Novel Fluorine-Containing Ferroelectric Side Chain Liquid-Crystalline Polysiloxanes Showing Bistable Fast Switching

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ABSTRACT: A series of new ferroelectric liquid-crystalline polymers consisting of a polysiloxane main chain with a side chain of 4-([1-(trifluoromethyl)alkoxy(*n*)]carbonyl)phenyl 4′-alkoxy(*m*)biphenyl-4-carboxylate (**5**) were synthesized by the direct polycondensation of the corresponding liquid crystalline dichlorosilane monomers with water. The mesogenic dichlorosilanes were prepared by the hydrosilylation of the mesogenic compounds possessing terminal olefine with dichloromethylsilane in the presence of hexachloroplatinic acid. The liquid crystalline polymers were characterized by differential scanning calorimetry (DSC), optical polarizing microscopy (OPM), and electrooptical studies as well. All the polymers displayed an enantioropic smectic A phase (S_A) and a broad chiral smectic C (S_c*) phase, where the S_c* phase persisted even below 20 °C. The polymer molecular weights were in the range of 4.5×10^3 to 11.0×10^3. These materials showed bistable fast switching in the oriented samples (2.7-μm cells) having the response time of a few hundred microseconds, the shortest response time reported so far for liquid crystalline polymers, driven by a rectangular wave voltage of ±50 V. Spontaneous polarization of the polymers was found to be in the range of 32–122 nC/cm² at T_c −30 °C (T_c = S_A–S_C* transition temperature).

Introduction

The discovery[1] of ferroelectricity in the chiral smectic C phase of liquid crystals and the concept of developing a fast switching bistable device based on this principle[2] have resulted in a concerted effort to synthesize new compounds which show the ferroelectric liquid crystalline behavior (FLC). This mesophase has a good potential as electrically active media in a wide variety of applications including displays,[3] light valves,[4] spatial light modulators,[5] and optical processing.[6] To be a good candidate in electrically active devices, a FLC material should possess some vital requirements such as low rotational viscosity, high spontaneous polarization, and a broad S_C* phase at around room temperature. Chemists have successfully prepared a large number of low molecular weight FLC compounds, and some of them have spontaneous polarization as large as 1.5 mC/m² or more.[7]

In contrast, studies on polymeric FLC systems, which possess better mechanical properties compared with monomeric ones and structural features of liquid crystals, are fairly new. Although several FLC polymers have been reported, in only a few cases, ferroelectric properties such as spontaneous polarization and response time have been given.[8-15] Among them the fastest response time of 300 μs has been reported by Dumon et al.[12] Recently, antiferroelectric ordering was also reported in LC side group polymers.[15-19]

Polymeric liquid crystals, in comparison with monomeric ones, clearly show superiority with regard to chemical resistance, high modulus, and ease of processing. The main disadvantage of these polymers is high viscosity and, hence, longer response time to an external electric field. This severely limits the applicability of FLC polymers in fast switching devices. Therefore in order to answer this challenge, it is obviously useful to synthesize various kinds of FLC polymers and then explore their application potentials.

In this study we have synthesized a series of new FLC polymers containing polysiloxane main chain with side chain of 4-([1-(trifluoromethyl)alkoxy(*n*)]carbonyl)phenyl 4′-alkoxy(*m*)biphenyl-4-carboxylate. One of the authors reported that the low molecular weight liquid crystals corresponding to the side chain group showed not only ferroelectric but also antiferroelectric ordering.[7] In addition, it has also been reported[13] that the side chain liquid crystalline polymethacrylates possessing some of these mesogens exhibited S_c* phase with a response time less than 10 ms.

Polysiloxane backbone, because of its extreme flexibility, gives liquid crystalline polymers with the lowest glass transition temperatures among all known mesomorphic polymers.[20] Therefore, in this study polysiloxane backbone was used in order to obtain polymers with broad mesomorphic range, even at room temperature. Side chain liquid crystal polysiloxane polymers are commonly prepared by the hydrosilylation reaction of poly(hydrogen methylsiloxane) with appropriate mesogens terminated with a vinyl function in the presence of a platinum catalyst. This conventional method, however, has some major problems, such as nonreproducability, and cross-linking of the resulting polymers due to incompletion of hydrosilylation reaction. To overcome these shortcomings, as Subramaniam et al.[21] have reported, polymers were prepared by the direct polycondensation of appropriate mesogenic dichlorosilane in the presence of water. In spite of the relatively low molecular weight, this method has some merits, which include the presence of a consecutive mesogenic pendant over the entire polymer length, free of cross-linking, and narrow molecular weight distribution.

