C for 1 day after purification. Polymerization was carried out in benzene, THF, or bulk using AIBN as an initiator at 80 °C or at 60 °C with a concentration [M] of about 0.1−0.3 mol/mL (reaction time 24 h). Formed polymers were recovered by precipitation into hexane or methanol from chloroform or dichloromethane solution and were purified by repeated reprecipitation. The absence of monomer in the polymerization product was checked by thin-layer chromatography and GPC.

The names of the 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.

The characterization data of the polymers by NMR (200 MHz, $CDCl_3$) are shown.

PB-CN-6. Chemical shifts: 1.35(broad s, 6H), 1.75(broad s, 2H), 2.05(broad s, 6H), 3.90(broad s, 2H), 4.60−5.35(main peak 5.15, b with a small peak in the higher field, 1H), 6.85-(d, 2H), 7.47(d, 2H), 7.58(d, 4H).

PB-F-6. Chemical shifts: 1.35 (b, 6H), 1.75 (b, 2H), 2.05 (b, 6H), 3.90 (b, 2H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.85 (d, 2H), 7.00 (t, 2H), 7.40 (d, 4H).

PB-1-6. Chemical shifts: 1.35 (b, 6H), 1.75 (b, 2H), 2.05 (b, 6H), 3.75 (s, 3H), 3.90 (b, 2H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.85 (b, 2H), 7.45 (b, 4H).

PB-6-6. Chemical shifts: 0.89 (b, 3H), 1.35 (b, 12H), 1.75 (b, 4H), 2.05 (b, 4H), 3.95 (b, 4H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.85 (d, 2H), 7.47 (d, 2H), 7.58 (d, 4H).

PB-CN-EO5. Chemical shifts: 2.07 (b, 4H), 2.35 (b, 2H), 3.60 (b, 2H), 3.78 (b, 2H), 4.10 (b, 2H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.85 (d, 2H), 7.47 (d, 2H), 7.58 (d, 4H).

PB-F-EO5. Chemical shifts: 2.07 (b, 4H), 2.35 (b, 2H), 3.60 (b, 2H), 3.78 (b, 2H), 4.10 (b, 2H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.89 (b, 2H), 7.08 (b, 2H), 7.42 (b, 4H).

PB-1-EO5. Chemical shifts: 2.07 (b, 4H), 2.35 (b, 2H), 3.60 (b, 2H), 3.78 (b, 5H), 4.10 (b, 2H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.89 (b, 4H), 7.39 (d, 4H).

PB-6-EO5. Chemical shifts: 0.90 (s, 3H), 1.0−1.55 (b, 6H), 1.75 (b, 2H), 2.07 (b, 4H), 2.35 (b, 2H), 3.55 (b, 2H), 3.75 (b, 5H), 3.95 (b, 2H), 4.10 (b, 2H), 4.60−5.35 (main peak 5.15, b with a small peak in the higher field, 1H), 6.91 (b, 4H), 7.42 (b, 4H).

PB-CN-EO6. Chemical shifts: 1.65 (b, 2H), 2.01 (b, 6H), 3.46 (b, 2H), 3.74 (b, 2H), 4.09 (b, 2H), 4.7−5.5 (main peak

5.15, b with a small peak in this region, 1H), 6.94 (d, 2H), 7.45 (d, 2H), 7.59 (dd, 4H).

PB-F-EO6. Chemical shifts: 1.65 (b, 2H), 2.01 (b, 6H), 3.46 (b, 2H), 3.74 (b, 2H), 4.09 (b, 2H), 4.7–5.5 (main peak 5.15, b with a small peak in this region, 1H), 6.94 (d, 2H), 7.02 (d, 2H), 7.43 (b, 4H).

PB-1-EO6. Chemical shifts: 1.65 (b, 2H), 2.01 (b, 6H), 3.46 (b, 2H), 3.74 (b, 2H), 4.09 (b, 2H), 4.7–5.5 (main peak 5.15, b with a small peak in this region, 1H), 6.94 (b, 4H), 7.45 (b, 4H).

PB-6-EO6. Chemical shifts: 0.90 (s, 3H), 1.0–1.55 (b, 6H), 1.65 (b, 2H), 1.75 (b, 2H), 2.01 (b, 6H), 3.55 (b, 2H), 3.74 (b, 2H), 3.95 (b, 2H), 4.09 (b, 2H), 4.7–5.5 (main peak 5.15, b with a small peak in this region, 1H), 6.94 (b, 4H), 7.45 (b, 4H).

PB-CN-S6. Chemical shifts: 0.08 (s, 6H), 0.14 (s, 6H), 0.62 (b, 2H), 1.80 (b, 2H), 2.18 (b, 4H), 3.90 (t, 2H), 5.88 (b, 1H), 6.95 (d, 2H), 7.45 (d, 2H), 7.59 (dd, 4H).

PB-F-S6. Chemical shifts: 0.05 (s, 6H), 0.15 (s, 6H), 0.59 (b, 2h), 1.75 (b, 2H), 2.17 (b, 4H), 3.85 (b, 2H), 5.70–6.15 (main peak 5.88, b with a small peak in the lower field, 1H), 6.83 (d, 2H), 7.00 (t, 2H), 7.40 (d, 4H).

