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Synthesis and X-ray diffraction of ferroelectric liquid crystalline polysiloxanes containing 4′-(2-chloro-3-methylpentanoyloxy)-4-alkanyloxybiphenyl side groups

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SUMMARY

The synthesis and characterization of side-chain liquid crystalline polysiloxanes containing (2S,3S)-4'-(2-chloro-3-methylpentanoyloxy)-4-alkanyloxybiphenyl side groups are presented. All the obtained polymers exhibit smectic mesomorphism. Those polymers containing a spacer length longer than 8 methylene units reveal respectively enantiotropic S_A, S_C^* and S_B phases. The result demonstrates that the tendency toward the S_C^* phase increases with increasing the spacer length.

INTRODUCTION

Ferroelectric liquid crystals(FLCs) have attracted growing interest over recent years because of their bistability in displays and their short switching times[1,2]. Besides low molar mass FLCs, ferroelectric LC polymers[3-14] have also been well investigated. Ferroelectric LC polymers show response times in the range of mili-seconds by applying weak electric field[14]. They also show bistability that is comparable to low-molecular-mass FLCs. An advantage of such material in display applications is their applicability as flexible display devices.

Presenting the synthesis of some chiral smectic liquid crystalline polysiloxanes containing (2S, 3S)-4'-(2-chloro-3-methylpentanoyloxy)-4-alkanyloxy biphenyl side groups is the goal of this study. Their characterizations by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction are presented.

EXPERIMENTAL

Materials

Poly(methylhydrogen siloxane) ($\overline{Mn}$ = 4500) and divinyltetramethyldisiloxane platinum catalyst were obtained from Patrarch System Inc. and used as received. Biphenol and all other reagents were purchased from Aldrich and used as received. Toluene used in the hydroxylation reaction were first refluxed over sodium and then distilled under nitrogen.

Techniques

Experimental techniques used in the characterization of intermediate compounds and of polymers are identical to those previous reported[15-18].

Synthesis of monomers 1M~5M

The synthetic routes used for the preparation of monomers 1M~5M are outlined in Scheme 1.

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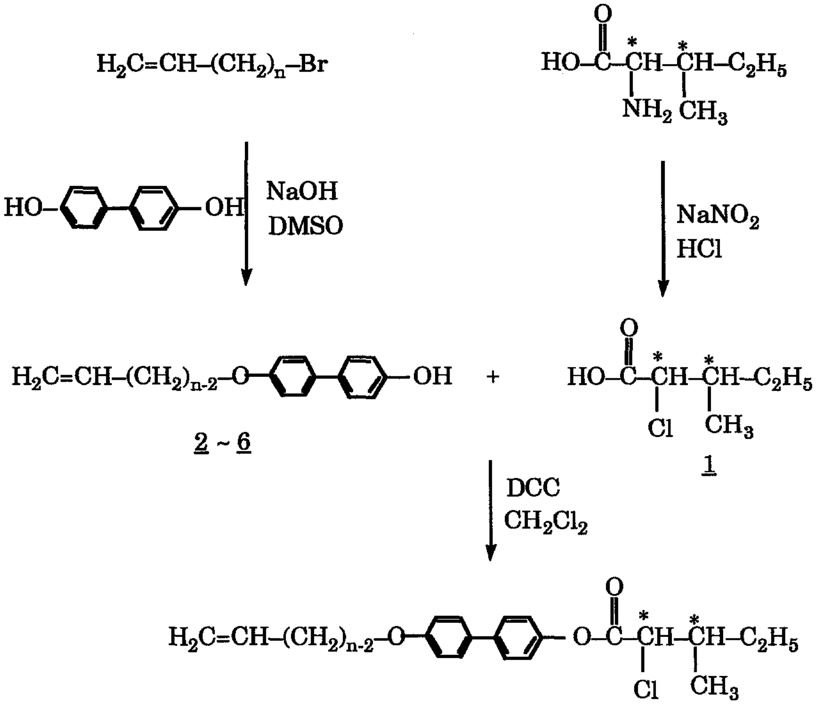


n = 3, 6, 8, 10, 11

monomer	1M	2M	3M	4M	5M
n	3	6	8	10	11

Scheme 1 : Synthesis of monomers 1M ~5M.

