Synthesis and Characterization of Monodisperse Ferroelectric Side Chain Liquid-Crystalline Siloxane Oligomers

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Received February 25, 1994; Revised Manuscript Received August 22, 1994®

ABSTRACT: The synthesis and characterization of monodisperse ferroelectric side chain liquid-crystalline siloxane oligomers (from monomer to pentamer) having a mesogenic group consisting of (*S*)-(−)-4-(((2-methylbutyl)oxy)carbonyl)phenyl 4′-(octyloxy)biphenyl-4-carboxylate are described. The controlled hydrolysis of dichloromethylsilane with water resulted in a mixture of α,ω-dichloro-α,ω-dimethylsiloxane oligomers. These were then fractionated by distillation and end-capped with trimethylsilanol sodium salt. The products were purified by distillation and characterized by gas chromatography/mass spectroscopy (GC/MS) analysis. The hydrosilylation of the methylsiloxane oligomers with the vinyl mesogen was carried out in the presence of platinum divinyltetramethylsiloxane catalyst. The products were purified by column chromatography. The liquid-crystalline properties of the oligomers were confirmed by differential scanning calorimetry (DSC), optical polarized microscopy (OPM), and electro-optical measurement. All the oligomers displayed S_A and S_C* mesophases. A very steep increase of transition temperatures (clearing as well as S_A−S_C* transition) was observed until the trimer, and then the increase became less steep as the degree of polymerization increased. The *d*-spacing of the oligomers in the S_A phase, determined by X-ray diffraction studies, agreed with the length of the repeat unit which was calculated by molecular simulation. This suggested that the S_A phase had a monolayer structure. The tilt angle of the S_C* phase reached saturation at about 20 °C below the S_A−S_C* transition point (T_c − 20 °C). The fastest response time of 260 μs was observed with the dimer. At T_c − 10 °C, P_s values varied in the order monomer < trimer < dimer < pentamer < tetramer, revealing an odd−even effect, wherein the largest P_s value of 90 nC/cm^2 was observed for the tetramer.

Introduction

Liquid crystal (LC) materials with a chiral smectic C (S_C*) phase have received much attention because of their interesting ferroelectric,[1] antiferroelectric,[2] and ferrielectric[3] behaviors. This mesophase has many potential applications in electroactive media such as displays,[4] light valves,[5] etc., where the electronic and physical properties are manipulated by an external electric field altering the alignment of mesogens.

Although monomeric ferroelectric liquid crystals (FLC) have been extensively investigated, their associated polymers have received sporadic attention. Polymeric LCs clearly show superiority, in comparison with monomers, in chemical resistance, high modulus, and ease of processing. The main disadvantages of these liquid-crystalline polymers include (1) high viscosity and hence slow response time to an applied field and (2) poorly reproducible synthesis, mainly due to batch to batch variation of molecular weights and molecular weight distribution. These factors limit the applicability of FLC polymers in display devices.

LC oligomers have better mechanical properties than monomers. The oligomers also exhibit enhanced FLC capabilities compared with FLC polymers. Therefore, if reproducible methods for the synthesis of oligomers can be found, these may become candidate materials for use in display devices. Especially, it is clearly useful to focus more attention on the synthesis and characterization of monodisperse FLC oligomers.

Phase transition temperatures of some side chain LC oligomers with narrow molecular weight distributions have been reported,[6,7] in which the samples have been prepared by the preparative GPC method. Systematic syntheses of some linear[8] and cyclic[9] main chain LC oligoethers have recently been reported. Since the preparation of pure oligomers and their large-scale production by preparative GPC seem to be very difficult, we became interested in the systematic preparation of side chain LC siloxane oligomers, which has not been reported previously.

In this study, the synthesis and characterization of a series of monodisperse side chain FLC siloxane oligomers (from monomer to pentamer) having (*S*)-(−)-4-(((2-methylbutyl)oxy)carbonyl)phenyl 4′-(octyloxy)biphenyl-4-carboxylate as the side chain mesogenic group are discussed. The effect of degree of polymerization (DP) on ferroelectric properties such as response time and spontaneous polarization are also described.

