

Effect of Lateral Substituents on the Mesomorphic Properties of Side-Chain Liquid Crystalline Polysiloxanes Containing 4-[(*S*)-2-Methyl-1-butoxy]phenyl 4-(Alkenyloxy)benzoate Side Groups

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ABSTRACT: The synthesis of side-chain liquid crystalline polysiloxanes containing either 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-(alkenyloxy)benzoate or laterally fluoro-, chloro-, bromo-, and methoxy-substituted 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-(alkenyloxy)benzoate mesogenic side groups is presented. The mesomorphic properties of the synthesized polymers have been characterized by optical polarizing microscopy, differential scanning calorimetry, and X-ray diffraction measurements. The effects of spacer length and lateral substituent on the mesomorphic properties of the obtained polymers are examined. The five polymers which contain three methylene units in the spacers show no mesophase, while the five polymers which contain eleven methylene units in the spacer display smectic mesomorphism. Among the other fifteen polymers which contain respectively four, five, or six methylene units in the spacers, those with small fluoro and chloro substituents reveal respectively an S_A phase, while those with bulky bromo and methoxy substituents show no liquid crystalline behavior. The experimental results demonstrate that introducing a bulky lateral substituent into the mesogenic core of a polymer depresses the tendency to form a mesophase. Furthermore, the technique of thermally stimulated current has been used to study the dipolar relaxation mechanisms in a side-chain liquid crystalline polysiloxane. © 1997 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* **35**: 2793–2800, 1997

Keywords: polysiloxanes; liquid crystalline polymers; lateral substitution effect; thermal stimulated current

INTRODUCTION

In 1975, Mayer¹ presented theoretically and then proved experimentally that the chiral smectic C (S_C^*) mesophase was ferroelectric. A bistable, fast switching, electrooptical device which uses the ferroelectric liquid crystals (FLCs) was demonstrated a few years later by Clark and Lagerwell.² An increasing interest in the synthesis of low molar mass S_C^* liquid crystals has since then developed. Numerous FLC compounds and room-tem-

perature mixtures have so far been prepared for fast electrooptical applications. Besides low molar mass liquid crystals, a number of side-chain liquid crystalline polymers (LCPs) exhibiting an S_C^* mesophase have been successfully prepared during the past few years.^{3–14}

The effect of molecular structure on the occurrence of tilted smectic C phases is very different from that on the nematic or orthogonal smectic phases. The molecules should possess some degree of steric asymmetry so that the molecules can arrange themselves in a tilted layer when they are packed together. Some reports^{15–17} on low molar mass liquid crystals in the literature also showed that introduction of a suitable lateral substituent, e.g., a fluoro group, into the mesogenic core of a molecule can enhance the possibility to form a chiral

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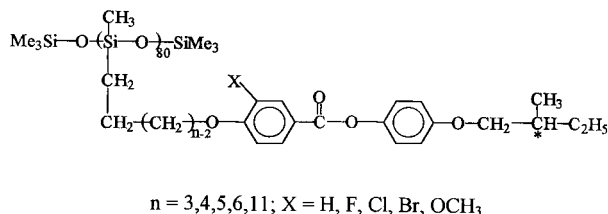


Figure 1. Molecular structure of the side-chain LC polysiloxanes.

smectic *C* phase. The goal of this paper is to present the synthesis and characterization of several series of side-chain liquid crystalline polymers containing laterally substituted mesogens. The particular examples described here refer to polysiloxanes containing 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-(alkenyloxy)benzoate, 4-[(*S*)-2-methyl-1-butoxy]phenyl 3-fluoro-4-(alkenyloxy)benzoate, 4-[(*S*)-2-methyl-1-butoxy]phenyl 3-chloro-4-(alkenyloxy)benzoate, 4-[(*S*)-2-methyl-1-butoxy]phenyl 3-bromo-4-(alkenyloxy)benzoate, and 4-[(*S*)-2-methyl-1-butoxy]phenyl 3-methoxy-4-(alkenyloxy)benzoate side groups (Fig. 1).