Preparation of (–)-(2S, 3S)-2-chloro-3-methylpentanoic acid (1)

(–)-(2S, 3S)-2-chloro-3-methylpentanoic acid was prepared by chlorination of diazonium salt of L-isoleucine according to a literature procedure[19].

Preparation of 4'-alkenyloxy-4-hydroxybiphenyl (2~6)

Compounds **2** ~ **6** were synthesized by monoetherification of the corresponding alkenyl halides with 4,4-biphenol. An example is described below. 4,4'-Biphenol (6.32 g, 34 mmol) was added to a solution of sodium hydroxide (2.72 g, 68 mmol) in 40 ml of DMSO. The solution was stirred at room temperature for 1 h. 1-Chloro-10-undecene (3.77 g, 20 mmol) was added dropwise and the reaction mixture was heated to 110°C and stirred overnight. The solution was cooled, acidified with 6N HCl aqueous solution and extracted with diethylether. The collected diethylether solution was washed with water, dried over anhydrous $MgSO_4$ and then evaporated to dryness. The obtained product was purified by column chromatography (silica gel, chloroform as eluent) to yield 3.72 g (55%) of white crystals.

Preparation of monomers 1M~5M

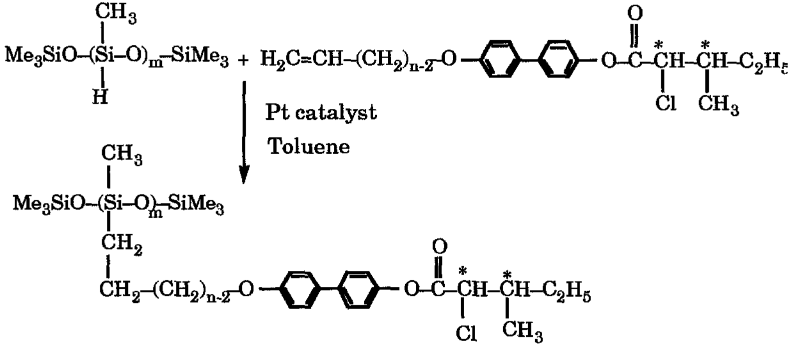
The olefinic monomers 1M~5M were synthesized by the esterification of (–)-(2S, 3S)-2-chloro-3-methylpentanoic acid with 4'-alkenyloxy-4-hydroxybiphenol (**2** ~ **6**). An example is described below. (–)-(2S, 3S)-2-Chloro-3-methylpentanoic acid (1.50 g, 10 mmol), 4'-(10-undecenyloxy)-4-hydroxybiphenyl (3.38 g, 10 mmol) dicyclohexylcarbodiimide (DCC) (2.06 g, 10 mmol) and 4-dimethy-laminopyridine (DMAP) (0.24 g, 2.0 mmol) were dissolved in dichloromethane (50 ml) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was washed with dilute HCl aqueous solution, water, dried over anhydrous $MgSO_4$ and then evaporated to dryness. The crude product was purified by column chromatography (silica gel, chloroform as eluent) to yield 3.81 g (81%) of white crystals. Table I summarized the ^{1}H-NMR chemical shifts for all synthesized monomers 1M~5M.

Table I : ^{1}H-NMR Chemical Shifts of Monomers 1M~5M.

