

## Preparation and Properties of Ferroelectric Liquid-Crystalline Polysiloxanes Possessing (S)-(-)-4-(2-methylbutyloxycarbonyl)phenyl 4'-(5-hexyloxy)biphenyl-4-carboxylate as Side Chain Mesogen Unit

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**ABSTRACT:** New ferroelectric liquid crystalline polysiloxanes **5** containing a side chain mesogenic group were prepared by the reaction between poly(methylsiloxane) **4** with various degrees of polymerization and the mesogenic compound possessing terminal olefin, (S)-(-)-4-(2-methylbutyloxycarbonyl)phenyl 4'-(5-hexyloxy)biphenyl-4-carboxylate **3**, in the presence of a platinum catalyst. The polarized microscopic observation indicated that both the olefinic precursor **3** and the resulting polysiloxanes **5** displayed enantiotropic smectic A ( $S_A$ ) and smectic C ( $S_C^*$ ) mesophases. The polymers showed transitions from isotropic to  $S_A$  phases and from  $S_A$  to  $S_C^*$  phases in the range of 250—220°C and 215—188°C, respectively, where the  $S_C^*$  phase was exhibited even at room temperature. The phase transition temperature increased with increasing molecular weight of the polysiloxane backbone. The small angle X-ray diffraction study indicated that the layer spacing increased and the tilt angle of the mesogenic side chain unit decreased with increasing temperature, and they became constant after a particular temperature of  $S_C^*$ - $S_A$  transition. The observed layer spacing of 2.9 nm in  $S_A$  phase agreed with the calculated value of 3.1 nm. The polymers are switchable by an electric field and the minimum response time was 175 ms.

**KEY WORDS** Polysiloxane / Side Chain Liquid Crystal Polymer / Smectic A Phase / Chiral Smectic C Phase /

Side chain liquid crystalline polymers have been introduced only in 1970s.<sup>1</sup> During this period several hundred polymers have been synthesized. In most these polymers, the monomeric mesogen links to the main chain via a flexible spacer. First synthesized side chain polymer had a polymethacrylate backbone,<sup>1</sup> and to date almost all polymers are polyacrylate, polymethacrylate, and polysiloxane. These comb-like liquid crystalline polymers have been interested for their mesophase properties caused by the low molecular weight

liquid crystalline side chain and the excellent mechanical properties offered by the polymeric backbone. Among them polysiloxanes have several advantages particularly because of flexibility of the backbone, which confer a low glass transition temperature ( $T_g$ ) of the resulting polymers.<sup>2</sup>

Chiral smectic C liquid crystals have attracted much attention for their ferroelectric nature, first demonstrated by Mayer,<sup>3</sup> and have been used in a new type of electro-optic display devices.<sup>4</sup> Although a lots of works concerning

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low molecular weight ferroelectric liquid crystals (FLC) have been reported, there have been a few reports on polymeric FLC materials. Some successful works on the synthesis and characterization FLC side chain polysiloxanes have been reported recently.<sup>5-11</sup> Therefore it is obviously useful to synthesize various kinds of liquid crystalline polysiloxanes in order to explore their application potentials.

It is generally accepted that mesomorphic phase transition temperatures increase up to a certain degree of polymerization (DP) with increasing molecular weight of the liquid crystalline polymers.<sup>12-17</sup> Concerning the value of the critical DP, some papers claimed that the required DP was about 10-15,<sup>12,13,16,18</sup> 30-50<sup>19</sup> while two groups<sup>14,17</sup> pointed out a value as high as a few hundreds. In addition some authors showed that the type of mesophase is molecular weight independent,<sup>13,20</sup> however, there are some recent publications<sup>14,21</sup> discussing the opposite phenomenon.

In this paper, the synthesis and characterization of new ferroelectric liquid crystalline polysiloxanes having (*S*)-(-)-4-(2-methylbutyloxycarbonyl)phenyl 4'-(5-hexyloxy)biphenyl-4-carboxylate as the mesogenic side chain group with various degree of polymerization are discussed. As our purpose was to obtain the ferroelectric LC polysiloxanes, the mesogen should possess a asymmetric carbon center to show the chiral smectic C (*S*<sub>c</sub><sup>\*</sup>) phase. Mesogenic unit in the present study was (*S*)-(-)-4-(2-methylbutylcarboxy)phenyl-4'-(5-hexyloxy)biphenyl-4-carboxylate, and has been reported<sup>22</sup> to show three kinds of smectic phases. However, attempts to incorporate this low molecular weight liquid crystal with polysiloxanes have not yet reported.

## EXPERIMENTAL

### *Preparation of Mesogenic Precursor Possessing Terminal Olefin Unit*

The chiral mesogenic precursor compound

**3** possessing terminal olefin unit was synthesized by the analogous method reported on the synthesis of the corresponding saturated liquid crystalline compounds.