The effects of lateral fluoro, chloro, bromo, and methoxy substituents on the mesomorphic properties of the obtained polysiloxanes are discussed.

The molecular dynamics behavior of side-chain LCPs has been extensively studied by dielectric relaxation spectroscopy,^{18–21} but the correlation of the motions of the main chain with those of the pendant mesogenic units is not clearly understood yet. The thermally stimulated current (TSC) technique is another very suitable method for study of the molecular dynamics behavior of side-chain LCPs. The first TSC study of a side-chain LCP was published by Simon²² in 1989, and since then several works have also been reported on this subject.^{23–27} In this study, we report some TSC results on a polysiloxane showing liquid crystalline behavior. The dielectric relaxation mechanisms of the side-chain LC polysiloxane are discussed.

EXPERIMENTAL

Materials

Poly(methylhydrogensiloxane) ($M_n = 4500\text{--}5000$) and divinyltetramethyldisiloxane–platinum catalyst were obtained from Petrarch Systems Inc. (Bristol, PA) and used as received. (*S*)-(-)-2-Methyl-1-butanol, $[\alpha]_D^{25} = -6.5^\circ$ (from Merck), 3-methoxy-4-hydroxybenzoic acid, 3-bromo-4-hy-

droxybenzoic acid, 3-chloro-4-hydroxybenzoic acid (from Janssen Inc.), and all other reagents (from Aldrich) were used as received. Dichloromethane used in the esterification was refluxed over calcium hydride and then distilled under nitrogen. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under nitrogen. 4-[(*S*)-2-Methyl-1-butoxy]phenol, 10-undecen-1-yl tosylate, and 3-fluoro-4-hydroxybenzoic acid were synthesized according to literature procedures.^{11,28}

Techniques

¹H-NMR spectra (400 MHz) were recorded on a Varian VXR-300 spectrometer. FT-IR spectra were measured on a Nicolet 520 FT-IR spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid-nitrogen cooling accessory. Heating and cooling rates were 10°C/min. Thermal transitions reported were collected during the second heating and cooling scans. A Carl-Zeiss Axiophot optical polarized microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Preparative gel permeation chromatography (GPC) was run on a Waters 510 LC instrument equipped with a 410 differential refractometer and a preparative GPC column (22.5 mm × 60 cm) supplied by American Polymer Standard Co. X-ray diffraction measurements were performed with nickel-filtered Cu K α radiation with a Rigaku powder diffractometer. TSC experiments were carried out with a TSC/RMA spectrometer (Solomat Instruments, Stamford, CT) covering the range -170 to 200°C . In each experiment, the sample was polarized for several minutes by a polarization voltage V_p at a temperature T_p and the polarization was frozen-in by cooling to a temperature $T_o \ll T_p$ in the presence of the electric field. With the field off the depolarization current was then measured as the sample was heated at a constant rate to T_f ($T_f > T_p$).

Synthesis of Monomers and Polymers

The synthetic routes used to prepare the following olefinic monomers 1M–25M and polymers 1P–25P are outlined in Schemes 1 and 2: 4-(alkenyloxy)benzoic acid (1–5); 3-fluoro-4-(alkenyloxy)benzoic acid (6–10); 3-chloro-4-(alkenyloxy)benzoic acid (11–15); 3-bromo-4-