PB-1-S6. Chemical shifts: 0.08 (s, 6H), 0.14 (s, 6H), 0.62 (b, 2H), 1.80 (b, 2H), 2.18 (b, 4H), 3.72 (s, 3H), 3.90 (t, 2H), 5.80 (b, 1H), 6.85 (b, 4H), 7.38 (b, 4H).

PB-6-S6. Chemical shifts: 0.08 (s, 6H), 0.14 (s, 6H), 0.59 (b, 2H), 0.87 (s, 3H), 1.15–1.70 (b, 6H), 1.75 (b, 2H), 1.80 (b, 2H), 2.18 (b, 4H), 3.85 (b, 4H), 5.82 (b, 1H), 6.85 (m, 4H), 7.38 (d, 4H).

Results and Discussion

Synthesis. 4-Monoalkoxy-4′-hydroxybiphenyl can be synthesized in high yield by the use of dialkyl sulfate or bromoalkane as an alkylating agent only if a large excess of 4,4′-dihydroxybiphenyl is used. In the synthesis of B-Z-6's and B-Z-EO6's, where hexamethylene or trimethylene is first introduced into the diene function by a cross-coupling reaction of 2-(1,3-butadienyl)magnesium chloride with alkylene dihalide derivatives. The alkyl iodide function showed a higher reactivity than the alkyl chloride function. The iodide group could be selectively coupled with the Grignard reagent even in the presence of the alkyl chloride function in the same molecule.[29] B-Z-EO6's were synthesized by the ether formation reaction of 2-(3-chloropropyl)-1,3-butadiene with (4-functionalized-4′-yloxy)ethanol (see Scheme 2). In the synthesis of B-Z-EO5's, a spacer group was first connected with a mesogenic group in order to make the purification easy by avoiding the contamination of a bis(diene-functionalized) product. Caution must be given in order to avoid unnecessary polymerization of the diene derivatives in the synthesis, since the reaction system was heated in the cross-coupling stage. A siloxane linkage was finally formed in the synthesis of B-Z-S6's (see Scheme 1). Caution must be taken to purify the product very carefully in order to avoid the contamination of a bis(diene-functionalized) product.

Polymerization. The results of polymerization are shown in Table 1.

All the monomers gave rather poor to reasonable yields in the polymerization. In the polymerization of B-Z-6's, bulk polymerization resulted in the formation of considerable amounts of insoluble product. Solution polymerization in benzene gave a soluble product; however, the yield became a little low. The polymerizability of B-Z-EO5 and B-Z-EO6 monomers seems to be low. Especially, B-Z-EO5's gave low yield and molecular weight of the products. The reason is not clear. Solution polymerization of B-Z-S6's usually gave a rather poor yield and lower molecular weight of the polymer. Bulk polymerization of the monomers gave improved yield (PB-CN-S6, 56%; PB-F-S6, 21%; PB-1-S6, 42%; PB-6-S6, 40%).

Table 1. Radical Polymerization of Monomers by AIBN[a]

monomer	solvent	yield (%)	M_w ($\times 10^4$)[d]	M_n ($\times 10^4$)[d]	M_w/M_n[d]
B-CN-6	benzene	32.6	2.0	1.4	1.43
B-F-6	benzene	25.6	2.2	1.5	1.51
B-1-6	benzene	23.2	1.2	0.87	1.39
B-6-6	benzene	34.8	3.4	1.6	2.09
B-CN-EO5[b]	benzene	trace	0.38	0.26	1.44
B-F-EO6	benzene	15.0	0.59	0.42	1.38
B-1-EO5	THF	19.8	0.54	0.35	1.53
B-6-EO5	THF	21.8	0.44	0.25	1.74
B-CN-OE6[c]	benzene	42.0	1.0	0.86	1.23
B-F-EO6[c]	benzene	57.9	1.0	0.68	1.55
B-1-EO6[c]	benzene	53.4	0.68	0.52	1.29
B-6-EO6[c]	benzene	52.9	0.86	0.65	1.33
B-CN-S6	benzene	20.2	1.4	1.0	1.41
B-CN-S6	bulk	55.6	9.6	6.8	1.40
B-F-S6	bulk	21.2	2.7	1.9	1.42
B-1-S6	bulk	41.6	11.9	8.4	1.41
B-6-S6	bulk	39.8	29.1	14.9	1.94

[a] At 80 °C, [M]/[I] = 100. [b] At 60 °C, [M]/[I] = 100. [c] At 60 °C, [M]/[I] = 10. [d] Estimated by GPC using standard polystyrene.