### *S*-(-)-2-Methylbutyl 4-Hydroxybenzoate **1**

Crude 4-benzyloxybenzoyl chloride, obtained from 2.28 g (10 mmol) of 4-benzyloxybenzoic acid with excess thionyl chloride and a few drops of *N,N*-dimethylformamide (DMF) at 60°C for 2 h, dissolved in 25 ml of dichloromethane was added dropwise to a mixture of 0.88 g (10 mmol) of (*S*)-2-methyl-1-butanol and 1.11 g (11 mmol) of triethylamine in 100 ml of dichloromethane at room temperature under Nitrogen atmosphere. After the mixture was stirred for 12 h, the solution was neutralized with 1M hydrochloric acid and the precipitate of triethylamine hydrochloride was filtered, and the solvent was evaporated. (*S*)-(-)-2-Methylbutyl 4-benzyloxybenzoate was obtained as a colorless liquid using silica gel column chromatography with a mixture of toluene and ethyl acetate (10:1) as the eluent. The yield was 80%. IR (neat)  $\text{cm}^{-1}$  1771 (s), 1279 (s), 1256 (s); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 8.1-7.9 (2H, d, Ar-H), 7.5-7.3 (5H, m, Ar-H), 7.1-6.9 (2H, d, Ar-H), 5.1 (2H, s,  $\text{OCH}_2\text{-Ar}$ ), 4.3-4.1 (2H, dd,  $\text{OCH}_2\text{-CH}$ ), 2.0-1.6 (1H, m, CH), 1.1-1.6 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 1.1-0.8 (6H, m,  $2 \times \text{CH}_3$ ).

In a flask, 2.40 g (8 mmol) of (*S*)-(-)-2-methylbutyl 4-benzyloxybenzoate, 0.24 g (10% weight of the substrate) of 10% Pd-C and 50 ml of ethanol were placed, and then was stirred for 12 h under hydrogen atmosphere at 25°C. Crude (*S*)-(-)-2-methylbutyl 4-hydroxybenzoate **1** was obtained by evaporation of the solvent of the filtrate. The yield of *S*-(-)-2-methylbutyl 4-hydroxybenzoate **1** was 90%. IR (neat)  $\text{cm}^{-1}$ ; 3375 (b), 1712 (s), 1280 (s). <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 8.1-7.9 (2H, d, Ar-H), 6.8-7.0 (2H, d, Ar-H), 5.8-6.2 (1H, b, OH), 4.0-4.2 (2H, dd,  $\text{OCH}_2$ ), 2.0-1.6 (1H, m, CH), 1.5-1.1 (2H, m,  $\text{CH}_2$ ), 1.1-0.8 (6H, m,  $2 \times \text{CH}_3$ ).

**4'-(5-Hexenyloxy)biphenyl-4-carboxylic Acid 2**

In a flask, 4.28 g (20 mmol) of 4'-hydroxybiphenyl-4-carboxylic acid was refluxed with 2.46 g (44 mmol) of potassium hydroxide and few crystals of potassium iodide in 100 ml of 90% ethanol, and 3.00 g (22 mmol) of 6-bromohexene was added to this solution. After the mixture was refluxed over night, the mixture was neutralized with 6M hydrochloric acid. The resulting white precipitate obtained by pouring the solution into ice-water was recrystallized from ethanol. The yield of 4'-(5-hexenyloxy)biphenyl-4-carboxylic acid **2** was 72%. IR (KBr)  $\text{cm}^{-1}$ ; 1686 (s), 1288 (s). Three mesogenic transitions were observed by DSC and microscope at 204, 234, and 266°C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  ppm 8.1–8.0 (2H, d, Ar-H), 7.7–7.6 (4H, m, Ar-H), 7.0–6.9 (2H, d, Ar-H), 6.0–5.6 (1H, m,  $\text{CH}_2=\text{CH}$ ), 5.1–4.9 (2H, m,  $\text{CH}_2=\text{CH}$ ), 4.1–3.8 (2H, t,  $\text{OCH}_2$ ), 2.2–1.4 (6H, m,  $3 \times \text{CH}_2$ ).

**(S)-(-)-4-(2-Methylbutyloxycarboxy)phenyl 4'-(5-Hexenyloxy)biphenyl-4-carboxylate 3**

In a flask, 2.96 g (10 mmol) of 4'-(5-hexenyloxy)biphenyl-4-carboxylic acid was reacted at 60°C with excess thionyl chloride containing a few drops of DMF for 2 h. Excess thionyl chloride was removed under reduced pressure. The product was dissolved in 25 ml of dichloromethane and this was added dropwise to a mixture of 2.08 g (10 mmol) of **1**, and 1.11 g (11 mmol) of triethylamine in 100 ml of dichloromethane. After the mixture was stirred for 12 h at 25°C under nitrogen atmosphere, the white precipitate of triethylamine hydrochloride was filtered, and the solvent was evaporated. The crude product was purified by silica gel column chromatography eluting with a mixture of hexane and ethyl acetate (10:1). Recrystallization from ethanol afforded a white crystals of (S)-(-)-4-(2-methylbutyloxycarboxy)phenyl 4'-(5-hexenyloxy)biphenyl-4-carboxylate **3** with 60% yield.