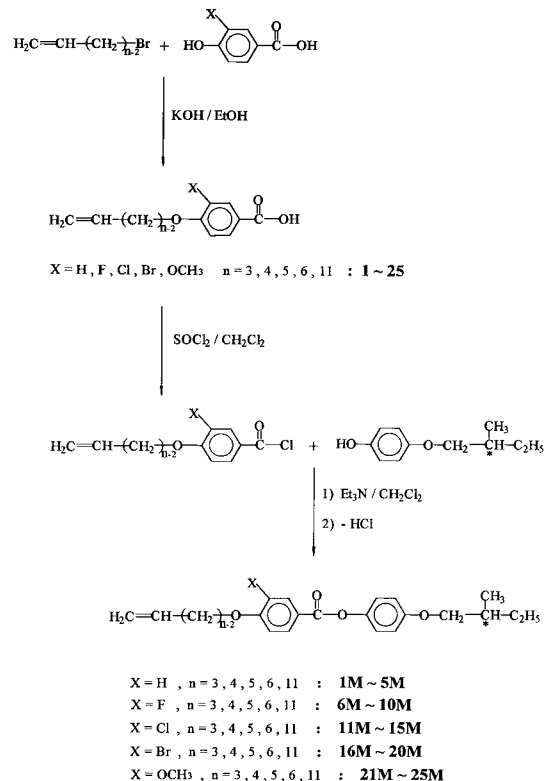
(alkenyloxy)benzoic acid (**16–20**); 3-methoxy-4-(alkenyloxy)benzoic acid (**21–25**).

The compounds **1–25** were prepared by the etherification of alkenyl bromides or undecenyl tosylate with 4-hydroxybenzoic acid, 3-fluoro-4-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, 3-bromo-4-hydroxybenzoic acid, and 3-methoxy-4-hydroxybenzoic acid, respectively. The synthesis of 3-methoxy-4-(allyloxy)benzoic acid (**21**) is described below.

3-Methoxy-4-hydroxybenzoic acid (4.00 g, 0.024 mol) was added to a solution of KOH (2.98 g, 0.052 mol) and KI (0.5 g) in 95 wt % ethanol (150 mL). The solution was refluxed for 1 h, and allyl bromide (5.07 g, 0.048 mol) was added dropwise. The resulting solution was refluxed for 20 h and cooled to room temperature, and 100 mL of water was added. The solution was acidified with dilute hydrochloric acid. The precipitate was filtered out and recrystallized from MeOH/H₂O (1/2 v/v) to yield 3.69 g (74.5%) of white crystals. ¹H-NMR (CDCl₃, TMS, ppm): δ 3.94 (s, 3H, —OCH₃), 4.69 (d, 2H, —CH₂O—), 5.34 (m, 2H —CH=CH₂), 6.04 (m, 1H, —CH=), 6.90–7.74 (m, 3 aromatic protons).

Synthesis of Monomers **1M–25M**

All olefinic monomers (**1M–25M**) were prepared by a same method. The synthesis of monomer **21M** is described below. 3-Methoxy-4-(allyloxy)benzoic acid (2.62 g, 0.011 mol) was reacted at room temperature with excess thionyl chloride (6 mL) containing a few drops of dimethylformamide in methylene chloride (7 mL) for 2 h. The solvent and excess thionyl chloride were removed under reduced pressure to give the corresponding acid chloride. The product was dissolved in 20 mL of methylene chloride and slowly added to a cold solution of 4-[(S)-2-methyl-1-butoxy]phenol (1.80 g, 0.01 mol) and triethylamine (3 mL) in 100 mL of methylene chloride. The solution was stirred at room temperature. The solvent was then distilled. The obtained crude product was dissolved in methylene chloride and passed through silica gel. The solvent was removed in a rotary evaporator. The crude product was recrystallized from ethanol to yield 3.47 g (87.0%) of white crystals. ¹H-NMR (CDCl₃, TMS ppm): δ 0.92–1.80 [m, 9H, CH(CH₃)(C₂H₅)], 3.70 (d, 2H, —O—CH₂—), 3.88 (s, 3H, —OCH₃), 4.64 (d, 2H, =CH—CH₂—O—), 5.33 (m, 2H, CH₂=), 4.64 (m, 1H, =CH—), 6.86–7.74 (m, 7 aromatic protons).



Scheme 1. Synthesis of monomers **1M–25M**.