Experimental Section

Measurements. ^{1}H NMR spectra were recorded on a Bruker AMX 400 spectrometer. IR spectra were recorded on a Shimadzu FT/IR 800 spectrometer. Molecular weights of the oligomers were determined by gel permeation chromatography (GPC) at room temperature with a Shodex KF 802.5 column equipped with a Shimadzu RID-60A refractive index detector using THF as the eluent. The GPC column was calibrated using polystyrene standards having molecular weights ranging from 5.8 × 10^2 to 6.8 × 10^4. Differential scanning calorimetry (DSC) was carried out with a Rigaku DSC-8240D instrument at rates of 20 and 10 °C/min under nitrogen for both cooling and heating processes.

GC/MS analyses were carried out with a Hewlett-Packard 5890 GC apparatus connected to a Hewlett-Packard 5970 MS

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® Abstract published in *Advance ACS Abstracts*, November 15, 1994.

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Scheme 1. Preparation of Vinyl Mesogen

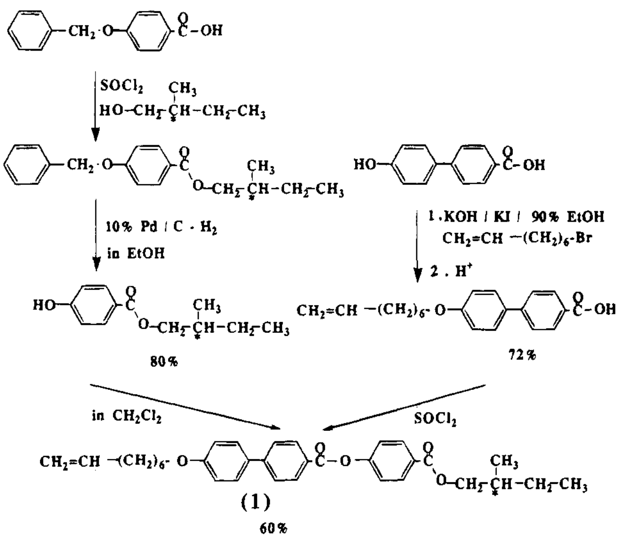


Table 1. Characterization of α,ω-Dichloro-α,ω-dimethylsiloxanes (2)

frac no.	bp (°C) (mmHg)	¹H NMR peak ratio[a] a:b:c:d (required)	yield (%)
1	51–52 (120)	–:3:–:1 (–:1:–:3)	15
2	56–60 (60)	3:6:1:2 (3:6:1:2)	11
3	75–80 (20)	6.2:6:2.1:2 (6:6:2:2)	6
4	110–113 (20)	10:6.3:4:2 (9:6:4:2)	5

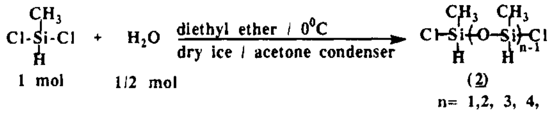
[a] See Figure 1.

instrument. The GC conditions were as follows: column material, OV 101; column length, 2 m; column diameter, 2 mm; injector temperature, 260 °C; detector temperature, 260 °C; column temperature program, 60–260 °C(8 °C/min); carrier gas flow rate, 50 mL/min. MS conditions: ionization voltages, 70 V; ionization current, 300 mA; acceleration voltage, 2–20 V; scan speed, 44 amu/s.

The optical polarizing microscope (OPM) studies were made at a heating rate of 1.0 °C/min using an Olympus BH 2 polarizing instrument fitted with a Mettler FP-82 hot stage. Homogeneously aligned cells (2.7 μm thick) were prepared by rubbing after coating indium tin oxide (ITO) deposited glass plates with polyimide films and filling with the liquid crystalline materials in their isotropic state. The response times were measured by applying a rectangular wave voltage of ±50 V at 1 Hz. The spontaneous polarization was measured by the triangular wave voltage method[10] (±50 V, 10 Hz). X-ray diffraction studies were made using a Rigaku RU-200 (60 kV, 200 mA) instrument equipped with a temperature control unit.