Elemental analysis Calcd for  $\text{C}_{31}\text{H}_{34}\text{O}_5$ : C, 76.44%; H, 6.94%. Found: C, 76.52%; H, 7.04%. IR (KBr)  $\text{cm}^{-1}$ ; 1737 (s), 1271 (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 8.30–8.05 (4H, m, Ar-H), 7.75–7.55 (4H, m, Ar-H), 7.40–7.20 (2H, m, Ar-H), 7.05–6.85 (2H, m, Ar-H), 6.10–5.60 (1H, dd,  $\text{OCH}_2\text{-CH}$ ), 4.10–3.90 (2H, t,  $\text{OCH}_2\text{-CH}_2$ ), 2.25–1.25 (9H, m,  $4 \times \text{CH}_2 + \text{CH}$ ), 1.10–0.90 (6H, m,  $2 \times \text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 166.0, 165.6, 159.6 (158.1), 154.7 (156.3), 146.3 (145.7), 138.5 (139.0), 131.9 (133.3), 131.8 (130.4),\* 130.8 (130.1),\* 128.5 (128.1), 128.0 (128.0), 127.0 (127.3), 126.7 (126.3), 121.9 (121.4), 115.1 (114.4), 114.9 (114.6), 69.7 (73.0), 68.0 (68.4), 34.3 (37.0), 33.4 (33.5), 28.7 (28.9), 26.2 (26.8), 25.3 (25.3), 16.6 (17.1), 11.3 (12.6).

**Poly(methylsiloxane)'s 4**

Poly(methylsiloxane)'s **4** were synthesized from dichloromethylsilane and chlorotrimethylsilane in the presence of hydrochloric acid and water. The molecular weight of **4** was controlled by the amount of chlorotrimethylsilane.

The general procedure is as follows: In a three-necked flask 12M hydrochloric acid and tetrahydrofuran (THF) were placed. The amount of these reagents were controlled so that 1 mol of water and 0.01 mol of THF were present for each mole of hydrolyzable chlorine atoms in chlorosilanes. To this was added a mixture of appropriate amount of dichloromethylsilane and chlorotrimethylsilane at  $-10^\circ\text{C}$ . The reaction mixture was stirred for 24 h, and then extracted with toluene. Toluene was removed *in vacuo*. The unreacted monomers and low molecular products were removed by distillation at  $150^\circ\text{C}$  *in vacuo*. A typical  $^1\text{H}$  NMR spectrum of **4a** is presented in Figure 1.

**Liquid Crystalline Polysiloxane 5d**

In a flask, 1.0 g (2.0 mmol) of the mesogenic

\* Interchangeable. Calculated values are in parentheses.

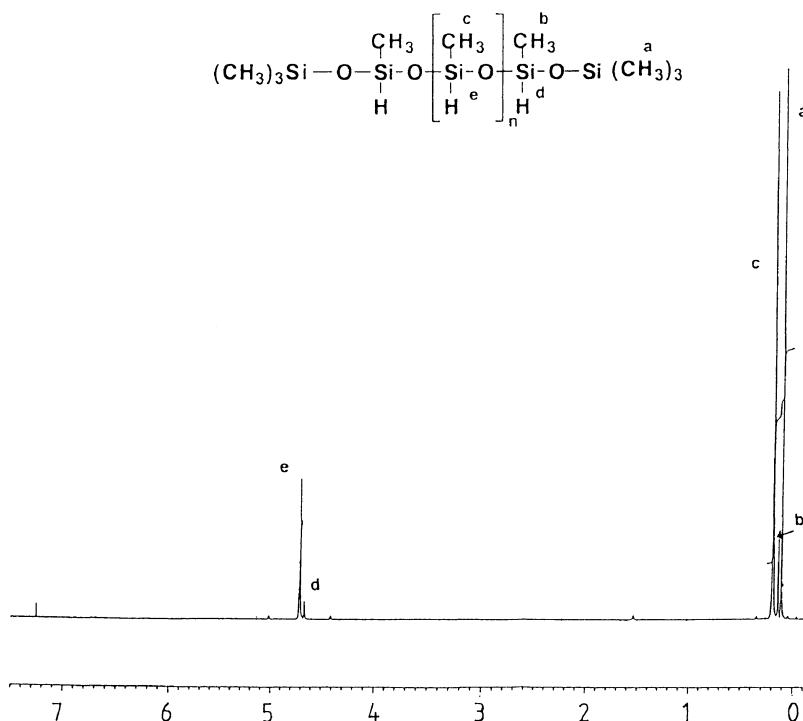


Figure 1.  $^1\text{H}$  NMR spectrum of poly(methylsiloxane) with molecular weight of 1400 measured in  $\text{CDCl}_3$ .