Synthesis of Polysiloxanes **1P–25P**

The olefinic derivative, 0.8 g (10 mol % excess versus the Si—H groups present in polysiloxane), was dissolved in 80 mL of dry, freshly distilled toluene together with the proper amount of poly-(methylhydrogensiloxane). The reaction mixture was heated to 110°C under nitrogen, and 100 μg of divinyltetramethyldisiloxane–platinum catalyst was then injected with a syringe as a solution in toluene (1 mg/mL). The reaction mixture was refluxed (110°C) under nitrogen for 24 h. After this reaction time, both the ¹H-NMR and FT-IR analyses showed that the hydrosilylation reaction was almost complete. The polymers were separated and purified by several reprecipitations from tetrahydrofuran solution into methanol, further purified by preparative GPC, and then dried under vacuum.

RESULTS AND DISCUSSION

Effects of Lateral Substituent on the Mesomorphic Properties of Polysiloxanes

The synthetic route used for the preparation of monomers **1M–25M** is outlined in Scheme 1. The

Table I. Phase Transitions and Phase Transition Enthalpies for Monomers **1M–25M**

Monomer	n^a	X ^a	Phase Transitions in °C
			(Corresponding Enthalpy Changes in kcal/mol) ^b of Heating Scan
1M	3	H	K 71.3 (5.7) I
2M	4	H	K 61.7 (6.8) I
3M	5	H	K 66.0 (6.1) I
4M	6	H	K 62.8 (5.6) I
5M^c	11	H	K 44.1 (7.4) S _A 55.2 (1.2) I
6M	3	F	K 83.2 (5.2) I
7M	4	F	K 61.4 (6.3) I
8M	5	F	K 83.1 (4.8) I
9M	6	F	K 74.0 (5.8) I
10M^d	11	F	K 38.4 (6.4) I
11M	3	Cl	K 77.1 (8.48) I
12M	4	Cl	K 52.9 (6.59) I
13M	5	Cl	K 82.0 (7.34) I
14M	6	Cl	K 79.7 (7.23) I
15M	11	Cl	K 47.1 (7.88) I
16M	3	Br	K 84.0 (8.91) I
17M	4	Br	K 56.1 (7.41) I
18M	5	Br	K 71.6 (7.46) I
19M	6	Br	K 70.7 (7.60) I
20M	11	Br	K 52.4 (9.01) I
21M	3	OCH ₃	K 65.1 (7.85) I
22M	4	OCH ₃	K 61.0 (6.93) I
23M	5	OCH ₃	K 69.0 (7.54) I
24M	6	OCH ₃	K 66.7 (7.84) I
25M	11	OCH ₃	K 47.1 (6.29) I

^a n and X according to Scheme 1.

^b K = crystalline, I = isotropic, S_A = smectic A, S_C* = chiral smectic C.

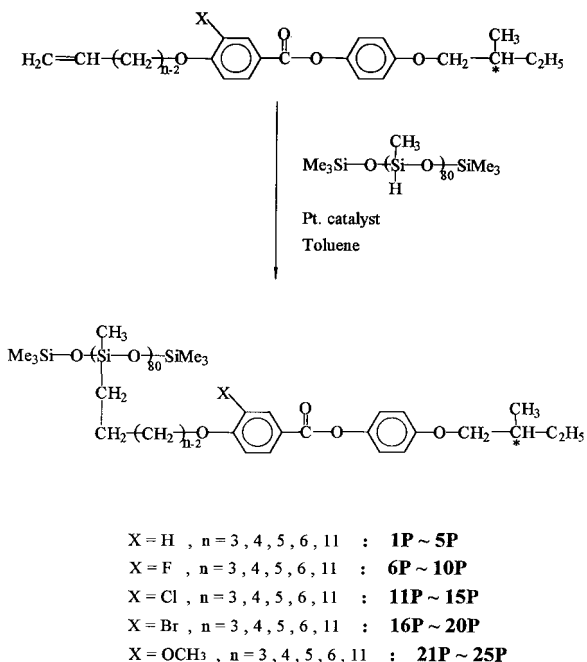
^c Monomer **5M** shows S_A, S_B, and S_C* phases on DSC cooling scan: I 52.6°C, S_A 25.4°C, S_C* 17.6°C, S_B 6.9°C K.