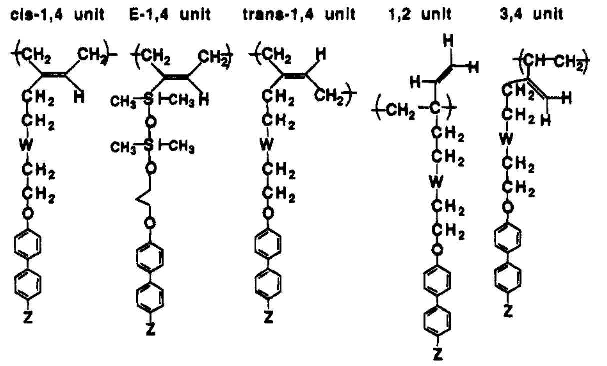


Figure 1. Structural isomerism of a 2-substituted polydiene main chain.

In the GPC chromatogram of polymers before purification, a low molecular weight fraction was sometimes observed. Such an oligomer fraction was removed by reprecipitation. The weight-average molecular weight of polymers estimated by GPC using polystyrene standards is reasonably high, ranging from 1.2 to 3.4 × 10^4 (M_w/M_n = 1.39–2.09) for PB-Z-6 and from 2.7 to 29.1 × 10^4 (M_w/M_n = 1.40–1.94) for PB-Z-S6. The molecular weight distribution of the polymers is considerably narrow as a polymer formed by radical polymerization.

Polymer Structure by ^{1}H NMR and ^{13}C NMR.[30,31] There are four structural isomers, namely, cis-1,4, trans-1,4, 1,2, and 3,4 structures in the polydiene main chain having a substituent at the 2-position as shown in Figure 1. In the case of polydiene with a siloxane linkage in the spacer, cis-1,4 and trans-1,4 structures correspond to (*E*)-1,4 and (*Z*)-1,4 structures, respectively.

The ratio of the structural units very much depends on the method of polymerization.[30–32] For instance, polyisoprene rich in trans-1,4 structure is obtained by the radical polymerization; meanwhile anionic polymerization by an organolithium reagent or coordination polymerization by a transition-metal catalyst gives cis-1,4 structure. Since the structure of the main chain affects the characteristics of the polymer, the control of the structure is one of the most important factors.

A typical ^{1}H NMR spectrum of PB-CN-6 and those of the olefinic proton region of polyisoprene, PB-CN-6, PB-CN-EO5, and PB-CN-EO6 are shown in Figures 2 and

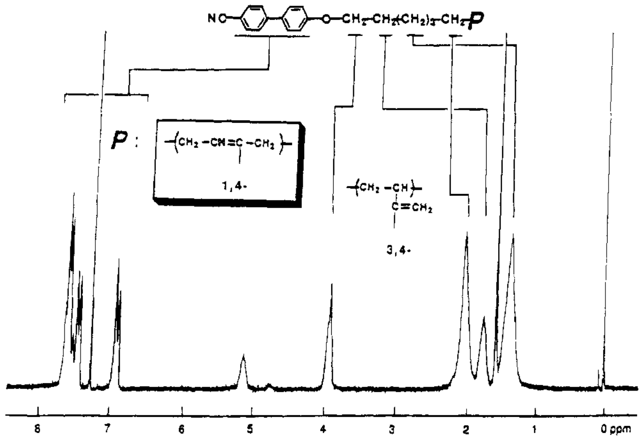


Figure 2. ^{1}H NMR spectrum of PB-CN-6 (200 MHz, room temperature in $CDCl_3$).

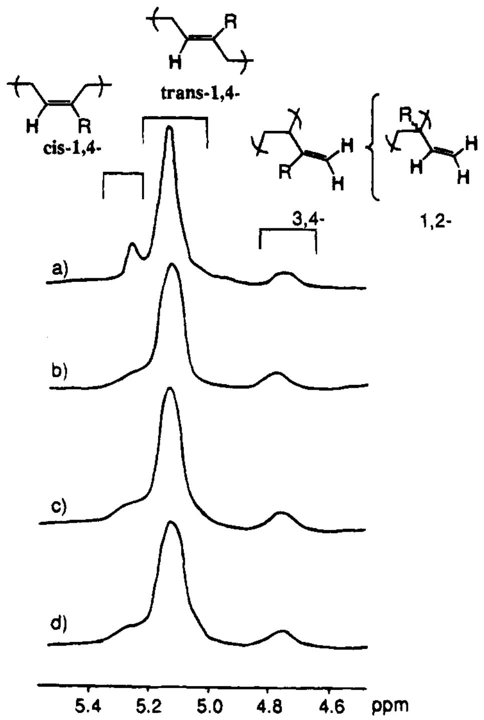


Figure 3. ^{1}H NMR spectra of the olefinic region of polymers (200 MHz, room temperature in $CDCl_3$): (a) polyisoprene, (b) PB-CN-6, (c) PB-CN-EO5, (d) PB-CN-EO6.

3. In the spectrum of polyisoprene, the appearance of three kinds of olefinic signals indicates the presence of trans-1,4, cis-1,4, and 1,2 and 3,4 structures in the main chain. The ratio is 75:15:10. It can be seen that the polymer was formed by the consumption of the diene function also in the case of PB-CN-6. The appearance of three singlet signals at 4.76, 5.15, and 5.25 (shoulder) ppm in the case of PB-CN-6 clearly indicates the presence of two types of 1,4-structural isomeric units and a 3,4 unit in the main chain. Two singlets at the lower field seem to correspond to the olefinic protons of cis-1,4 and trans-1,4 structures. The spectra are similar for PB-Z-EO5 or PB-Z-EO6. The major structural isomeric unit of these polymers is trans-1,4.