terminal olefin compound **3**, 10% mol excess over the silylhydride groups present in the poly(methylsiloxanes), PHMS, was dissolved in 100 ml of dried toluene. Into this was pipetted 0.11 g (0.0052 mmol) of **4d**. The mixture was heated to  $110^\circ\text{C}$  under nitrogen, and  $200\ \mu\text{l}$  of dicyclopentadienyl platinum(II) chloride<sup>23</sup> dissolved in methylene chloride with a concentration of  $1\ \text{mg ml}^{-1}$  was then injected to the mixture. The reaction was carried out for 24 h. The extent of the reaction was monitored by the disappearance of absorption of silyl hydride at  $2160\ \text{cm}^{-1}$  in the IR spectrum. The polymer was isolated by precipitation into excess amount of methanol. Polymer purification was done by repeated precipitation from toluene with excess methanol and subsequent centrifugal treatment. Polymer purity was checked by thin layer chromatography (silica gel, hexane:ethylacetate = 10:1) and gel permeation chromatog-

raphy (GPC). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ ; 1736 (s), 1716 (s), 1216, 1070, 760 (b), 670 (s).  $^1\text{H}$  NMR spectrum of the polymer is given in Figure 2.

Other liquid crystalline polysiloxane polymers were also prepared by the similar way. Polymer **5a** and **5g** were further purified by preparative GPC.

#### Measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX 400 spectrometer. IR spectra were recorded on a JASCO FT/IR 5000 spectrophotometer. Differential scanning calorimetry (DSC) were carried out with a Shimadzu thermal analyzer DSC-41M at a rate of  $5^\circ\text{C min}^{-1}$  under nitrogen on both heating and cooling. The optical polarization microscopic studies were made at a heating rate of  $10^\circ\text{C}$  and  $2^\circ\text{C min}^{-1}$  using a NIKON OPTIPHOT-POL polarizing instrument fitted with a metler FP82HT hot stage. Polymer molecular

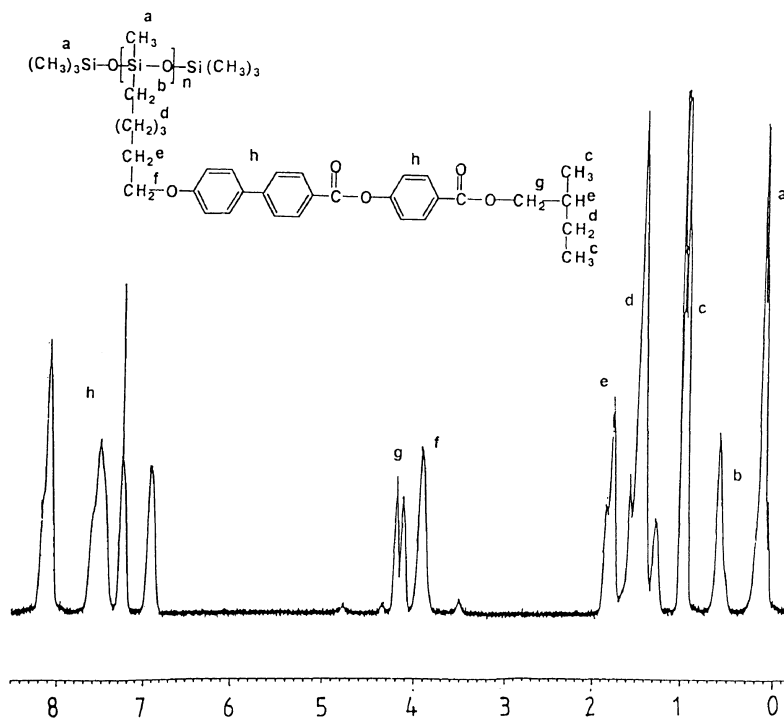


Figure 2.  $^1\text{H}$  NMR spectrum of liquid crystalline polymer **5c** measured in  $\text{CDCl}_3$ .