^d Monomer **10M** shows S_A and S_B phases on cooling scan: I 37.6°C, S_A 18°C, S_B 11.1°C K.

chiral end group was inserted into these mesogenic compounds starting with the commercially available (*S*)-(-)-2-methyl-1-butanol. This was done by a sequence of reactions which avoided its racemization. All monomers were characterized by differential scanning calorimetry and optical polarizing microscopy. The phase transitions and corresponding enthalpy changes of monomers **1M–25M** are summarized in Table I. As can be seen from Table I, all monomers with short spacer length (i.e., $n = 3–6$) display no mesomorphic behavior. Among five monomers containing eleven methylene units in the spacers, monomer **5M** without a lateral substituent and monomer **10M** with a small fluoro substituent are the only two showing mesomorphic behavior while the other three monomers which contain respectively a chloro, bromo, or methoxy substituent display no liquid crystalline phase. Monomer **5M** reveals an enantiotropic S_A phase and two monotropic

S_C* and S_B phases, while monomer **10M** reveals only two monotropic S_A and S_B phases. The experimental results demonstrate that introducing a more bulky lateral substituent into the mesogenic core of a monomer dramatically decreases the tendency to form a mesophase.

The synthesis of polysiloxanes **1P–25P** is described in Scheme 2. An excess amount of olefinic monomers was usually used to carry the hydrosilylation reaction to completion. The unreacted monomers were removed by several reprecipitations from tetrahydrofuran solution into methanol and by preparative GPC. Therefore, the polymers were isolated with high purity. The obtained polymers were characterized by differential scanning calorimetry and optical polarizing microscopy. Table II summarized the phase transitions and corresponding enthalpy changes of the obtained polysiloxanes **1P–25P**. Representative DSC traces of polymer **13P** are presented in Fig-



Scheme 2. Synthesis of polysiloxanes **1P–25P**.

ure 2. On the heating scan (curve A), it shows a glass transition temperature (T_g) at 17.0°C followed by a smectic A to isotropic phase transition at 59.1°C. The cooling scan (curve B) looks almost identical to the heating scan except that a small amount of supercooling is observed for the exothermic transition. The phase assignment was conducted by optical polarizing microscopic observations and X-ray diffraction measurements. The structures of side-chain liquid crystalline polymers have been extensively studied by X-ray diffraction measurements.^{29,30} Structure models of side-chain LC polymers in the smectic phase are mostly derived from the ideas of Liebert and Strzelecki.³¹ They picture the mesogenic side chains with positional order along a director packed in a lamellae type of arrangement. The polymer backbone to which the mesogenic side chains are attached is placed between the lamellae and is able to form a two-dimensional sheaf-like or coil-like structure. The sheaf-like structure is very much supported by packing consideration. In these models the main chain is considered to be of minor importance. Figure 3 presents the temperature-dependent X-ray diffraction diagrams obtained from powder samples of **13P** at 50, 40, and 30°C. A broad reflection at wide angles (associated with the lateral packings) and a sharp reflection at low angles (associated with the smectic layers) are respectively shown by all curves.

Curve A presents a diffuse reflection at about 4.5 Å, which corresponds to the lateral spacing of two mesogenic side groups, a sharp first-order reflection at 21.3 Å, and a second-order reflection at 10.4 Å, which correspond to the d spacing of smectic layers. When the measuring temperature has been lowered from 50 to 40 and 30°C, the d spacings of the first-order reflection are basically kept at about the same value (curves B and C). The result indicates the formation of a smectic A phase. This result is also in agreement with the optical microscopic observation which reveals a typical smectic A texture (Fig. 4).