Monomer	400 MHz, $CDCl_3$, δ in ppm
1M	0.90 (t, 3H, $-CH_2C\underline{H}_3$), 0.97 (d, 3H, $-CHC\underline{H}_3-$), 1.27 and 1.58 (m, 2H, $-C\underline{H}_2-CH_3$), 2.03 (m, 1H, $-C\underline{H}-CH_3$), 4.37 (d, 1H, $-C\underline{H}Cl$), 4.52 (m, 2H, $-C\underline{H}_2-O-$), 5.23-5.42 (m, 2H, $\underline{H}_2C=CH-$), 5.78 (m, 1H, $H_2C=C\underline{H}-$), 6.82-7.42 (m, 8 aromatic protons)
2M	0.97 (t, 3H, $-CH_2C\underline{H}_3$), 1.14 (d, 3H, $-CHC\underline{H}_3-$), 1.40 and 2.10 (m, 8H, $-(C\underline{H}_2)_3-CH_2-O-$ and $-CH_2-CH_3$), 2.22 (m, 1H, $-C\underline{H}-CH_3$), 3.97 (t, 2H, $-C\underline{H}_2-O-$), -4.37 (d, 1H, $C\underline{H}Cl-$), 4.92-5.00 (m, 2H, $-H_2C=CH-$), 5.78 (m, 1H, $H_2C=CH-$), 6.82-7.42 (m, 8 aromatic protons)
3M	0.97 (t, 3H, $-CH_2C\underline{H}_3$), 1.13 (d, 3H, $-CHC\underline{H}_3-$), 1.36 and 2.08 (m, 12H $-(C\underline{H}_2)_5-CH_2-O-$ and $-C\underline{H}_2-CH_3$), 2.22 (m, 1H, $-C\underline{H}-CH_3$), 3.97 (t, 2H, $-C\underline{H}_2-O-$), -4.37 (d, 1H, $-C\underline{H}Cl-$), 4.92-5.02 (m, 2H, $\underline{H}_2C=CH-$),5.78 (m, 1H, $H_2C=C\underline{H}-$), 6.82-7.42 (m, 8 aromatic protons)
4M	0.95 (t, 3H, $-CH_2C\underline{H}_3$), 1.12 (d, 3H, $-CHC\underline{H}_3-$), 1.25-2.05 (m, 16H, $-(C\underline{H}_2)_7-CH_2-O-$ and$-C\underline{H}_2-CH_3$), 2.21(m, 1H, $-C\underline{H}-CH_3$), 3.96 (t, 2H, $-C\underline{H}_2-O-$), -4.37 (d, 1H, $C\underline{H}Cl-$), 4.90-5.00 (m, 2H, $\underline{H}_2C=CH-$), 5.78 (m, 1H, $H_2C=C\underline{H}-$), 6.90-7.54 (m, 8 aromatic protons)
5M	0.90 (t, 3H, $-CH_2C\underline{H}_3$), 1.09 (d, 3H, $-CHC\underline{H}_3-$), 1.12 and 2.00 (m, 16H, $-(C\underline{H}_2)_8-CH_2-O-$ and $-C\underline{H}_2-CH_3$), 2.17 (m, 1H, $-C\underline{H}-CH_3$), 3.92 (t, 2H, $-C\underline{H}_2-O-$), -4.32 (d, 1H, $C\underline{H}Cl-$), 4.85-4.95 (m, 2H, $\underline{H}_2C=CH-$), 5.75 (m, 1H, $H_2C=C\underline{H}-$), 6.88-7.47 (m, 8 aromatic protons)

Synthesis of polymers 1P~5P

All of the polymers 1P~5P were synthesized by the hydrosilylation of poly(methylhydroyer siloxane) with the olefinic monomers 1M~5M in the presence of Pt catalyst (Scheme 2). A general synthetic procedure is described below. The olefinic derivative (1.0 g, 10 mol % excess versus the Si-H groups present in polysiloxane) was dissolved in 100 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 divenyltetramethyldisiloxane 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 24h. After this reaction time the FT-IR analysis showed that the hydrosilation reaction was complete. The polymers were separated, purified by several reprecipitations from a tetrahydrofuran solution into methanol and further purified by preparative GPC, and then dried under vacuum.



m ≑ 80,n = 3, 6, 8, 10, 11

1P : n = 3, 2P : n = 6, 3P : n = 8, 4P : n = 10, 5P : n = 11.