Experimental Section

Materials. Bromoolefins such as 6-bromohexene and 8-bromooctene were obtained from Aldrich and used as received, and 10-bromohexene was prepared by treatment of 9-decene-1-ol with

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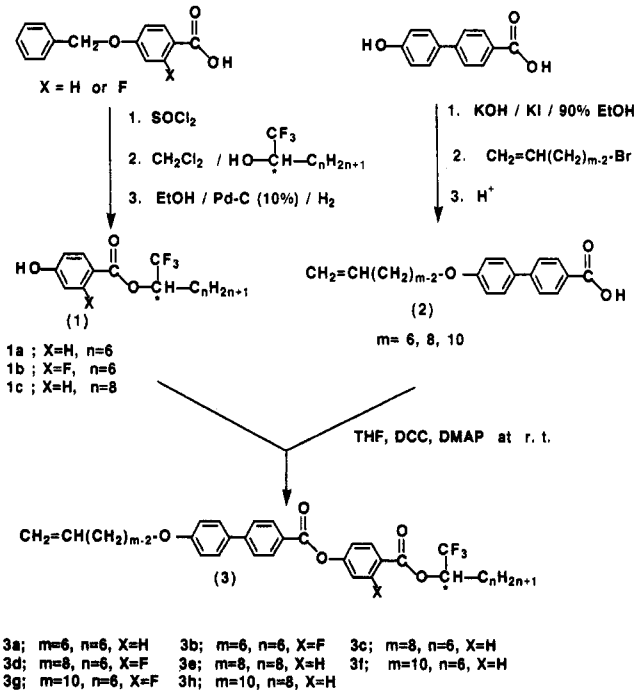
Scheme 1. Synthesis of Vinyl Mesogenic Precursors (3)



3a; m=6, n=6, X=H 3b; m=6, n=6, X=F 3c; m=8, n=6, X=H
3d; m=8, n=6, X=F 3e; m=8, n=8, X=H 3f; m=10, n=6, X=H
3g; m=10, n=6, X=F 3h; m=10, n=8, X=H

phosphorus tribromide under the reported conditions.[22] The other reagents, 4'-hydroxybiphenyl-4-carboxylic acid, 9-decene-1-ol, dimethylcholorsilane, and hexachloroplatinic acid hydrate were purchased from Tokyo Kasei Co., Japan. Tetrahydrofuran (THF) and toluene were distilled over sodium under nitrogen atmosphere.

Measurements. ^{1}H-NMR spectra were recorded on a JEOL FX90Q instrument. Obvious multiplicities and routine coupling constants were usually not listed here. IR spectra were recorded on a Shimadzu FT/IR 8000 spectrophotometer. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) at room temperature with a Shodex KF 802.5 column equipped with Shimadzu RID-60A refractive index detector using THF as the eluent. GPC column was calibrated using polystyrene standards ranging from 5.8×10^2 to 6.8×10^4. Preparative GPC was run with a Shodex H 20025 column using chloroform as the solvent. Differential scanning calorimetry (DSC) was carried out with a Rigaku DSC-8240D instrument at a heating rate of 3.0 °C/min under nitrogen on both heating and cooling processes.

The optical polarization microscopic studies were made at a heating rate of 1.0 °C using an Olympus BH2 polarizing instrument fitted with a Mettler FP-82 hot stage. General procedure for electrooptical measurements are as follows: Cells (2.7 μm thick), aligned by rubbing after coating the indium tin oxide (ITO) deposited glass plates with polyimide films, were filled with the liquid-crystalline compounds in their isotropic state. The resulting cell was slowly cooled at a rate of 0.1 or 1.0 °C/min to orientate the liquid-crystalline molecules. While cooling, a triangular wave voltage of ±40 V at 1 Hz was applied. The cell was set between a pair of cross polarizers in such a manner that the direction of the longer axis of the molecule was parallel to one of the polarizers when there is no applied voltage, and changes of transmittance were monitored by oscilloscope. The spontaneous polarization was measured by the triangular wave voltage method[23] (±50 V, 10 Hz). The response time was determined by applying a rectangular wave voltage of ±50 V at 1 Hz.