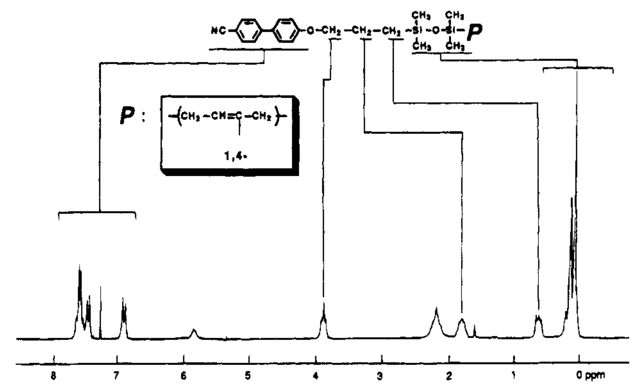


Figure 4. ^{1}H NMR spectrum of PB-CN-S6 (200 MHz, room temperature in $CDCl_3$).

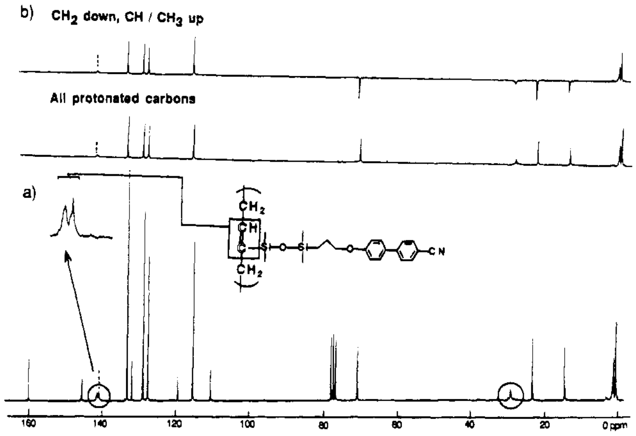


Figure 5. (a) ^{13}C NMR spectrum and (b) DEPT spectra of PB-CN-S6 (50 MHz, room temperature in $CDCl_3$).

The ^{1}H NMR spectrum of PB-CN-S6 is shown in Figure 4. The newly seen signals in the region of 5.88 ppm as a singlet correspond to the olefinic proton of the main chain. The area of the singlet is one-fourth of that of methylene protons of the main chain. This fact excludes the possibility that polymers were formed through 3,4- or 1,2-addition to the diene functions. With respect to the structure of the PB-Z-S6's, it can be said that only one isomeric structure is predominant. However, the mode of addition, namely, 1,4-trans or 1,4-cis, was not clear at this point.

The DEPT spectrum of PB-CN-S6 is shown in Figure 5. The spectrum also supports that the signal at 5.8 ppm is that of CH, which is consistent with the assignment of the signal to a trisubstituted olefinic proton. The NOESY spectrum of the polymer is shown in Figure 6. Interaction between methyl protons of the trimethylsilyl group and the olefinic proton was observed, which supports that the olefinic proton and the trimethylsilyl groups are situated in a cis relation concerning the carbon–carbon double bond. This cross relation was not observed in the COSY spectrum. The polymer main chain takes one predominant stereochemistry namely, (*E*)-1,4. This stereochemistry was also suggested by Nakahama.[33–36] This may be because the bulky mesogen-containing substituent tends to be incorporated at the trans position to polymer main chain (*E* form) in the repeating monomer unit. Similarly it is also concluded that the main-chain structure of other PB-Z-S6's takes the (*E*)-1,4 form. The stereochemistry is generally seen for other polydienes with a siloxane linkage in the spacer.

Thermal Behavior of Monomers and Polymers. Transition temperatures of monomers are shown in Table 2. Monomers with a S6 spacer except for B-F-S6 showed only one transition. These monomers did not show any liquid crystalline state. Monomers with a hexamethylene spacer except for B-CN-6 showed two transition temperatures. This apparent trend was not observed for the transition temperatures of monomers with ethyleneoxy spacers. Monomers B-CN-EO5, B-CN-