Synthesis. Vinyl Mesogen (1). Vinyl mesogen **1** was synthesized as shown in Scheme 1. The synthesis of **1** is described elsewhere.[11]

α,ω-Dichloro-α,ω-dimethylsiloxane Oligomers (2). Compound **2** was prepared according to the method reported by Patnode and Wilcock[12] as shown in eq 1. A typical procedure is as follows.



$$\underset{\text{1 mol}}{\mathrm{Cl\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}\text{-}Cl}} + \underset{\text{1/2 mol}}{H_2O} \xrightarrow[\text{dry ice / acetone condenser}]{\text{diethyl ether / }0^0\text{C}} \underset{\substack{(\mathbf{2})\\ n=\ 1,2,\ 3,\ 4,}}{\mathrm{Cl{-}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}{-}\!\left(O{-}\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}\right)_{n-1}\!{-}Cl}} \qquad (1)$$

Into a three-necked flask, fitted with a dropping funnel, a magnetic stirrer, a dry ice–acetone condenser, and a nitrogen inlet–outlet purge system, were placed 115 g (1 mol) of dichloromethylsilane and 100 mL of dried ethyl ether. The solution was cooled to 0 °C, and a mixture of 9 g (0.5 mol) of water and 10 mL of THF was added dropwise over a 1 h period. The reaction product, which contained a mixture of α,ω-dichloro-α,ω-dimethylsiloxane oligomers, was fractionally distilled.

Table 2. Characterization of Methylsiloxane Oligomers (3)

			GC/MS data for the major component		
n	bp (mmHg)	frac yield (%)	R_t[a] (min)	peak %[b]	MS pattern
1	83–87 (85)	48	5.4	68.5	207, 191, 133, 73
2	110–114 (85)	35	7.6	58.5	267, 251, 193, 133, 73
3	58–60 (20)	51	10.7	78.0	327, 269, 253, 133, 73
4	75–80 (5)	24	13.7	48.0	387, 313, 253, 193, 133, 73
5	115–120 (5)	22	17.9	47.0	447, 373, 313, 253, 193, 133, 73

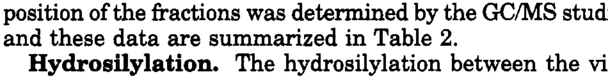
[a] Retention time was measured by using the following conditions: column material, OV 101; column length, 2 m; carrier gas, Ar (50 mL/min); injector temperature, 260 °C; detector temperature, 260 °C; column temperature program, 60–260 °C (8 °C/min). [b] Peak area percent of the required compound **3**.

Table 3. Characterization of LC Siloxane Oligomers (4)

			elemental anal. data			
			found		calc	
oligomer (n)	TLC R_f value[a]	yield[b] (%)	% C	% H	% C	% H
vinyl mesogen	0.64		77.04	7.39	77.42	7.02
1	0.73	72.0	65.24	8.29	65.22	8.15
2	0.48	69.0	68.24	8.17	67.79	7.79
3	0.31	55.0	68.79	7.64	68.66	7.42
4	0.17	40.0	69.32	7.57	68.75	7.75
5		34.0	69.55	7.51	69.23	7.79

[a] Measured on silica gel with hexane:THF (10:2) as the solvent. [b] Yield of the recovered oligomers; calculated based on the percentage of **3** in the corresponding fractions.

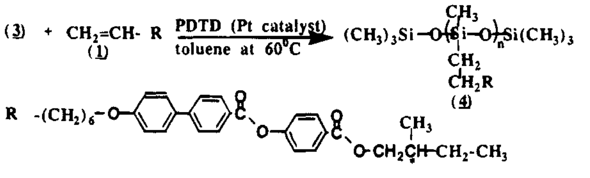
Methylsiloxane Oligomers (3). A typical procedure for the preparation of methylsiloxane trimer is given below (eq 2).



$$(\mathbf{2}) + \mathrm{(CH_3)_3Si\text{-}O^-\ Na^+} \xrightarrow[\text{at room t}]{\text{diethyl ether}} \underset{(\mathbf{3})}{\mathrm{(CH_3)_3Si{-}O\!\left(\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}{-}O\right)_{n}\!Si(CH_3)_3}} \qquad (2)$$

In a three-necked flask equipped with a dropping funnel, an argon inlet–outlet purge system, and a magnetic stirrer were placed 9.4 g (40 mmol) of 1,5-dichloro-1,5-dimethyltrisiloxane (trimer) and 100 mL of ethyl ether. To this solution was added dropwise 8.9 g (80 mmol) of trimethylsilanol sodium salt[13] in 100 mL of diethyl ether. The mixture was filtered under nitrogen, and the solvent was evaporated. The product was separated by fractional distillation. The chemical composition of the fractions was determined by the GC/MS studies, and these data are summarized in Table 2.