Monomer Synthesis. Vinyl monomers *3* were synthesized according to Scheme 1. Chiral alcohols (*R*)-(+)-1,1,1-trifluoro-2-octanol and (*R*)-(+)-1,1,1-trifluorodecanol were prepared by the procedure reported in the literature.[7]

1-(Trifluoromethyl)heptyl 4-hydroxybenzoate (**1a**) was prepared as follows. Crude 4-benzyloxybenzoyl chloride, which was obtained by the reaction of 4-benzylbenzoic acid (2.28 g, 0.010 mol) with excess thionyl chloride and a few drops of *N,N*-dimethylformamide (DMF) at 60 °C for 2 h, was dissolved in dichloromethane (25 mL), and the solution was added dropwise to a mixture of (*R*)-(+)-1,1,1-trifluoro-2-octanol (1.84 g, 0.010 mol), triethylamine (1.01 g, 0.011 mol), and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine in dichloromethane (25 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h, poured into ice-water, and extracted with dichloromethane. The organic layer was successively washed with 1 M hydrochloric acid, 1 M sodium carbonate, and water and dried over anhydrous magnesium sulfate. The crude product, obtained by removing the solvent, was purified by column chromatography using silica gel with *n*-hexane/ethyl acetate (10:1) as the eluent in 41% (1.6 g) yield.

A mixture of the resulting ester compound (1.6 g) and 10% palladium on carbon (0.16 g) in ethanol (50 mL) was stirred for 24 h at 25 °C under hydrogen atmosphere. Filtration of the mixture followed by evaporation of the solvent yielded 1.18 g of 1-(trifluoromethyl)heptyl 4-hydroxybenzoate (**1a**): ^{1}H NMR ($CDCl_3$, δ, ppm) 8.00 (2H, d, Ar–H), 7.43 (1H, s, OH), 6.93 (2H, d, Ar–H), 5.49 (1H, m, $CHCF_3$), 1.84–1.20 (10H, m, $(CH_2)_5$), 0.88 (3H, t, CH_3).

1-(Trifluoromethyl)heptyl 2-fluoro-4-hydroxybenzoate (**1b**) and 1-(trifluoromethyl)nonyl 4-hydroxybenzoate (**1c**) were prepared by the same procedure.

1-(Trifluoromethyl)heptyl 2-fluoro-4-hydroxybenzoate (**1b**): ^{1}H NMR ($CDCl_3$, δ, ppm) 7.87 (1H, m, Ar–H), 7.08 (1H, s, OH), 6.75–6.61 (2H, m, Ar–H), 5.60–5.39 (1H, m, $CHCF_3$), 2.20–1.10 (10H, m, $(CH_2)_5$), 0.86 (3H, t, CH_3).

1-(Trifluoromethyl)nonyl 4-hydroxybenzoate (**1c**): ^{1}H NMR ($CDCl_3$, δ, ppm) 7.97 (2H, d, Ar–H), 7.39 (H, s, OH), 6.90 (2H, d, Ar–H), 5.50 (1H, m, $CHCF_3$), 1.84–1.20 (14H, m, $(CH_2)_7$), 0.83 (3H, t, CH_3).

4'-(5-Hexenyloxy)biphenyl-4-carboxylic acid (**2a**) was prepared as follows. In a flask, 4'-hydroxybiphenyl-4-carboxylic acid (4.28 g, 0.020 mol) was refluxed with potassium hydroxide (2.46 g, 0.044 mol) and a few crystals of potassium iodide in 90% ethanol (200 mL). After 1 h, 6-bromohexene (3.00 g, 0.022 mol) was added dropwise to the mixture, and the resulting solution was refluxed for 20 h. The mixture was neutralized with 6 M hydrochloric acid. The resulting white precipitate, obtained by pouring the solution into ice-water, was recrystallized from acetic acid. The yield was 72% (4.30 g). IR (KBr, cm^{-1}): 1686 (s), 1288 (s). Three mesogenic transitions were observed at 204, 234, 266 °C.

4'-(7-Octenyloxy)biphenyl-4-carboxylic acid (**2b**) and 4'-(9-decenyloxy)biphenyl-4-carboxylic acid (**2c**) were also prepared by the same procedure. ^{1}H NMR spectra of all three acids were identical (DMSO-d_6, δ, ppm) 8.07–7.97 (2H, d, Ar–H), 7.68–7.51 (4H, m, Ar–H), 7.03–6.89 (2H, d, Ar–H), 5.98–5.61 (1H, m, CH=C), 5.12–4.92 (2H, m, CH_2=C), 4.08–3.84 (2H, t, OCH_2), 2.24–1.39 ($2(n-3)$H, m, $(CH_2)_{n-3}$).