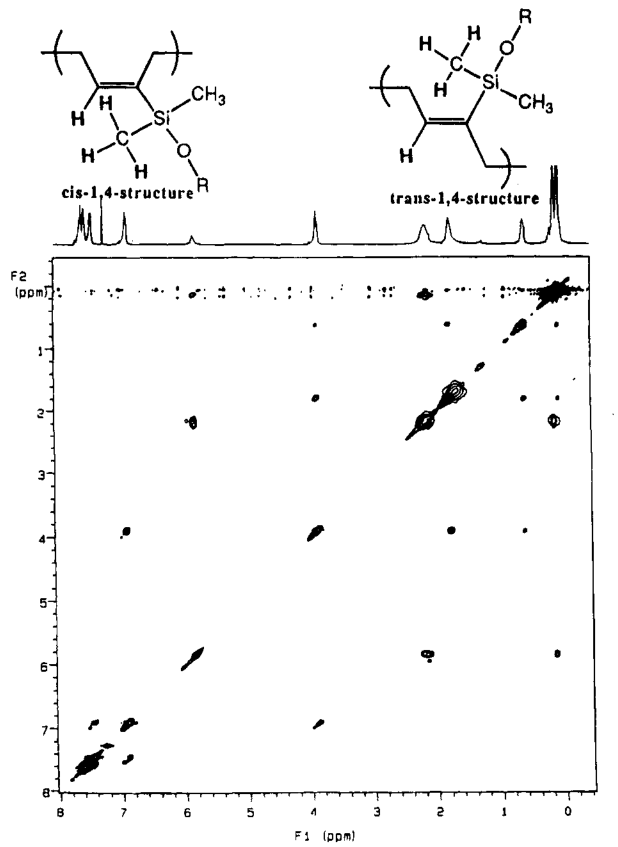


Figure 6. NOESY spectrum of PB-CN-S6 (400 MHz, room temperature in $CDCl_3$).

Table 2. Transition Temperatures of Monomers

monomer	DSC (heating): transition (°C); ΔH (mJ/mg)
B-CN-6	53.6; 120.3
B-F-6	30.8; 68.9 and 49.5; 29.3
B-1-6	84.5; 138.7 (broad) and 118.7; 1.9
B-6-6	91.5; 21.6 and 115.0; 23.6 (broad)
B-CN-EO5	oil
B-F-EO5	46.5; 135.0
B-1-EO5	87.5; 54.1 and 108.5; 13.7 (shoulder)
B-6-EO5	114.7; 32.3 (broad)
B-CN-EO6	oil
B-F-EO6	43.4; 35.5
B-1-EO6	100.0; 38.0 (broad)
B-6-EO6	81.8; 54.8 and 103.7; 6.6
B-CN-S6	35.38; 26.3
B-F-S6	oil
B-1-S6	72.5; 30.7
B-6-S6	41.5; 12.5

EO6, and B-F-S6 are oil at room temperature. Further accurate thermal analyses are needed.

The results of DSC analysis of polymers are shown in Figure 7. In the figure, only heating traces are shown.

Polymers with hexamethylene and S6 spacers except for PB-6-6, PB-F-S6, and PB-6-S6 showed a single transition temperature (Table 3). PB-6-6, PB-F-S6, and PB-6-S6 showed two transition temperatures. Polymers with ethyleneoxy spacers (PB-Z-EO5 and PB-Z-EO6) except for PB-CN-EO5 and PB-CN-EO6 showed broad, although single, transition. PB-CN-EO6 did not show any thermal transition other than the glass transition temperature. Roughly speaking, the transition temperatures of polymers having the same spacer become higher in the order of fluoro, cyano, methoxy, and hexyloxy groups as the tail group. Although it is very difficult to see a consistent trend, it can be said that the hexyloxy group is a good tail group for stabilizing the mesophase to result in the higher transition temperature.

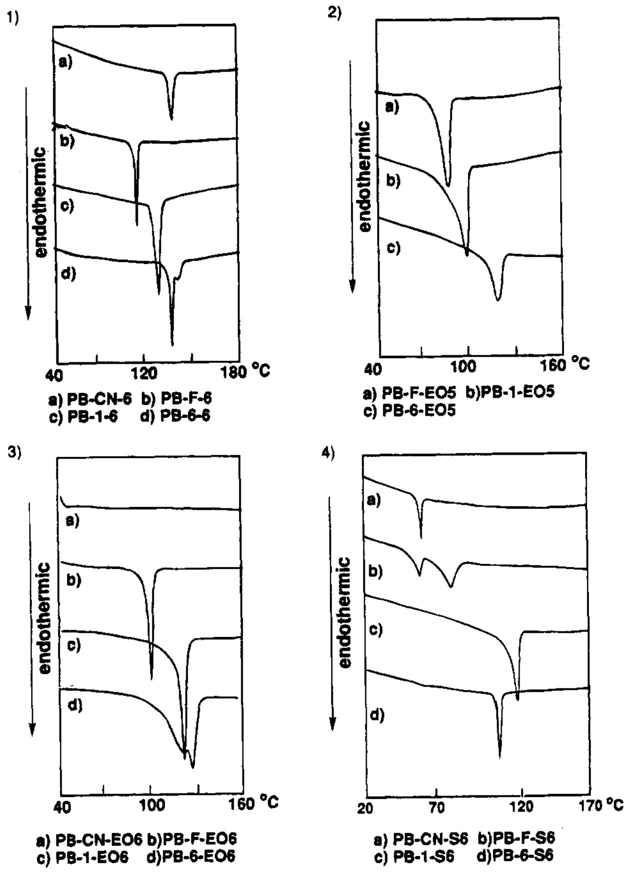


Figure 7. DSC curves of polymers: (1) PB-Z-6, (2) PB-Z-EO5, (3) PB-Z-EO6, (4) PB-Z-S6.