Scheme 2 : Synthesis of polysiloxanes 1P-5P.

RESULTS AND DISCUSSION

Olefinic monomers with chiral end group were synthesized via Scheme 1. (2S, 3S)-2-Chloro-3-methyl-pentanoic acid was prepared from isoleucine by a Sandmeyer reaction. The reaction is performed with retention of configuration[19]. The esterification of (2S, 3S)-2-chloro-3-methylpentanoic acid with 4'-alkenyloxy-4-hydroxybiphenyl is also achieved with retention of its configuration. The prepared monomers were characterized by differential scanning calorimetry and optical polarizing microscopy. Thermal transitions and thermodynamic parameters of monomers 1M~5M are summarized in Table II. Monomer 1M show no mesophase. The reason could be due to the short spacer length. Monomer 2M presents an enantiotropic S_A phase, both monomers 3M and 4M display an enantiotropic S_A and a monotropic S_C^* phase while monomer 5M reveals enantiotropic S_A and S_C^* phases. Representative DSC traces of monomer 3M are presented in Figure 1. It exhibits a melting transitions at 41°C and smectic A to isotropic phase transition at 51°C on the heating scan (curve A). On the cooling scan, it reveals an isotropic to smectic A phase transition at 47°C, a monotropic smectic A to chiral smectic C phase transition at 35°C and a crystallization transition at 21°C. Figure 2 displays respectively the smectic A and chiral smectic C textures exhibited by monomer 3M. As can be seen from the data listed in Table II, the tendency toward the S_C^* phase increases with increasing the spacer length.

The synthesis of polymers 1P~5P was described in Scheme 2. An excess amount of olefinic monomers was usually used to carry the hydrosilation reaction to completion. The unreacted monomers were removed by several reprecipitation from tetrahydrofuran solution into methanol and by preparative GPC. Therefore the polymers were isolated with high purity. Table III summarizes the thermal transitions and thermodynamic parameters of the obtained polymers 1P~5P. Polymer 1P and 2P show respectively a glass transition (Tg) and an enantiotropic S_A phases while polymers 3P~5P reveal respectively a Tg and enantiotropic S_A, S_C^* and S_B phase. Figure 3 illustrates the representative DSC traces of polymer 3P. On the heating scan (curve A), it shows a Tg at 21°C, a S_B to S_C^* transition at 75°C, a S_C^* to S_A transition at 124°C. The cooling scan (curve B) looks almost identical to the heating scan except that a very small supercooling (less than 10°C) is observed for three exothermic transitions. Figure 4 presents the typical S_A, S_C^* and S_B textures exhibited by 3P.

Table II : Thermal transitions and thermodynamic parameters of monomers 1M~5M.

Monomer	n	Thermal transition, phase transition and enthalpy T (°C) / ΔH (J/g) $\frac{\text{heating}}{\text{cooling}}$
1M	3	K 91 (32.5) I K 87 (34.5) I
2M	6	K 48 S_A 55 (21)^a I K 42 S_A 50 (19)^a I
3M	8	K 41 (40) S_A 51 (6.6) I K 21 (6.6) S_C^* 35 (2.0) S_A 47 (7.4) I
4M	10	K 49 (53.6) S_A 52 (0.7) I K 24 (52.5) S_C^* 33 (1.7) S_A 49 (6.7) I
5M	11	K 36 (30.6) S_C^* 46 (2.8) S_A 59 (5.34) I K 20 (40.5) S_C^* 38 (1.2) S_A 54 (8.47) I

a : overlapped transitions; K : crystalline; I : isotropic; S_A : smectic A; S_C^* : chiral smectic C.