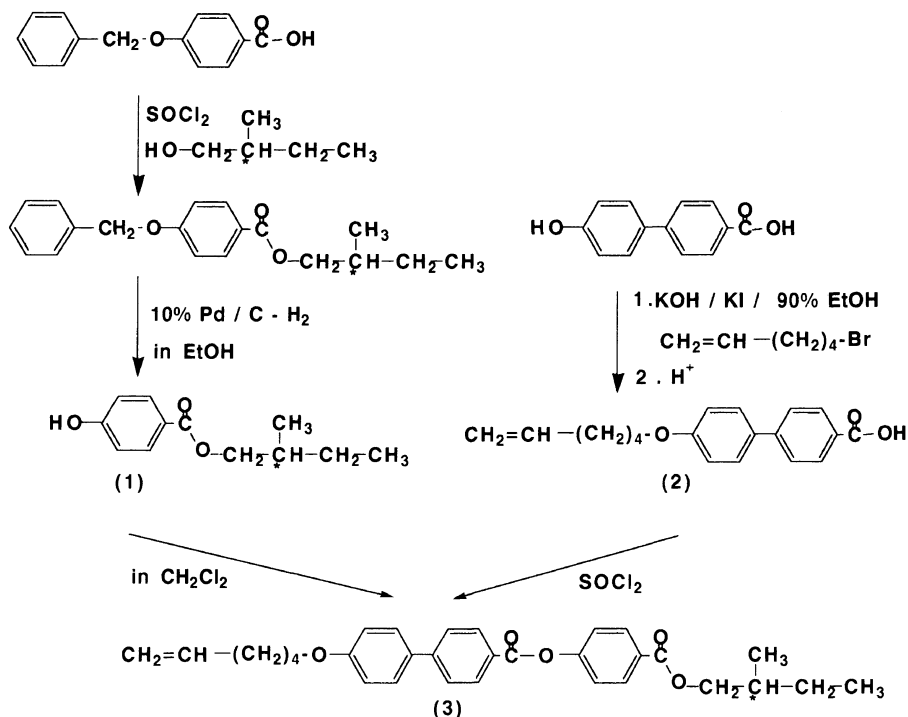
weight was determined by GPC equipped with Shimadzu RID-60A refractive index detector using toluene as the eluent. Vapor pressure osmometry was conducted in benzene with Corona 117 instrument. X-ray diffraction experiments were carried out on a Rigaku RU 200 instrument with flat film using Ni filtered  $\text{Cu-K}_\alpha$  radiation. The polymer sample (melt drawn fiber) was sealed in a glass capillary and placed on hot stage. Diffraction patterns were taken at regular intervals from 50 to  $240^\circ\text{C}$ . Homogeneously aligned cells of  $2\ \mu\text{m}$  thickness were prepared by rubbing thin polyimide films coated on the substrate plates. Response time was measured by applying electric field ( $\pm 80\ \text{V}$  and  $1\ \text{Hz}$ ) on the sample. Changes of the optical transmittance was recorded through a photomultiplier and an oscilloscope. The time measured was that required to change the light transmittance from 0 to 90%.

## RESULTS AND DISCUSSION

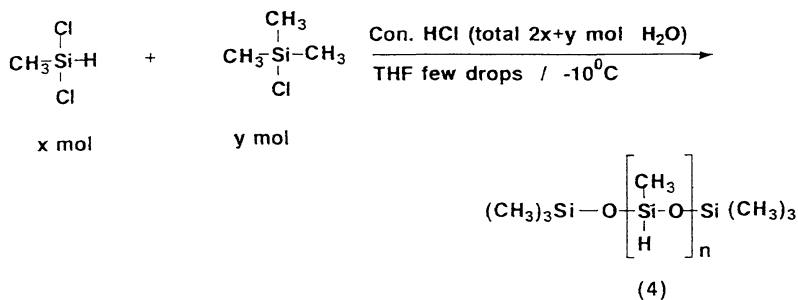
The side chain liquid crystalline polysiloxanes **5** were synthesized by the hydrosilylation reaction between polysiloxanes **4** possessing silylhydride group and the mesogenic compound **3** functionalized by terminal olefin.

The ferroelectric liquid crystalline polysiloxanes **5** should possess a mesogen with an asymmetric carbon center to show the chiral smectic C ( $\text{S}_\text{C}^*$ ) phase. The mesogenic unit in the present study was (*S*)-(-)-4-(2-methylbutyloxycarboxy)phenyl 4'-(5-alkyloxy)biphenyl-4-carboxylate, which has been reported<sup>22</sup> to show three kinds of smectic phases. For instance, the reported phase transition temperatures on heating was reported as follows (the long alkyl group was nonyl); from crystal (C) to smectic I ( $\text{S}_\text{I}$ ),  $52.5^\circ\text{C}$ ; from  $\text{S}_\text{I}$  to  $\text{S}_\text{C}^*$ ,  $57.0^\circ\text{C}$ ; from  $\text{S}_\text{C}^*$  to smectic A ( $\text{S}_\text{A}$ ),  $143.5^\circ\text{C}$ ; from  $\text{S}_\text{A}$  to isotropic (I),  $184.5^\circ\text{C}$ .