Hydrosilylation. The hydrosilylation between the vinyl mesogen **1** and the methylsiloxane oligomers **3** was carried out in the presence of platinum divinyltetramethyldisiloxane (PDTD) catalyst as shown in eq 3). The detailed procedure was



(3)

reported previously.[11] The products were purified by column chromatography on silica gel with the following solvent systems: monomer and dimer, hexane/EtOAc (20:1); trimer, hexane/EtOAc (10:2); tetramer, hexane/THF (10:2); pentamer, hexane/THF (10:2.5). The R_f values in thin-layer chromatography and the elemental analysis data of these oligomers are given in Table 3. A typical ¹H NMR spectrum of the oligomer (tetramer) is illustrated in Figure 2.

Results and Discussion

As mentioned above, there have been a few reports on the synthesis of side chain liquid crystal oligomers.

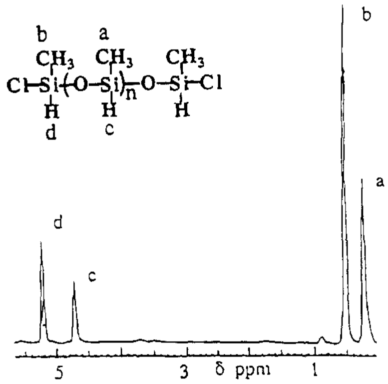


Figure 1. Typical ^{1}H NMR spectrum of α,ω-dichloro-α,ω-dimethylsiloxane oligomers.

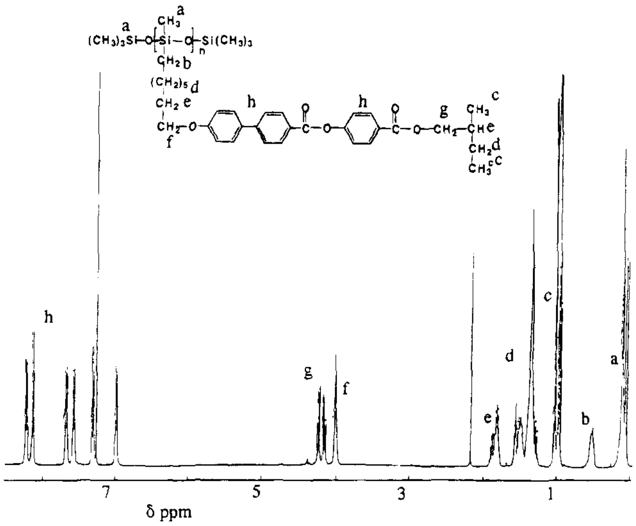


Figure 2. Typical ^{1}H NMR spectrum of side chain LC siloxane oligomers (tetramer).

In all cases, the samples have been separated by the preparative GPC method. Although this method is sufficient to obtain oligomers with a narrow molecular weight distribution, the preparation of monodisperse oligomers by this method is very difficult.

The synthesis of methylsiloxane oligomers **3** via α,ω-dichloro-α,ω-dimethylsiloxane oligomers **2**, is outlined in eq 1. A typical ^{1}H NMR spectrum of **2** is depicted in Figure 1. The characterization of these compounds is summarized in Table 1. Siloxane oligomers **3** obtained after fractional distillation were characterized by GC/MS analysis. As shown in Table 2, the percentage of the required compound **3** in the corresponding distillate varied between 47 and 79%.

The synthesis of the vinyl mesogen, (*S*)-(−)-4-(((2-methylbutyl)oxy)carbonyl)phenyl 4′-(7-octenyloxy)biphenyl-4-carboxylate, was carried out as described in our earlier report.[11] According to the DSC and optical microscopy studies, the phase sequence of the vinyl mesogen was observed to be as follows: I 180.1 °C S_A 129.9 °C S_C* 58.4 °C S_X 24.9 °C.