(*R*)-(+)-4-(((1-(Trifluoromethyl)heptyl)oxy)carbonyl)phenyl 4'-(5-hexenyloxy)biphenyl-4-carboxylate (**3a**) was prepared as follows. A solution of 4'-(5-hexenyloxy)biphenyl 4-carboxylic acid (**2a**) (2.20 g, 0.010 mol), 1,3-dicyclohexylcarbodiimide (DCC) (2.27 g, 0.011 mol), and 4-(*N,N*-dimethylamino)pyridine (0.12 g, 0.001 mol) in THF (50 mL) was stirred for 24 h at 30 °C. The white precipitate of 1,3-dicyclohexylurea was filtered and THF was removed in vacuo. The white solid was dissolved in dichloromethane and the resulting solution was successively washed with water, 5% acetic acid, and again with water, and dried over anhydrous magnesium sulfate. The solvent was removed and the resulting white solid was purified by column chromatography using silica gel with hexane/ethyl acetate mixture (20:1) as the eluent. Finally the product was recrystallized from ethanol.

Eight vinyl mesogenic precursor compounds (**3a–h**) were prepared by the same procedure.

The elemental analysis and ^{1}H NMR data of all the compounds **3** are summarized in Table 1. The phase transition temperatures are given in Table 2.

Polymer Synthesis. Polymer synthesis was carried out as given in Scheme 2. The detailed procedure is described below.

A mixture of **3a** (1.0 g, 1.6 mmol), hexachloroplatinic acid (0.12 M in THF, 2 drops), dried toluene (5 mL), and dichloromethylsilane (0.16 g, 1.6 mmol) was heated at 35–40 °C for 24 h. The mixture was filtered under nitrogen and the solvent was removed under reduced pressure. A pale yellow oily product of (*R*)-(+)-

Table 1. Characterization of Mesomeric Vinyl Precursors (3)

compound (formula)	elemental analyses % C found (calcd)	% H found (calcd)	^{1}H-NMR ($CDCl_3$, δ, ppm)
3a	69.74	6.25	0.88 (3H, t, CH_3), 1.20–2.20 (16H, m, CH_2), 4.05 (2H, t, CH_2O), 5.05 (2H, m, CH_2=), 5.40–6.10 (2H, m, $CHCF_3$ & CH=), 6.90–8.40 (12H, m, ArH)
($C_{34}H_{37}O_5F_3$)	(70.10)	(6.36)	
3b	68.91	5.86	0.89 (3H, t, CH_3), 1.20–2.28 (16H, m, CH_2), 4.03 (2H, t, CH_2O), 5.05 (2H, m, CH_2=), 5.45–6.05 (2H, m, $CHCF_3$ & CH=), 6.95–8.28 (11H, m, Ar–H)
($C_{34}H_{36}O_5F_4$)	(68.60)	(6.00)	
3c	70.72	6.89	0.87 (3H, t, CH_3), 1.10–2.20 (20H, m, CH_2), 4.00 (2H, t, OCH_2), 5.00 (2H, m, CH_2=), 5.45–6.05 (2H, m, $CHCF_3$ & CH=), 6.95–8.35 (12H, m, ArH)
($C_{36}H_{41}O_5F_3$)	(70.80)	(6.72)	
3d	68.79	6.37	0.88 (3H, t, CH_3), 1.20–2.20 (20H, m, CH_2), 4.02 (2H, t, OCH_2), 5.00 (2H, m, CH_2=), 5.50–6.10 (2H, m, $CHCF_3$ & CH=), 6.94–8.24 (11H, m, ArH)
($C_{36}H_{40}O_5F_4$)	(68.91)	(6.79)	
3e	71.08	7.10	0.87 (3H, t, CH_3), 1.20–2.20 (24H, m, CH_2), 4.02 (2H, t, OCH_2), 5.01 (2H, m, CH_2=), 5.40–6.0 (2H, m, $CHCF_3$ & CH=), 6.95–8.28 (12, m, Ar-H)
($C_{38}H_{45}O_5F_3$)	(71.47)	(7.05)	
3f	71.00	7.25	0.88 (3H, t, CH_3), 1.10–2.20 (24H, m, CH_2), 4.01 (2H, t, OCH_2), 5.00 (2H, m, CH_2=), 5.40–6.05 (2H, m, $CHCF_3$ & CH=), 6.95–8.28 (12H, m, ArH)
($C_{38}H_{45}O_5F_3$)	(71.47)	(7.05)	
3g	69.74	6.61	0.87 (3H, t, CH_3), 1.20–2.20 (24H, m, CH_2), 4.00 (2H, t, OCH_2), 5.07 (2H, m, CH_2=), 5.45–6.05 (2H, m, $CHCF_3$ & CH=), 6.94–8.22 (11H, m, ArH)
($C_{38}H_{44}O_5F_4$)	(69.51)	(6.71)	
3h	72.71	7.34	0.88 (3H, t, CH_3), 1.05–2.20 (28H, m, CH_2), 4.02 (2H, t, OCH_2), 5.00 (2H, m, CH_2=), 5.35–6.10 (2H, m, $CHCF_3$ & CH=), 6.95–8.30 (12H, m, ArH)
($C_{40}H_{49}O_5F_3$)	(72.07)	(7.36)	