The thermal transitions and corresponding enthalpy changes of the obtained polymers **1P–25P** are summarized in Table II. Among polymers **1P–5P** containing no lateral substituent, polymer **1P** displays no mesophase, polymers **2P–4P** show respectively an enantiotropic S_A phase, while polymer **5P** reveals two enantiotropic S_A and S_B phases. As can be seen from the data listed in Table II, the spacer length has a profound effect on the mesomorphic behavior of the obtained polymers. As the spacer length increases, the glass transition temperature (T_g) decreases while the isotropization temperature increases. This result suggests that a longer spacer tends to stabilize the mesophase more than a shorter one since a longer spacer always gives higher degree of decoupling between the mesogenic side groups and the main chains. Polymers **5P–10P** and **11P–15P**, which contain respectively a lateral fluoro or chloro substituent, display mesomorphic behavior very similar to that of their corresponding polymers **1P–5P**. However, among polymers **16P–20P** and **21P–25P** which contain respectively a lateral bromo or methoxy substituent, **20P** and **25P** containing 11 methylene units in the spacers are the only two polymers showing liquid crystalline behavior. The experimental results demonstrate that introducing a bulky lateral substituent into the mesogenic core of a polymer dramatically depresses the tendency to form a mesophase. Furthermore, according to the data listed in Table II, all polymers show no S_C^* phase. The reason could be due to the short mesogenic core. For this kind of phenyl benzoate mesogen, incorporation of a lateral substituent in the mesogen does not enhance the tendency to form a S_C^* phase.

TSC Study of the Molecular Dynamics Behavior of a Side-Chain LC Polysiloxane

The side-chain liquid crystalline polymers constitute a major class of LCPs in which the mesogenic

Table II. Phase Transitions and Phase Transition Enthalpies for Polymers **1P–25P**

Polymer	n^a	R^a	Phase Transitions in °C
			(Corresponding Enthalpy Changes in kcal/mru ^b) for Heating Scan
1P	3	H	G 17.1 I
2P	4	H	G 10.2 S _A 35.5 (0.37) I
3P	5	H	G 10.9 S _A 72.0 (1.33) I
4P	6	H	G 7.2 S _A 76.8 (1.04) I
5P	11	H	G 4.8 S _X 45.1 (0.94) S _A 128.4 (1.4) I
6P	3	F	G 22.1 I
7P	4	F	G 17.9 S _A 67.7 (0.92) I
8P	5	F	G 12.66 S _A 74.4 (0.72) I
9P	6	F	G 4.3 S _A 60.2 (0.76) I
10P	11	F	G 10.8 S _A 41.3 (0.74) S _A 117.6 (1.2) I
11P	3	Cl	G 13.2 I
12P	4	Cl	G 26.5 S _A 43.3 (0.29) I
13P	5	Cl	G 17.0 S _A 59.1 (0.60) I
14P	6	Cl	G 14.0 S _A 53.4 (0.81) I
15P	11	Cl	G 8.1 K 58.2 (3.83) S _A 70.2 (–) I
16P	3	Br	G 24.0 I
17P	4	Br	G 27.9 I
18P	5	Br	G 21.0 I
19P	6	Br	G 17.2 I
20P	11	Br	G 3.1 K 56.7 (2.62) S _A 66.3 (–) I
21P	3	OCH ₃	G 22.6 I
22P	4	OCH ₃	G 24.5 I
23P	5	OCH ₃	G 21.0 I
24P	6	OCH ₃	G 20.0 I
25P	11	OCH ₃	G 8.4 S _A 68.9 (1.60) I

^a n and X according to Scheme II.^b mru = mole repeating unit; G = glassy; K = crystalline; S_A = smectic A; I = isotropic.