Liquid crystalline oligomers **4** were prepared by the hydrosilylation reaction between methylsiloxane oligomers **3** and vinyl mesogen **1** in the presence of the platinum catalyst as shown in eq 3. The products were purified by column chromatography on silica gel as described in the Experimental Section. The oligomers obtained after purification were characterized by IR, elemental analysis, ^{1}H NMR, and GPC studies. A typical ^{1}H NMR spectrum for the tetramer is shown in Figure 2 together with its proton assignments. The ratio of the integration of the $SiCH_3$ protons to aromatic protons in the mesogenic unit agreed with the expected values.

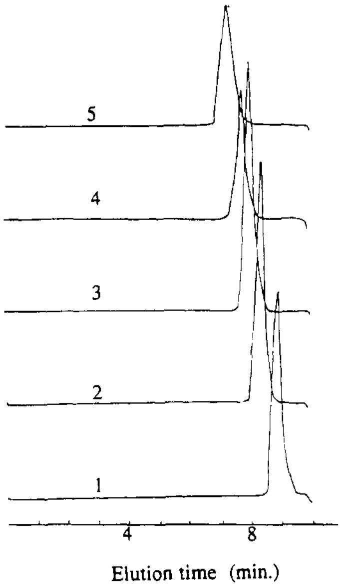


Figure 3. GPC traces of side chain LC siloxane oligomers. The degrees of polymerization (DP) are shown on each trace.

The thin-layer chromatography (TLC) R_f values and elemental analysis data of the LC oligomers are summarized in Table 3. The observed values of the elemental analysis were in good agreement with the calculated values. These data together with the very narrow molecular weight distribution (1.04–1.06) observed in the GPC traces (Figure 3) confirmed the monodisperse nature of the LC oligomers. It should be noted that the relative molecular weights observed by GPC were consistently 1.3 times higher than the calculated values. This behavior is due to the large hydrodynamic volumes of the samples compared with polystyrene standards.

As reported previously for the LC siloxane polymers with a hexyl spacer,[11] optical polarizing microscopy, DSC studies, and electro-optical measurements confirmed that all of the oligomers exhibited smectic A with the focal fan texture and smectic C with the broken focal fan texture. Upon heating, the monomer and the dimer gave sharp peaks at their melting transitions. But for the others, no peaks were observed for the melting transitions, suggesting an amorphous nature. The DSC traces of all the oligomers (second heating scan) and the vinyl mesogen are given in Figure 4. In the case of the monomer as well as the dimer, the peaks corresponding to S_A–S_C transitions were observed at 122.3 and 160.3 °C, respectively. For the other oligomers, this peak did not appear, but optical polarized microscopy revealed clearly the phase transitions from S_A to S_C*. We considered the enthalpies associated with these transitions to be very small and therefore they remained undetectable by DSC, as explained by Gray and Goodby.[14] The phase transition temperatures, measured by OPM, DSC, and electro-optical measurements, for all the oligomers are summarized in Table 4. These data are plotted in Figure 5 as a function of the degree of polymerization of the oligomers. On going from the vinyl mesogen to the LC siloxane monomer, the clearing temperature reduces drastically. This behavior could be due to the bulky nature of the trimethylsiloxy end group, which could be expected to dilute the mesophase. In other words, mesogens are loosely packed, resulting

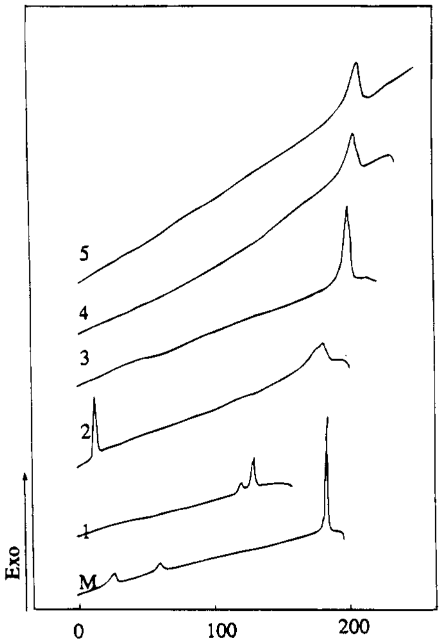


Figure 4. Representative DSC traces of side chain LC siloxane oligomers (second cooling scan); M = vinyl precursor, 1 = monomer, 2 = dimer, 3 = trimer, 4 = tetramer, 5 = pentamer.