Table 2. Phase Transition Temperatures of Vinyl Mesogenic Precursors (3)[a]

compound	transition temperature, °C (on cooling)						
3a	I	136.7	S_A	120.8	S_{CA}*	81.5	C
3b	I	117.1	S_A	114.3	S_{CA}*	40.4	C
3c	I	115.7	S_A	107.9	S_{CA}*	70.9	C
3d	I			100.5	S_{CA}*	13.8	C
3e	I	104.6	S_A	92.1	S_{CA}*	62.8	C
3f	I	99.7	S_A	97.4	S_{CA}*	-3.1	C
3g	I			90.4	S_{CA}*	1.1	C
3h	I	89.6	S_A	85.1	S_{CA}*	2.4	C

[a] I, isotropic; S_A, smectic A; S_{CA}*, antiferroelectric; C, crystal.

4-(((1-(trifluoromethyl)heptyl)oxy)carbonyl)phenyl 4-(6-dichloromethylsilyl)hexyloxybiphenyl-4-carboxylate (**4a**) was obtained.

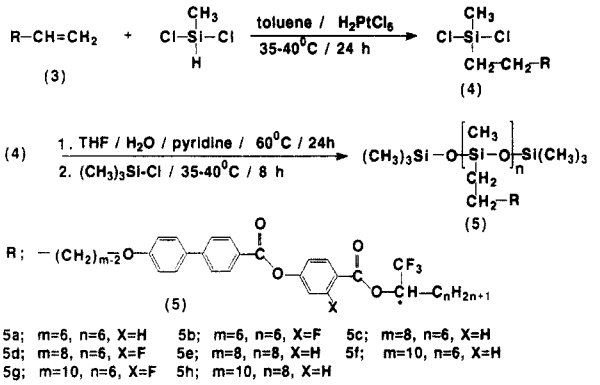
Water (0.3 mL) was added to the stirred solution of crude **4a** in THF (5 mL). After 15 min pyridine (0.2 mL) was added to the solution and the mixture was refluxed for 22 h, followed by the addition of trimethylchlorosilane (0.02 mL). The mixture was refluxed for another 5 h. The resulting polymer **5a** was precipitated by addition of excess methanol. The purification procedure of dissolving **5a** in THF and reprecipitation by adding excess methanol was repeated several times. Further purification of the polymer was conducted by preparative GPC. A typical ^{1}H NMR spectrum of the polymer **5e** is given in Figure 1b.

Results and Discussion

Monomers. All the vinyl precursors, (*R*)-(+)-4-([1-(trifluoromethyl)alkoxy]carbonyl)phenyl 4′-(ω-alkenyloxy)biphenyl-4-carboxylate (**3**), were synthesized by using known procedures as described in Scheme 1. The fluorine-containing starting chiral compounds, 1,1,1-trifluoro-2-octanol and 1,1,1-trifluoro-2-decenol, were prepared by the method reported by Suzuki et al.[7] Enantiomeric excess of these compounds was found to be 92–95%.