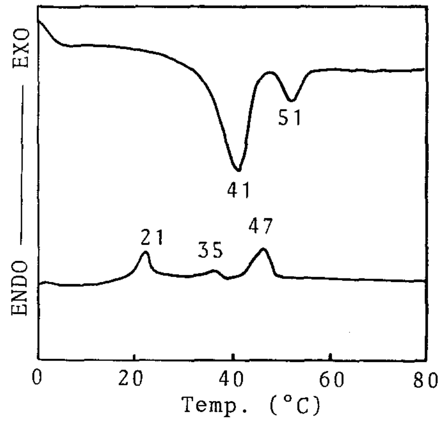
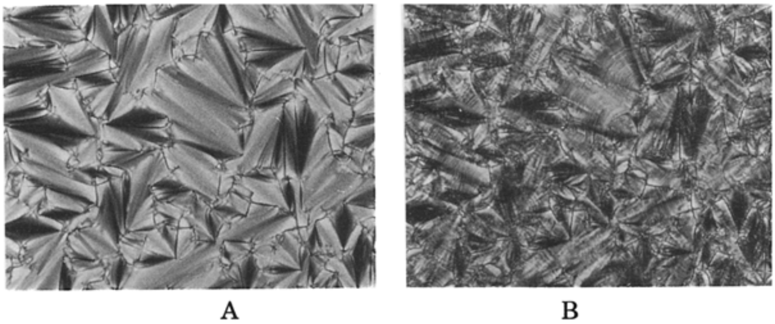


Figure 1 : DSC thermograms of 3M (10°C/min): (A) heating scan; (B) cooling scan.



A B

Figure 2 : Optical polarizing micrographs displayed by 3M : (A) S_A texture; (B) S_C^* texture.

Table III : Thermal transitions and thermodynamic parameters of polymers 1P~5P.

Polymer	n	Thermal transition, phase transition and enthalpy T (°C) / ΔH (J/g) heating	cooling
1P	3	g 21 S_A 63 (1.5) I	S_A 57 (1.2) I
2P	6	g 13 S_A 83 (2.5) I	S_A 77 (2.95) I
3P	8	g 21 S_B 57 (4.6) S_C^* 97 (1.0) S_A 124 (8.3) I	S_B 53 (2.1) S_C^* 93 (0.9) S_A 121 (5.5) I
4P	10	g 20 S_B 60 (9.2) S_C^* 96 (0.4) S_A 139 (2.6) I	S_B 53 (2.1) S_C^* 84 (0.3) S_A 131 (6.6) I
5P	11	g 10 S_B 57 (7.8) S_C^* 67 (7.3) S_A 143 (9.9) I	S_B 50 (11) S_C^* 78 (0.28) S_A 134 (9.8) I

g : glassy; S_A : smectic A; S_B : smectic B; S_C^* : chiral smectic C; I : isotropic.

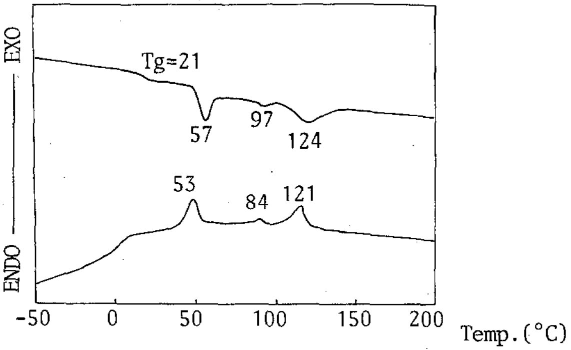
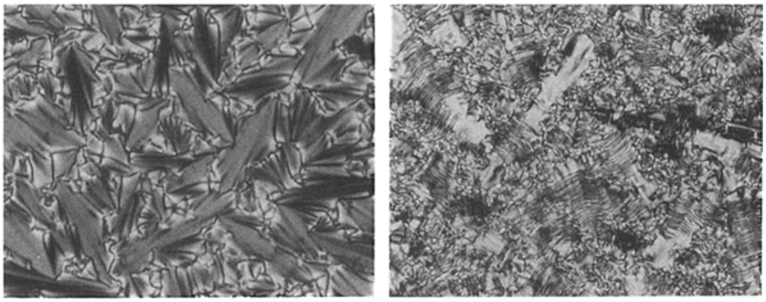


Figure 3 : DSC thermograms of 3P (10°C/min) : (A) heating scan; (B) cooling scan.