The precursor mesogenic compound **3**



Scheme 1.

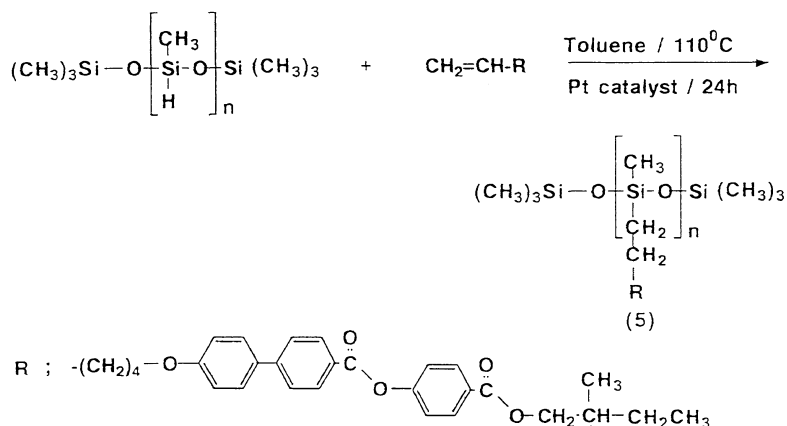


Scheme 2.

possessing terminal olefin was synthesized by the analogous method for the saturated liquid crystals as shown in Scheme 1 with the overall yield of 43%, where (*S*)-(-)-2-methylbutyl 4-hydroxybenzoate **1** and 4'-(5-hexenyloxy)-biphenyl-4-carboxylic acid **2** were connected *via* ester linkage. From the DSC curve shown in Figure 4(a) and the observation of polarized microscope, it was found that the precursor olefinic compound **3** also displayed the  $S_C^*$

phase as the case of the saturated analogs, and the phase transition temperatures was observed as follows on cooling: from I to  $S_A$ , 190°C: from  $S_A$  to  $S_C^*$ , 116°C: from  $S_C^*$  to  $S_X$  (unknown smectic phase suspected of being  $S_I$ ), 76.9°C: from  $S_X$  to C, 45°C. Here the  $S_C^*$  phase is broader compared with that of the corresponding saturated compound.

Poly(methylsiloxane)'s **4** with various degree of polymerization were synthesized by the



Scheme 3.

hydrolysis and condensation of dichloromethylsilane using hydrochloric acid, where the molecular weights of **4** were controlled by varying the amount of chlorotrimethylsilane, the end capping reagent. The molecular weights and the molecular weight distributions of **4** are summarized in Table I. The molecular weights of **4** were higher than the expected values calculated by the ratio of the monomer to the end capping reagent. This may be caused by the lower reactivity of chlorotrimethylsilane compared with dichloromethylsilane.

Liquid crystalline polysiloxanes **5** were prepared by the hydrosilylation reaction between poly(methylsiloxane)'s **4** and the olefin terminated mesogenic compound **3** in the presence of platinum catalyst. The major factors which may affect the quantitative understanding of the molecular weight on the phase transition are the polymer purity and the  $M_w/M_n$  ratio. In order to get a pure polymer, the reprecipitation was carried out several times until TLC and GPC showed no traces of the mesogenic compound. Polymers **5a** and **5g** were purified by preparative GPC. The  $M_w/M_n$  ratios of all the polymer samples were found to be in the range of 1.2–1.6.

A typical  $^1\text{H}$  NMR spectrum and a GPC chromatogram of liquid crystalline polysiloxane **5d** are given in Figures 2 and 3,

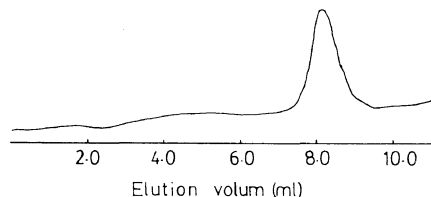
**Table I.** Molecular weight and  $M_w/M_n$  of poly(methylsiloxane), **4**

Sample	X:Y ratio <sup>a</sup>	$M_w/M_n$	Molecular weight ( $M_n$ )	
			GPC <sup>b</sup>	VPO <sup>c</sup>
<b>4a</b>	4:4	1.2	4200	1400
<b>4b</b>	4:3	1.3	6100	1800
<b>4c</b>	4:2	1.3	6600	1900
<b>4d</b>	4:1	1.5	7300	2100
<b>4e</b>	10:1	1.4	8200	2250
<b>4f</b>	20:1	1.4	9000	2500
<b>4g</b>	35:1	1.9	38000	9500

<sup>a</sup> See Scheme 2.