Table 4. Phase Transition Temperatures and FLC Properties of LC Siloxane Oligomers (4)

n	M_w/M_n	transition temp[a] (°C) (on cooling)	τ[b] (ms)	P_s (nC/cm^2)
1	1.05	I 130.8 S_A 122.3 S_C* −1.8 C[c]	1.48	4.8
2	1.04	I 169.3 S_A 160.3 S_C* 12.7 C	0.26	42.4
3	1.04	I 197.3 S_A 177.8 S_C* 21.7 G[c]	0.52	27.1
4	1.04	I 201.1 S_A 184.0 S_C* 24.0 G	1.78	90.8
5	1.06	I 204.6 S_A 187.2 S_C* 30.0 G	5.30	65.4
vinyl mesogen		I 182.1 S_A 129.9 S_C* 58.4 S_X 24.9 C		

[a] Phase transition temperatures were determined by combining the data from optical polarized microscopy, electro−optical measurements, and DSC studies. [b] Response times were measured with a rectangular voltage wave of 150 V at 1 Hz (at T_c − 10 °C). [c] C = crystal, G = glassy.

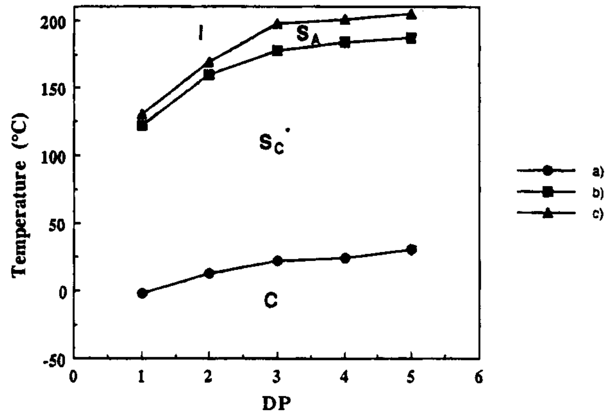


Figure 5. Dependence of phase transition temperature on degree of polymerization (DP): (a) S_C*−C; (b) S_A−S_C*; (c) I−S_A.

in a lower clearing temperature. On the other hand, due to this siloxane moiety, the S_C*−C transition point was notably depressed.

The transition temperatures of all the oligomers increased with increasing degree of polymerization (DP). This behavior is due to the decrease of the end group effects which produced well-aligned mesophases. A steep increase of the transition temperatures was observed from the monomer to the dimer as well as from the dimer to the trimer, and after that, transition temperatures were less affected.

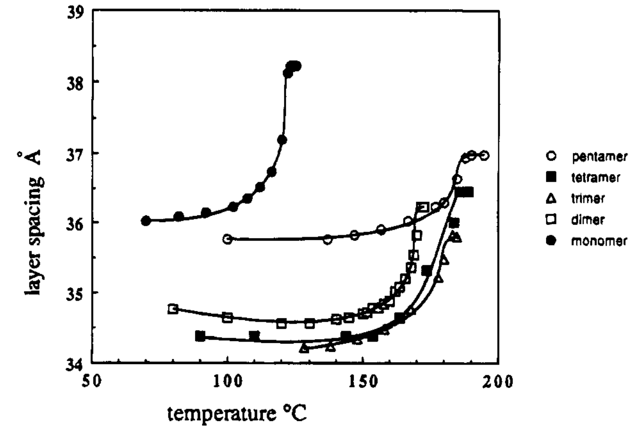


Figure 6. Effect of temperature on the layer spacing of the oligomers.

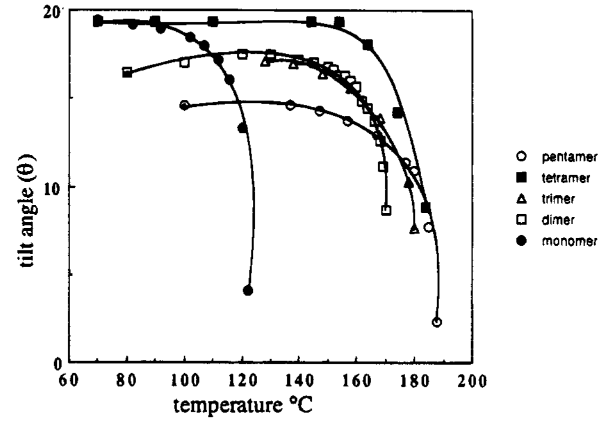


Figure 7. Effect of temperature on the tilt angle (θ) of the S_C* phase of the oligomers.