Table 3. Thermal Behavior of Polymers

polymer	DSC (heating): transition (°C)[a]; ΔH (mJ/mg)	texture
PB-CN-6	137.6; 10.0	fan
PB-F-6	114.5; 15.6	n.d.[b]
PB-1-6	133.0; 12.2	batonnet
PB-6-6	146.5; 9.6 and 151.6; 2.2	batonnet
PB-CN-EO5		
PB-F-EO5	87.5; 38.4 (broad)	
PB-1-EO5	98.4; 43.9 (broad)	
PB-6-EO5	100.5; 18.8 (broad)	
PB-CN-EO6		
PB-F-EO6	91.7; 37.4 (broad)	
PB-1-EO6	116.1; 41.9 (broad)	
PB-6-EO6	114.8 and 121.5; 36.5 (not separated)	n.d.[b]
PB-CN-S6	57.4; 2.8	fan
PB-F-S6	51.9; 2.2 and 73.4; 6.1	fan
PB-1-S6[c]	116.3; 16.9	n.d.[b]
PB-6-S6	107.8 (shoulder) and 110.3; 2.0	fan

[a] Determined by DSC at the starting point of the transition. [b] n.d.: Phase could not be determined. [c] Phase changed with prolonged annealing.

We can see the importance of the chemical structure, namely, the flexibility of the main chain, in determining the transition temperature (clearing point) by comparing the transition temperatures of the diene polymer having a hexamethylene spacer and cyanobiphenyl as a mesogen (PB-CN-6) with those of ordinary liquid crystalline polymers having the same spacer and mesogen. The glass transition temperature and clearing

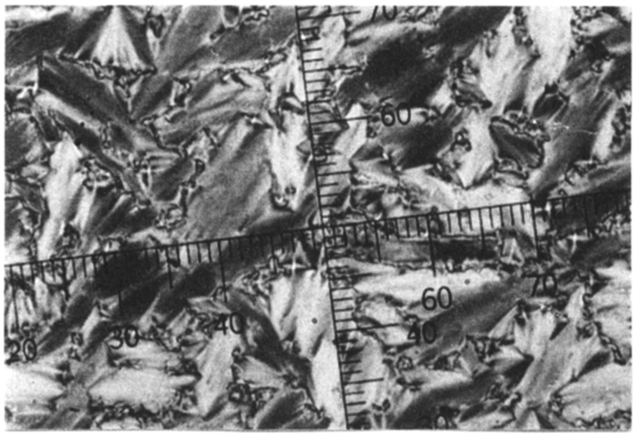


Figure 8. Optical polarization micrograph of PB-F-S6 annealed at 79.8 °C for 2 days.