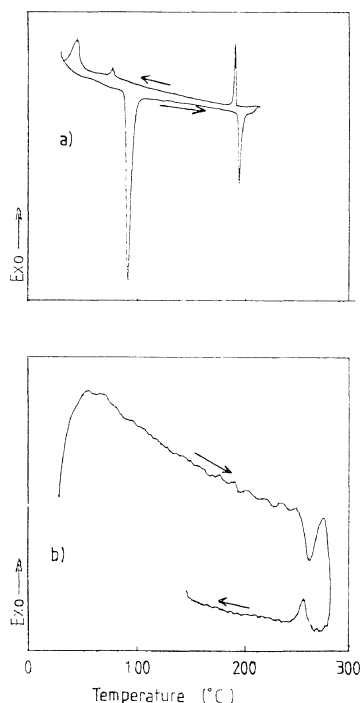
<sup>b</sup> Gel permeation chromatography was carried out with polystyrene standards using toluene as eluent.

<sup>c</sup> Vapor pressure osmometry was carried out in benzene with polystyrene standards.



**Figure 3.** Gel permeation chromatogram of liquid crystalline polymer **5c**.

respectively. The ratio of the integration of methyl protons of polysiloxane to aromatic protons of the mesogenic unit agreed with the



**Figure 4.** Heating and cooling scans of a) precursor alkene b) liquid crystalline polymer **5e**.

calculated value. Furthermore, the absorption corresponding to the silylhydride bond at  $2160\text{ cm}^{-1}$  was not observed in the IR spectra of the resulting polymers. These facts indicated that the hydrosilylation reaction was proceeded quantitatively.

A typical DSC trace of **5e** is presented in Figure 4(b). The polymers showed a single peak on both heating and cooling that corresponds to the  $S_A$ -I transition. As the liquid crystalline phase transitions could not be precisely identified by DSC analysis, they were determined by the optical polarizing microscopic observation. On cooling from the isotropic phase, it showed a fine grain batonnet texture in the beginning and then merged into a focal conic fan texture of  $S_A$  phase, followed by broken fan texture corresponding to the  $S_C^*$  phase. Heating process also gave clear textures for  $S_A$  and  $S_C^*$  mesophases. Phase transition behaviors of the polymers are given in Table

**Table II.** Phase transition temperatures of liquid crystalline polysiloxanes **5** measured on cooling

Polymer	$M_n^a$	$M_w/M_n$	Phase transition temperature/°C
<b>5a-1<sup>b</sup></b>	4800	1.04	I 220 SA 188 $S_C^*$ rt
<b>5a-2<sup>b</sup></b>	10500	1.16	I 222 SA 190 $S_C^*$ rt
<b>5g-1<sup>c</sup></b>	12000	1.08	I 227 SA 198 $S_C^*$ rt
<b>5b</b>	21000	1.33	I 241 SA 208 $S_C^*$ rt
<b>5c</b>	21200	1.26	I 241 SA 207 $S_C^*$ rt
<b>5d</b>	22800	1.46	I 240 SA 208 $S_C^*$ rt
<b>5e</b>	24000	1.33	I 249 SA 215 $S_C^*$ rt
<b>5f</b>	29800	1.61	I 249 — <sup>d</sup>
<b>5g-2<sup>c</sup></b>	36100	1.31	I 251 — <sup>d</sup>

<sup>a</sup> Measured by gel permeation chromatography with polystyrene standards using toluene as the eluent.

<sup>b</sup> Obtained by preparative GPC of polymer **5a**.

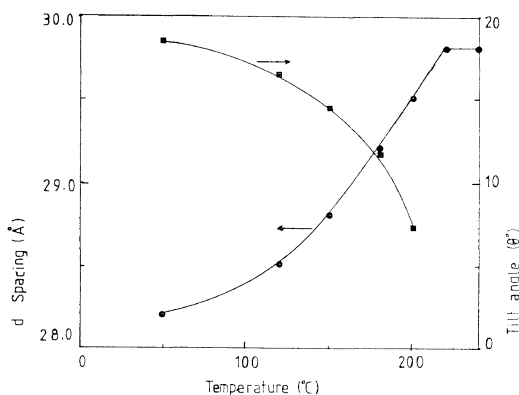
<sup>c</sup> Obtained by preparative GPC of polymer **5g**.

<sup>d</sup> Phase transition was not obvious.

II. The phase transition temperatures of polymers **5** were always higher than that of the precursor olefin terminated mesogenic compound **3**. The  $S_C^*$  phase temperature range of **5** was very broad and kept even at room temperature. However, in the polymers having high molecular weight such as **5f** and **5g-2**, well formed smectic texture could not be observed. Therefore, it is difficult at this time to discuss the mesomorphic behavior of these polymers. While polymer **5e** exhibited a very clear smectic textures, the uncertain nature of phase transition of **5f** (and **5g-2**) could be linked to the molecular weight increment of about 6000. Such behavior has also been reported,<sup>24,25</sup> and this may be due to the high polymer viscosity, which hinders a prompt formation of layer structures. In contrast, according to Percec *et al.*,<sup>21</sup> appearance of different smectic phases have been observed when the degree of polymerization higher than 12.