Table 5. *d*-Spacing of the S_A Phase (d_A)/Molecular Length of the Repeat Unit (*l*) of Some Oligomers

oligomer	d_A (Å)	l (Å)	d_A/l
monomer	38.21	37.36	1.02
dimer	36.26	34.74	1.05

X-ray Diffraction. The layer thicknesses (d) in the smectic A phase (d_A) and the chiral smectic C phase (d_C) were examined by X-ray diffraction studies. The tilt angles (θ) of the smectic C phases were calculated according to the equation $\theta = \cos^{-1}(d_C/d_A)$. The layer thickness of the smectic A phase was compared with the length of the repeat unit (l) of the oligomers. This repeat unit length was calculated for its most extended conformation by molecular simulation.[15] For all of the samples, the d_A/l ratio was found to be around 1.0. This suggests that the S_A phases had a monolayer structure.

The changes in layer spacing with temperature of the samples are given in Figure 6. The effect of the temperature on the tilt angles (θ) of the S_C* phase is depicted in Figure 7. The maximum tilt angles for the oligomers are as follows: monomer and tetramer, around 19°; dimer and trimer, 17°; pentamer, 15°.

Response Time. As can be seen from Figure 8, for all of the oligomers, the response became slower with decreasing temperature. Figure 9 presents the response time (measured at T_c − 10 °C) variation with the degree of polymerization (DP) of the oligomers. In this series, the quickest response time was observed in the dimer.

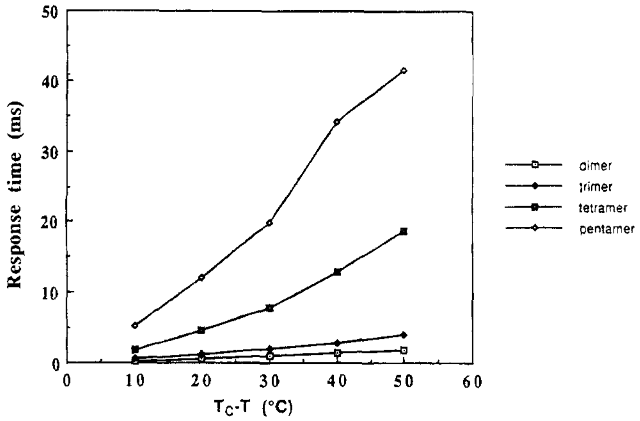


Figure 8. Effect of temperature on the response time of the LC oligomers.

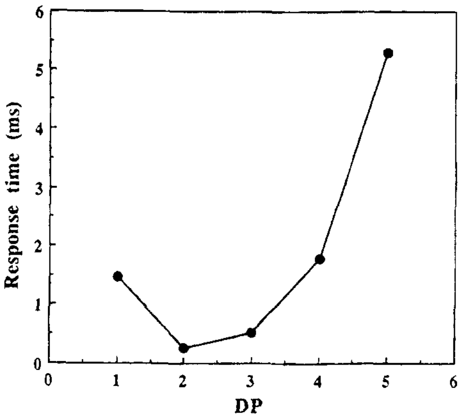


Figure 9. Effect of degree of polymerization (DP) on the response time (at 10 °C below the S_A–S_C* transition point).

Except for the monomer, the response became slower with increasing DP. In the case of the monomer, in which the siloxane moiety acted as the terminal group of the spacer, the response time was found to be notably slower than that of the dimer. One reason for this behavior may be due to the bulkiness of the trimethylsilyl end group of the spacer, which could be expected to dilute the mesophase. Therefore, the molecular dipole ordering for the monomer in one direction is hindered. This resulted in a small spontaneous polarization P_s,[16,17] which led to its slow response to an external field (E) as noted in the equation $\tau = \eta / P_s{\cdot}E$.[18] Also, the response time of the monomer was measured at a lower temperature (T_c − 10 = 110 °C) than the other samples. At this lower temperature, the viscosity (η) of the LC phase increased, thus increasing the response time τ.