units are attached laterally to the main chain via a flexible spacer. According to those reports^{22–27} in the literature, TSC spectra of side-chain LCPs generally show three different discharges: a lower temperature one in the vitreous state, a discharge peak which appears near T_g , and a relaxation above T_g . It seems that the lower temperature relaxation arises from localized noncooperative motions in the side group. The T_g peak seems to arise from the microbrownian motions of the dipole moment rigidly attached to the main chain and/or from the motions of the mesogenic side groups induced by the movements of the backbone. The relaxation above T_g corresponds to the motions of the longitudinal component of the dipole moment of the mesogenic side group.²⁷

In this work, polymer **14P**, which contains six methylene units in the spacer and a lateral chloro substituent, was chosen for TSC measurement. Polymer **14P** reveals a glass transition temperature at 14.0°C and an S_A to isotropic transition at

53.4°C on the DSC scans. Figure 5 shows the TSC global spectra of polymer **14P**. Two depolarization peaks are observed for curve A (polarization voltage $V_p = 50$ V/mm): one whose maximum occurs at 23.7°C (near T_g) and the other whose maximum is at ca. 53.7°C. In comparison with the DSC results, it seems that the first peak at 23.7°C corresponds to the glass transition relaxation and the second peak at 53.7°C corresponds to the S_A to isotropic phase transition. Curve A did not show the relaxation motions of the longitudinal component of the dipole moment of the mesogenic side group.²⁵ However, when the polarization voltage is increased to 500 V/mm, three depolarization peaks are observed for the TSC thermogram (curve B): a high-intensity peak with temperature of maximum at 17.4°C and two low-intensity peaks with temperatures of maxima at 49.5 and 56.5°C. It seems that the peak at 17.4°C is attributed to the motions of the glass transition relaxation and the peak at 56.4°C is attributed to the

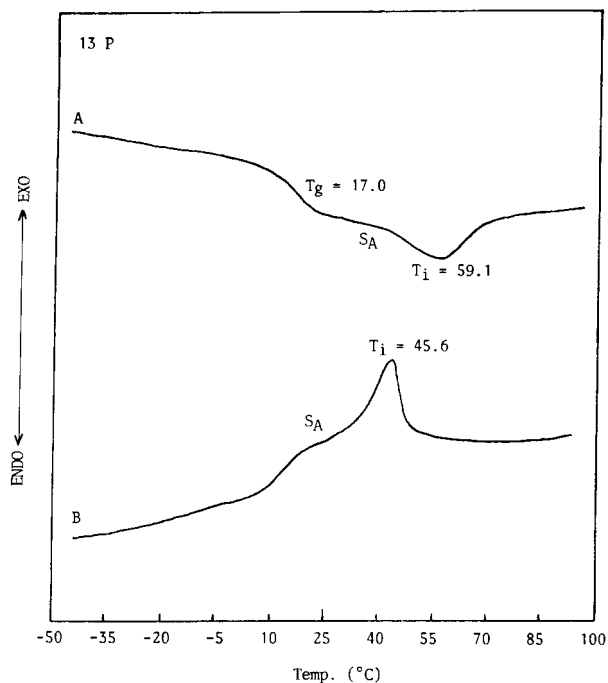


Figure 2. DSC thermograms (20°C/min) for polymer **13P**: (A) Second heating scan; (B) cooling scan.

S_A to isotropic phase transition. Besides the glass transition and the S_A to isotropic phase transition peaks, a depolarization peak at 49.5°C is also presented in curve B. It is thus reasonable to believe the peak at 49.5°C arises from rotations of the longitudinal component of the dipole moment of the mesogenic side group.²⁷

CONCLUSIONS

Five series of side-chain liquid crystalline polysiloxanes containing either 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-(alkenyloxy)benzoate or laterally substituted 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-(alkenyloxy)benzoate mesogenic side groups are prepared. Both lateral substituent and spacer length have profound effects on the thermal stability of mesophases formed. The bulky lateral bromo and methoxy substituents dramatically depress the tendency to form a mesophase, while the small lateral fluoro and chloro substituents do not. Due to the short phenyl benzoate mesogenic core, all synthesized polymers display no S_C^* phase. Incorporation of a lateral substituent in this kind of mesogenic core does not enhance the possibility to form a S_C^* phase, either. The dipolar relaxation mechanisms of a side-chain LC