Figure 5 shows the variation in the layer spacing ( $d$ ) and the tilt angle ( $\theta$ ) of the mesogenic unit determined by the small angle X-ray diffraction with changing temperature in the case of **5e**. The layer spacing gradually increased with increasing temperature, and it became constant above  $220^\circ\text{C}$ , which corre-

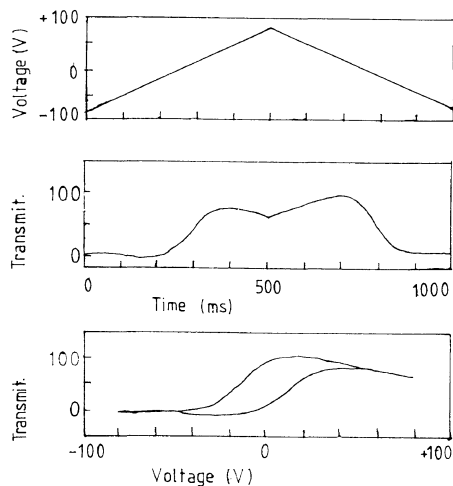




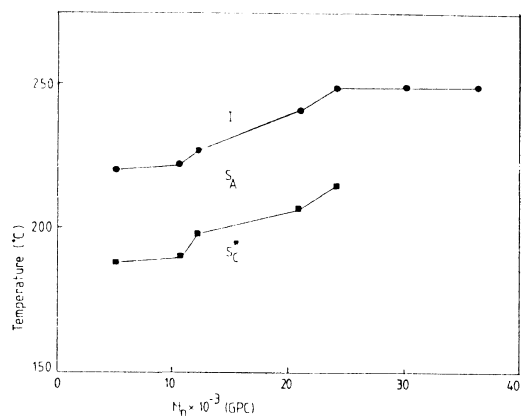
**Figure 5.** Variation of polymer layer spacing,  $d$  (Å)/tilt angle ( $\theta^\circ$ ) with temperature.

sponded to the  $S_C^* - S_A$  transition temperature. In the case of the  $S_A$  phase, the observed layer spacing was found to be 2.9 nm, which agreed with the calculated value of 3.1 nm including the length of mesogenic moiety, alkyl spacer unit, and  $\text{Si}-\text{CH}_3$ . These results indicated that the mesogenic unit on the side chain began to tilt at the  $S_C^* - S_A$  transition temperature on cooling, and then the tilting angle increased with decreasing temperature.

Due to the low glass transition temperature of polysiloxane backbone, liquid crystalline (LC) polysiloxanes are expected to be favorable candidate for fast switching polymers. To our knowledge, there have been very few reports on switchable LC polysiloxanes. Among them the fastest switching time has been reported by Dumon *et al.*<sup>10</sup> Here the backbone was methylhydrogen-dimethylsiloxane copolymer and only 30% of silyl hydrogen was replaced by the mesogenic unit. This fast switching behavior was probably due to the low viscosity caused by low molecular weight and low introduction ratio. Scherowsky *et al.*<sup>8</sup> have reported LC polysiloxane with response time of 200 ms. Figure 6 shows the optical responses to switching in a cell under a triangular wave voltage at 140°C for **5a**. This switchable nature further confirms the presence of  $S_C^*$  mesophase. The optimum response time of this



**Figure 6.** Polymer optical response to a triangular voltage wave of  $\pm 80$  V.



**Figure 7.** Effect of molecular weight on the phase transition temperature of liquid crystalline polymers.

polymer was found to be 175 ms at 140°C.

It is accepted that regardless of the nature of the backbone, the liquid crystalline transition temperatures increase up to a certain degree of polymerization and then remain constant. In this study, we found that the  $I - S_A$  and  $S_A - S_C^*$  transition temperatures gradually increased with increasing molecular weight as shown in Figure 7. As far as the  $I - S_A$  transition is concerned, the temperatures ceased to increase in the high molecular weight polymers such as **5f** and **5g-2**.

In conclusion, new ferroelectric liquid crystalline polysiloxanes were obtained by incorporating a mesomeric ester constructed with a chiral alcohol and 4-biphenylcarboxybenzoic acid core unit into the polysiloxane side chain via a flexible spacer. Mesomorphic range of the polymer is appreciably higher than that of the mesogenic precursor alkene. Polymer exhibits  $S_A$  and  $S_C^*$  phases and the  $S_C^*$  phase remains even at room temperature. When the degree of polymerization is above 40, the phase transition temperature became molecular weight independent. Polymers were switchable by electric field and the optimum response time was 175 ms.

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