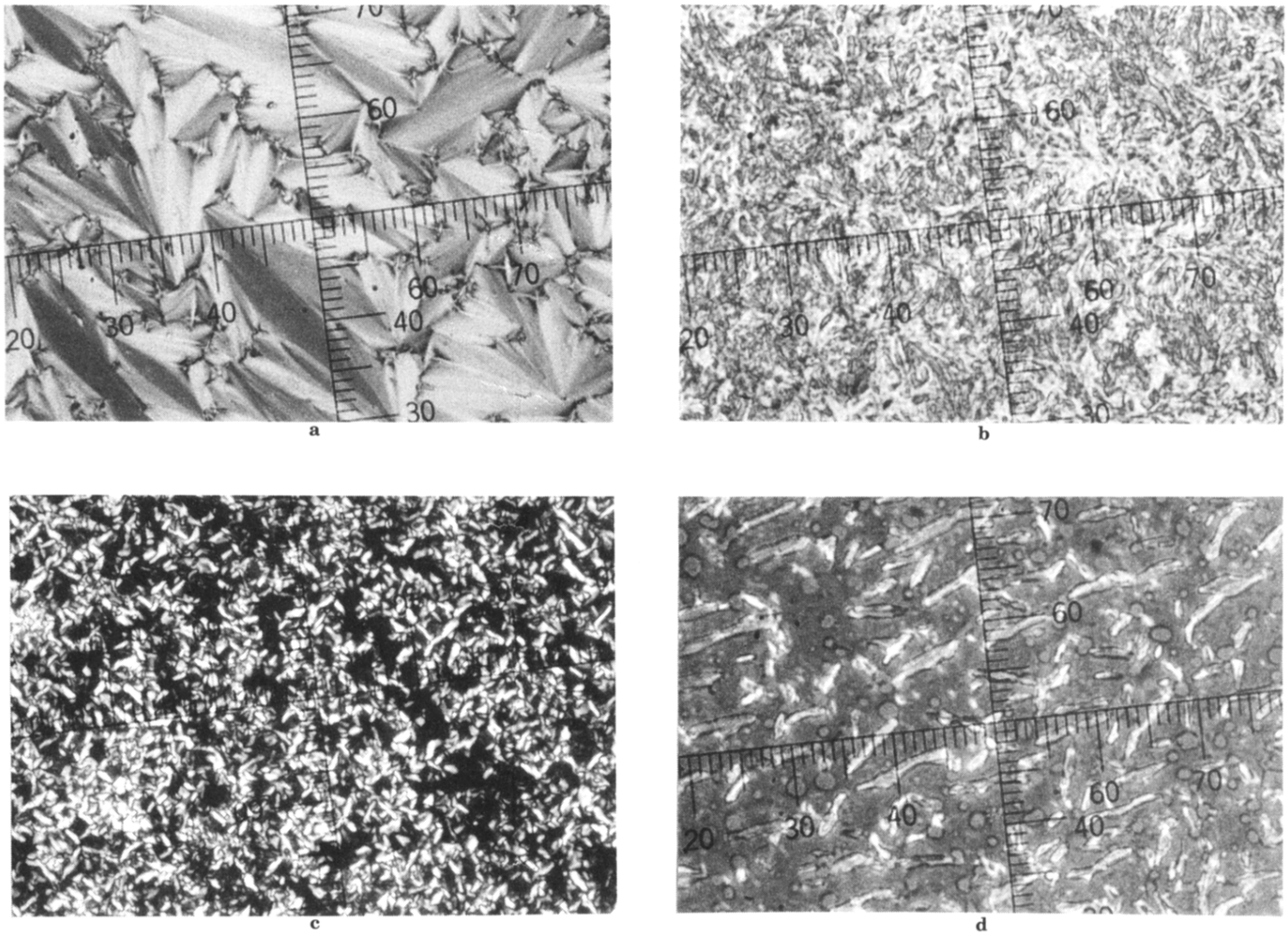
point of polymers of polysiloxane, polyacrylate, and polymethacrylate as the main chain are (12 °C; 166 °C), (35 °C; 135 °C), (60 °C; 100 °C), respectively.[1] The more flexible main chain gives the wider temperature range of the liquid crystalline state. Polydiene polymer, PB-CN-6, showed the clearing point at 137.6 °C. This temperature is between that of polysiloxane and polyacrylate main-chain polymers. This fact is considered to reflect that the flexibility of the polydiene main chain is between that of polysiloxane and polyacrylate. Although the glass transition temperature was not observed, PB-CN-6 is assumed to show a considerably wide temperature range of the liquid crystalline state.

When polymers of a different spacer group with a hexyloxy tail group are compared, an interesting trend is noticed; namely, the transition temperature drops in the order of hexamethylene, ether-containing spacers, and disiloxane-containing spacer. Introduction of a disiloxane linkage in the spacer is very effective to bring down the transition temperature.

Only the transition of polydiene side-chain liquid crystalline polymers having the spacer with a disiloxane linkage was enantiotropic. This may reflect the importance of the flexibility of the main chain and spacer of these polymers in making the mesogens easily organized. The transition temperatures of the polymers having the spacer with a disiloxane linkage range from room temperature to around 115 °C. This might be an advantage when an application is considered.

Phase Structure under Optical Polarization Micrograph. As mentioned in the preceding section, monomers with a hexamethylene spacer except for B-CN-6 showed two transition temperatures. Judging from the enthalpy of the transition, there is a possibility for these monomers to take a liquid crystalline state. However, a liquid crystalline state could not be seen, so far, under an optical polarization micrograph. No monomer was concluded to take a liquid crystallization state by an optical polarization micrograph.

The chemical structure of the main-chain polymer is an important factor in determining the liquid crystalline state. The flexible polydiene main chain made it possible for these polymers to take a liquid crystalline phase. Among polydiene polymers, those with a spacer



a

b

c

d

Figure 9. Optical polarization micrograph of PB-Z-6: (a) PB-CN-6 annealed at 138.3 °C for 4 h, (b) PB-F-6 annealed at 115.2 °C for 2 h, (c) PB-1-6 annealed at 134.5 °C for 2 h, (d) PB-6-6 annealed at 143.5 °C for 10 h.

containing an ether linkage did not give any mesophase except for PB-6-EO6 which showed an unidentified mesophase only in the heating process. Although an accurate reason is not clear, it may have some relation to the structure of the diethyleneoxy spacer. Polymers with a hexamethylene spacer (PB-Z-6) and those with a spacer containing a siloxane linkage (PB-Z-S6) took a smectic liquid crystalline state. The batonnet structure taken by both PB-6-6 and PB-6-S6 grew up to a well-developed focal conic fan structure only in the case of PB-6-S6. PB-6-S6 showed two transition temperatures at 107.8 and 110.3 °C. Although it could not be elucidated by now, there is a possibility for this polymer to take two different liquid crystalline phases between these temperatures. A trend was observed that the mesophase structure of the polymers with a disiloxane linkage in the spacer developed better compared to that of the polymers with a hexamethylene spacer. The structure of the spacer group is one of the important factors in determining the liquid crystalline state.