Spontaneous Polarization. The effect of temperature on the spontaneous polarization (P_s) of the oligomers is presented in Figure 10. Except for the monomer and the dimer, P_s increased in the beginning with decreasing temperature, and after about T_c − 20 °C it tended to decrease. This behavior can be explained by the tilt angle (θ) variation as noted in Figure 7. It is accepted that θ is a primary order parameter and P_s is a derived property.[16] In our samples, θ reached saturation at around T_c − 20 °C; hence we could not expect any increase in P_s. In addition, when the sample was cooled, the molecules became more rigid. This increased rigidity resulted in a lessened ability of molecules to respond to an external field, which led to a decrease in P_s.

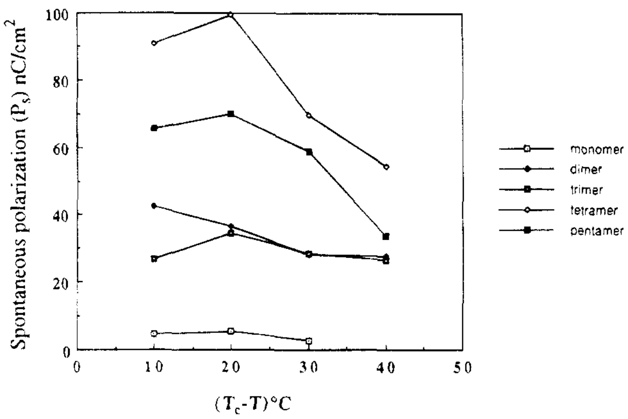


Figure 10. Effect of temperature on the spontaneous polarization of the LC oligomers.

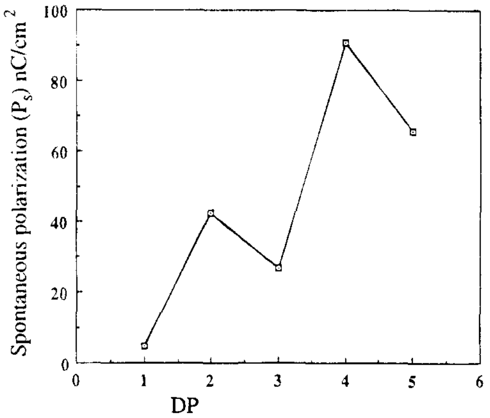


Figure 11. Effect of degree of polymerization (DP) on the spontaneous polarization (at 10 °C below the S_A–S_C* transition point).

At T_c − 10 °C, the LC siloxane monomer gave the smallest P_s of 5 nC/cm^{-1}. It is interesting to note that when progressing from the monomer to the dimer, even though $\theta_{\text{monomer}} > \theta_{\text{dimer}}$, a notable P_s increase was observed. This is because, in the dimer, the LC group is less diluted in comparison with the monomer due to the trimethylsiloxy end groups. This led to a better packing in the LC phase, thus affording a stronger coupling between the chiral group and the polar group. Therefore, it resulted in a stronger rotational hindrance of the side chain. Hence, dipolar ordering in one direction was favored in the dimer, leading to a larger P_s.

If the effect of the trimethylsiloxy end groups was the only reason for this behavior, for the other oligomers, P_s should increase with increasing DP. However, at T_c − 10 °C, P_s varies in the order monomer < trimer < dimer < pentamer < tetramer, revealing an odd–even effect (Figure 11). We assume that this behavior may be associated with two different phenomena. One could be the trimethylsiloxy end group effect, which states that P_s should increase as DP increases. Another one could be caused by the differences of the tilt angle (θ). At T_C − 10 °C, θ varied in the order pentamer < trimer < dimer < tetramer as shown in Figure 7; thus P_s also should increase in the same order. Therefore, the association of these two factors may result in the odd–even alteration of P_s with DP. However, the relationship between the observed tilt angles and the DP is not clear.

In conclusion, we have presented a successful synthesis of a series of new monodisperse ferroelectric side chain LC siloxane oligomers ranging from the monomer to the pentamer. This study leads the way for the reproducible synthesis of monodisperse side chain FLC siloxane oligomers, which have great potential for use as candidate materials in display devices. The effect of degree of polymerization of the oligomers on the ferroelectric properties was reported for the first time.

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MA941030N