Compound **1** was prepared starting from *p*-benzyloxybenzoic acid by successive procedures, i.e. the protection of the hydroxyl group, the conversion to acid chloride, the esterification, and the deprotection to form hydroxyl function. On the other hand, the direct etherification of 4′-(hydroxy)biphenyl-4-carboxylic acid with ω-alkenyl bromide afforded compound **2**. The coupling reaction between **1** and **2** was carried out by using 1,3-dicyclohexylcarbodiimide (DCC) as a dehydrating agent.

Scheme 2. Synthesis of Polysiloxanes (5)



The mesomorphic behavior of side chain units **3** was assigned on the basis of DSC pattern, optical textures, and electrooptical measurements. A typical DSC trace of monomer **3c** is given in Figure 2a. It exhibited two major peaks and another minor peak both in heating and cooling scans, giving evidence for the presence of two enantiotropic mesophases. When observed with optical polarization microscopy, the higher temperature mesophase exhibited the fan texture characteristic of a smectic A (S_A) phase. The lower temperature mesophase was confirmed to be antiferroelectric (S_{CA}*), as it gives a double hysteresis in electrooptical measurement studies.

Except for **3d** and **3g**, all the vinyl compounds display enantiotropic S_A and S_{CA}* mesophases as shown Table 2. A narrow S_C* phase, which has been reported[7] in the corresponding saturated analogs, was not observed with these compounds. In the case of **3d** and **3g**, which possessed an additional fluorine atom at the ortho position of the benzene ring, only the antiferroelectric mesophase was observed. The additional S_A mesophase observed with the corresponding saturated compounds did not appear. In addition, the clearing temperatures of these compounds are lower than their saturated counterparts.

Polymers. Regarding the synthesis of liquid-crystalline polysiloxane, several attempts were made by the conven-

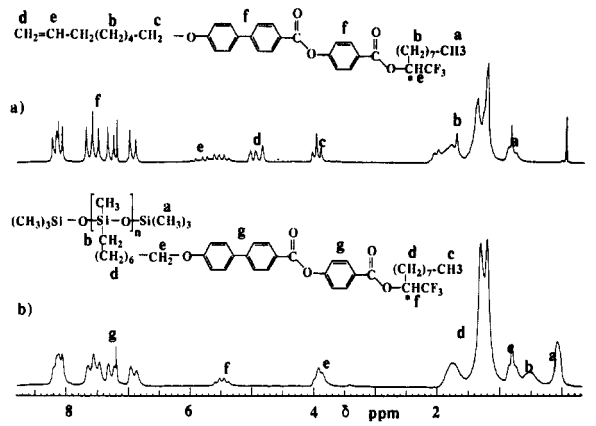


Figure 1. ^{1}H NMR spectra of (a) **3e** and (b) **5e**.

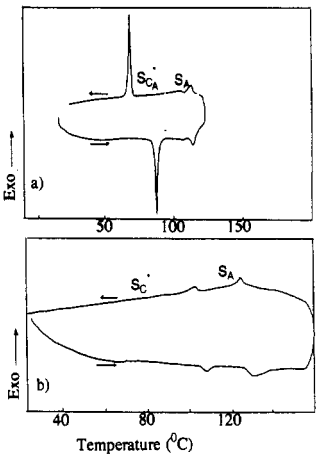


Figure 2. DSC patterns of (a) **3c** and (b) **5c**.

Table 3. Phase Transition Temperatures (°C) of the Polymers (5)

polymer	M_n[a]	M_w/M_n	transition temperature, °C (on cooling)						τ[b]	P_s[c]
5a	4500	1.2	I	113.0	S_A	86.0	S_c*	<20	5.60	<5
5b	6100	1.1	I	109.8	S_A	82.0	S_c*	<20	0.88	84
5c	6300	1.1	I	127.2	S_A	103.7	S_c*	<20	0.33	102
5d	5400	1.1	I	127.4	S_A	110.7	S_c*	<20	0.13	107
5e	11000	1.2	I	109.1	S_A	65.0	S_c*	<20	32.00	<5
5f	7000	1.1	I	134.8	S_A	100.3	S_c*	<20	0.51	122
5g	8100	1.7	I	111.5	S_A	107.8	S_c*	<20	0.24	32
5h	8800	1.3	I	109.5	S_A	66.9	S_c*	<20	6.00	<5