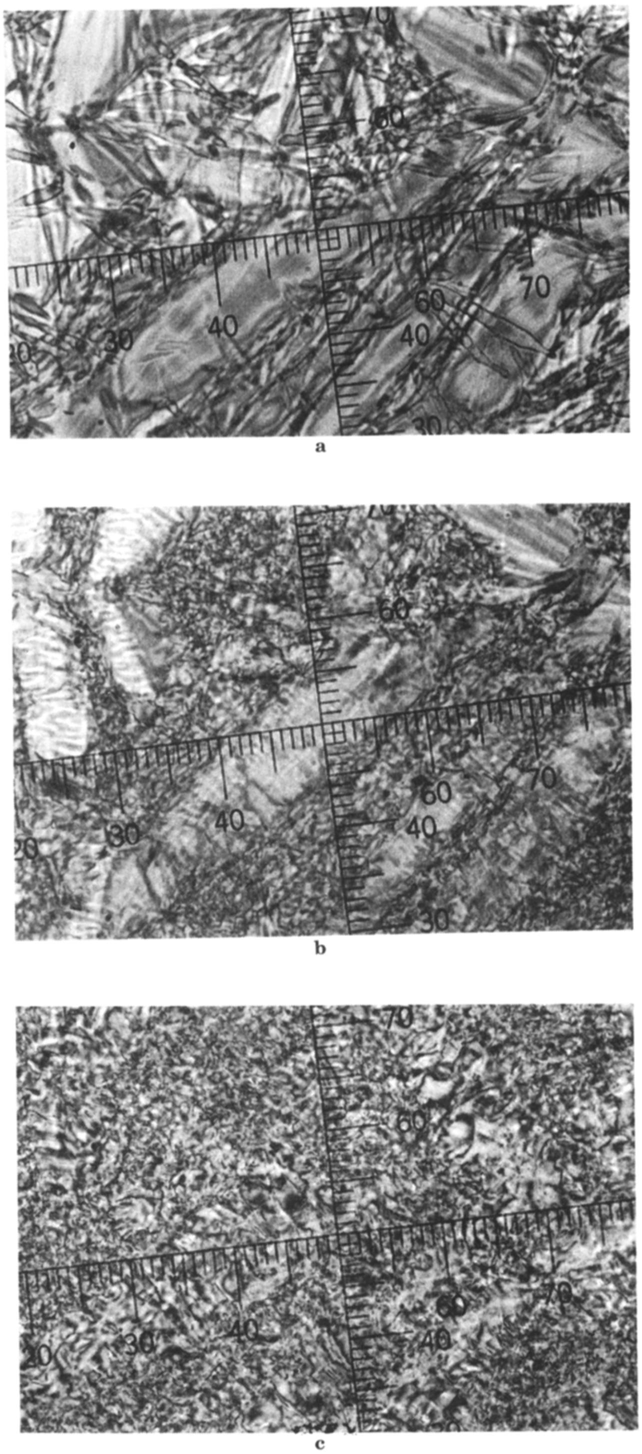
The structure of the mesogenic group is also one of the important factors in determining the mesophase structure. Although PB-1-S6 immediately forms a fine structure on cooling near the transition temperature, the phase could not be determined. PB-1-6 gave only a batonnet structure, and the structure was not developed further. Apparently, methoxybiphenyl is not a good mesogenic group for polydiene to take a well-organized structure. Contrary to the fact that polymers with methoxybiphenyl as a mesogen did not give a well-developed mesophase, cyanobiphenyl as a mesogen usually gives a better developed mesophase. An optical polarization micrograph of PB-CN-S6 was already reported.[25] That of PB-F-6, those of PB-Z-6, and the change of those of PB-6-S6 with time are shown in Figures 8–10.

The smectic A phase of PB-6-S6 shown by annealing at a temperature slightly below the main transition temperature (108.5 °C) turned into an unidentified fine structure on further cooling. This will be the subject of a future detailed study, especially by X-ray diffraction analysis, to clarify the detailed mesophase structure of these polymers. In accordance with the generally admitted fact that side-chain liquid crystalline polymers with a polar cyanobiphenyl mesogenic group give well-organized smectic phases, so does polydiene with cyanobiphenyl as the mesogenic group (PB-CN-6, PB-CN-S6). The polar interaction between mesogenic groups makes it easy for them to organize. Polymer with a fluorobiphenyl- and siloxane-containing spacer also showed a similar smectic phase with a focal conic fan structure (PB-F-S6).

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 mesogenic groups apart from each other along the polymer main chain, compared with ordinary vinyl polymers.

Conclusion

Polydiene was found to act as a suitable main-chain component for a side-chain liquid crystalline polymer with various biphenyl derivatives as the mesogenic group. Introduction of a siloxane linkage into the spacer group is an effective molecular design of the chemical structure of the polymer to give a better organized mesophase of lower transition temperature. The importance of the flexibility of the main chain and spacer was stressed.



a

b

c

Figure 10. Change in optical polarization micrographs of PB-6-S6: (a) annealed at 106.0 °C for 3 h, (b) kept at 103 °C for 0.5 h after being annealed at 106.0 °C for 3 h, (c) kept at 90 °C for 5 h after being kept at 103 °C for 5 h.

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