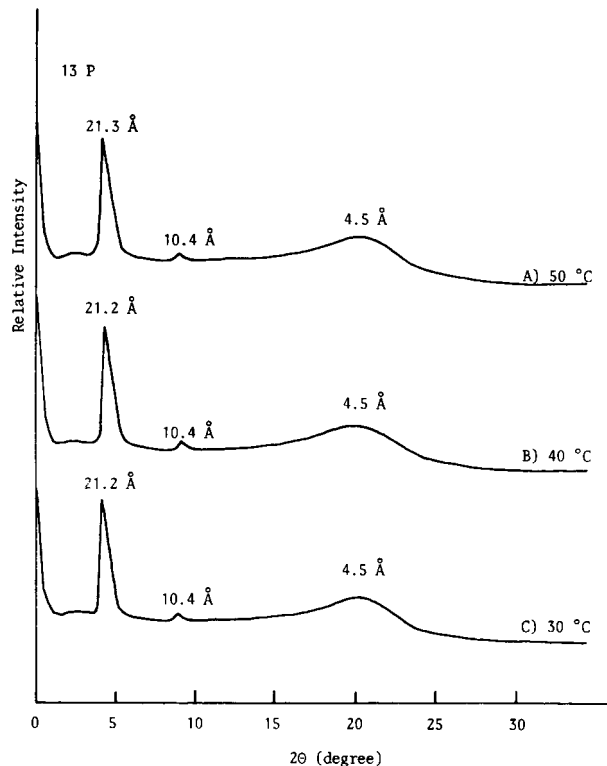


Figure 3. Temperature-dependent X-ray measurements for polymer **13P** at (A) 50°C, (B) 40°C, and (C) 30°C.

polysiloxane have also been studied by the TSC technique. A glass transition relaxation and two higher temperature relaxations are observed. Comparison of the DSC and TSC results seems to confirm that the TSC technique as a more powerful tool to resolve the dipolar relaxation mechanisms of a side-chain LCP.

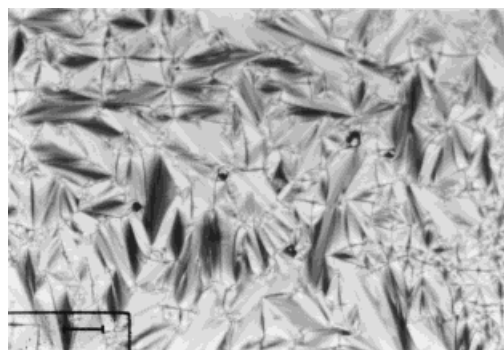


Figure 4. Optical polarizing micrographs (magnification 320×) displayed by polymer **13P**: S_A texture obtained at 45°C.

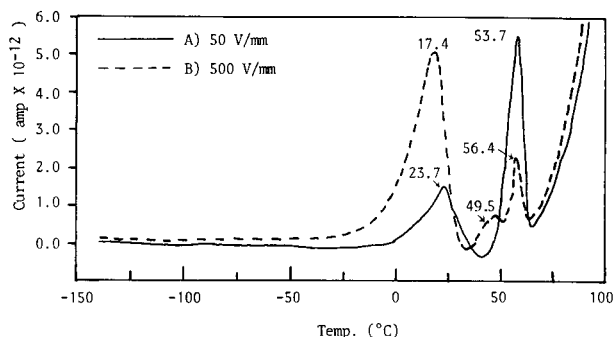


Figure 5. TSC global thermograms of polymer **14P** obtained at (A) $V_P = 50$ V/mm and (B) $V_P = 500$ V/mm. The experimental conditions were as follows: $T_P = 100^\circ\text{C}$; $T_o = -140^\circ\text{C}$; $T_f = 100^\circ\text{C}$; heating rate = $7^\circ\text{C}/\text{min}$.

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