[a] Measured by gel permeation chromatography with polystyrene standards using THF as the eluent. [b] Response time (ms) measured at T_c −10 °C, where T_c is the S_A–S_C* transition temperature. [c] Spontaneous polarization (nC/cm^2) measured at T_c −30 °C.

tional hydrosilylation of the vinyl mesogens with poly(hydrogen methylsiloxane) in the presence of hexachloroplatinic acid or dicyclopentadienylplatinum(II) chloride catalyst. Unfortunately, successful results could not be obtained by this method. Most probably, this could be due to the low efficiency of hydrosilylation reaction. Therefore in this study, the polymers were synthesized by the direct polycondensation of the mesogenic dichlolosilanes, as outlined in Scheme 2. The hydrosilylation reaction between the vinyl mesogen and dichlorosilane was conducted at 35–40 °C in the presence of hexachloroplatinic acid. The polycondensation of compound **4** with water was carried out for 24 h and then trimethylchlorosilane was added to give the trimethylsilyl-terminated polymers. They were purified by repeated precipitation from the THF and methanol system. One of the major shortcomings of this purification procedure was that a notable amount of the polymer was lost during the purification process. The white pastelike polymers obtained after purification were characterized by IR, ^{1}H NMR, and GPC analysis.

A representative ^{1}H-NMR spectra of polymer **5e** and the corresponding vinyl compound **3e** are shown in Figure 1, together with their proton assignments. The spectrum of polymer **5e** showed a broad resonance at δ 0.1–0.3 ppm for Si–CH_3 protons and at δ 0.5 ppm for Si–CH_2 protons, and a multiplet at δ 5.5 ppm for $CHCF_3$. The multiplicity pattern of aromatic protons is similar to that of the corresponding vinyl compound **3e**. These data were consistent with the expected structure. As there is no trace of signals for CH_2= at δ 4.5 ppm, the polymer was considered to be free of the vinyl precursor. A fairly narrow single peak in the GPC pattern further confirms the polymer purity. As given in Table 3, the number average molecular weight (M_n) of the polymers, relative to values determined by GPC using polystyrene as the calibration standard, were found to be in the range of 4500–11000. In addition, this polymerization method yielded the polymers with narrow polydispersity in the range of 1.1–1.7.

Mesophase Identification. Mesophase behavior of all the polymers were determined by DSC, thermal optical polarization microscopy, and electrooptical measurements. Figure 2b presents the DSC trace of polymer **5c**. It shows two transitions both in heating and cooling scans. According to the observation of the polarization microscopy, the polymer exhibited the usual focal conic fan texture of the smectic A phase, which then gave way on cooling to the typical broken fan texture with equidistant lines indicating the spiral structure of the chiral smectic C phase. This phase persisted even below 20 °C.

As we can observe from Table 3, all the polymers exhibit enantiotropic S_A and S_C* mesophases. It is well accepted that the mesophase formed by a side chain liquid-crystalline polymer is more ordered than the corresponding monomer.[24] This was observed to be the case here as well, since the clearing temperature elevated due to the polymerization in most of the polymers except **5a** and **5b**. In the case of the latter two polymers, the clearing temperature were lower than those of vinyl compounds. This behavior may be due to the shorter spacer, which results in a lower degee of order in the liquid crystal mesophase. Another important feature observed in the liquid-crystalline polymers is the appearance of the chiral smectic C (S_C*) phase, while antiferroelectric (S_{CA}*) ordering was observed in vinyl monomers. In addition, the S_C* phase was found to be much broader than the S_{CA}* phase of the monomers. A narrow S_C* phase has been reported[13] in polymethacrylates with some of these mesogenic side groups.

As molecular weights of the polymers were not high enough, in other words, molecular weights are within the range where phase transitions are molecular weight dependent, their phase transitions cannot be directly compared. However, inspection of the data in Table 3 revealed some possible trends as follows: (a) I–S_A as well as S_A–S_C* transition temperatures of polymers **5e** and **5h**, which consist of a longer tail group (n = 8), are lower than those of the other polymers (n = 6); (b) although there are a few anomalies due to small differences of molecular weights, the polymer clearing temperatures increase with increasing spacer (m) length. This phenomenon is well observed in side chain liquid crystal polymers.[25,26]

Polymer Switching Properties. Homogeneously aligned cells of the polymer samples were subjected to electrooptical measurements under a triangular wave voltage of ±40 V. The transmittance dependence upon voltage gives a single hysteresis in the mesophase of the

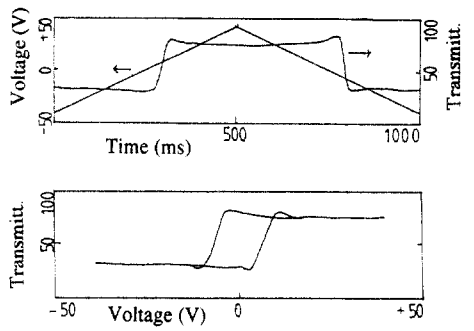


Figure 3. Polymer (**5h**) optical response to a triangular wave voltage of ±40 V at 1 Hz.

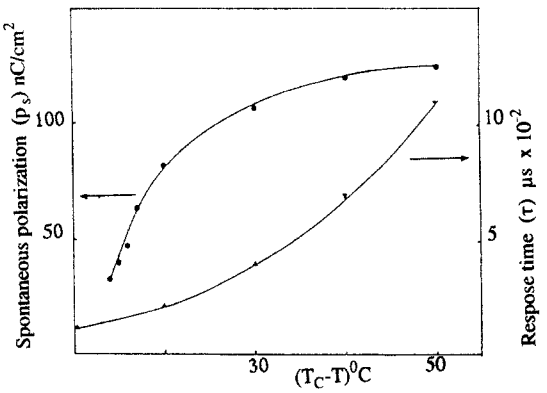


Figure 4. Effect of temperature on response time and spontaneous polarization of polymer **5d**.

lower temperature range, as shown in Figure 3. This switching behavior is due to the bistable nature, which further confirms the S_C^* mesophase.

Figure 4 illustrates the response time (τ) and the spontaneous polarization (p_s) as a function of differential temperature from S_A–S_C^* transition temperature (T_C) for polymer **5d**. The response time varies between 133 μs and 1.1 ms in the temperature range of T_c – 10 °C and T_c – 50 °C. According to our knowledge, this could be the quickest response time reported for polymers so far. As can be seen from Table 3, the polymer response times at T_c – 10 °C varies from 32 ms to 133 μs. The response times for **5b**, **5d**, and **5g**, which possessed a fluorine atom attached to the ortho position of the benzene ring, were shorter than those of the corresponding nonsubstituted samples. In the case of **5e** and **5h**, which possessed an *n*-octyl tail group, the response times were found to be notably higher than those of **5c** and **5f**. One reason for this behavior may be due to the low measuring temperature (where $T_c - 10 = \sim 50$ °C). The viscosity becomes higher at lower temperature; hence the response time τ ($=\eta/p_sE$) increases. In addition, the high molecular weight of **5e** is responsible for its slow response.

The effect of spacer length on the response time of side chain liquid crystalline polymers has been reported on only a very few cases. According to Kitazume et al.[13] for some side chain polymethacrylates, a shorter spacer resulted in a quicker response time, but Suzuki et al.[9] have reported the opposite phenomena for polysiloxanes. In the present study, when the switching times of **5a** and **5c** were compared at the constant temperature of ~80 °C, quicker response can be seen in the case of the longer spacer. A similar result was observed for **5b** and **5d** as well.

Figure 4 shows that for polymer **5d**, p_s increases monotonically and reaches a maximum with decreasing temperature. At 60 °C, P_s reaches about 125 nC/cm^2, which is the highest value ever reported in polymeric liquid crystals. P_s data for all the polymers measured at T_c – 30 °C are given in Table 3. Except for **5a**, **5e**, and **5h**, the other polymers gave large p_s values ranging 32–122 nC/cm^2. The p_s of **5a**, **5e**, and **5h** exhibited very low magnitude less than 5 nC/cm^2, and also these data are corresponding to the slow response times, respectively. Taking account of this experimental evidence, it can be said that the polymer structure, specially the side chain mesogenic unit, is not fully constructed to generate a large p_s. In other words, the steric structure, especially the length of the spacer and the tail group, is not really optimized so as to order the mesogenic unit, and then endow the mobility of the molecules. The introduction of a fluorine atom into the ortho position of the phenyl ring is profitable to enlarge the p_s and make the response time faster.

In conclusion, a series of fluorine-containing side chain ferroelectric polysiloxanes were prepared. They exhibited enantiotropic S_A and a broad S_C^* phase even below 20 °C. The switching properties of these polymers were found to be the best ever reported for polymeric liquid crystals.

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