A B

Figure 4 : Optical polarizing micrographs displayed by 3P : (A) S_A texture; (B) S_C^* texture.

The temperature-dependent X-ray diffraction diagrams obtained from powder sample of 3P are presented in Figure 5. The curve obtained at 110°C presents a diffuse reflection at about 4.8Å, which correspounds to lateral spacing of two mogenic side groups, and a sharp reflection at 30.0Å, which correspounds to smectic layers. This is typical X-ray diffraction pattern of a smectic A phase[8,20]. When the measuring temperature has been lowered form 110°C to 90°C, the d spacing of the sharp diffraction peak decreases from 30.0 to 28.6 Å. This gives the strong evidence for the formation of a tilted S_C^* phase. When the measuring temperature has been further cooled, the d-spacing first decreased and then increased (below 60°C). All the diffraction peaks became much sharper. This indicates the formation of smectic B phase. Polymers 4P and 5P show similar thermal behavior as polymer 3P.

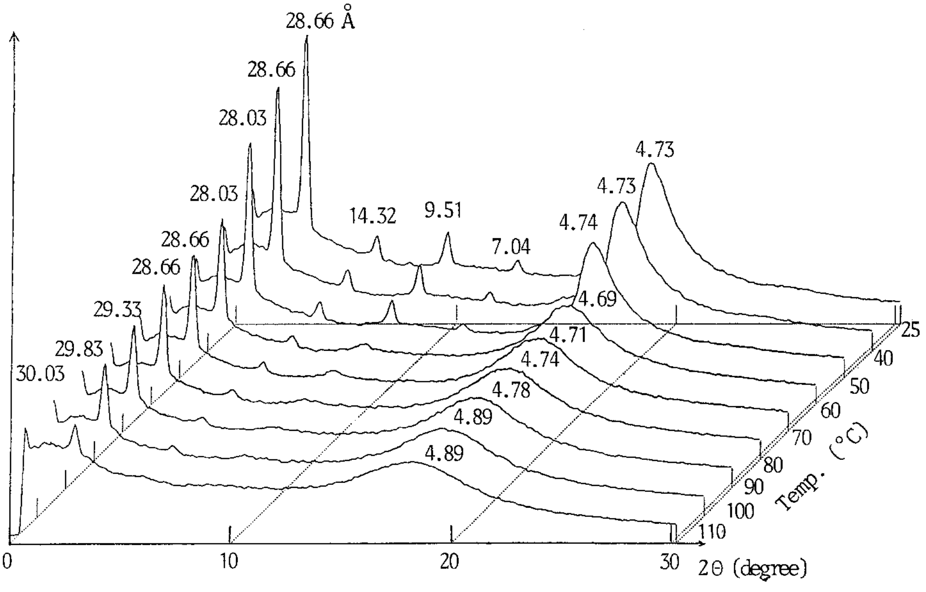


Figure 5 : Temperature-dependent X-ray diffraction diagrams for polymer 3P.

In conclusion, a series of side-chain liquid crystalline polysiloxanes containing (2S, 3S)-4'-(2-chloro-3-methylpentanoyloxy)-4-alkanyloxybiphenyl side groups have been prepared. All the obtained polymers have exhibited smectic mesomorphism. The tendency toward chiral smectic mesomorphism increases by increasing the length of alkyloxy spacers. It seems that a longer spacer enchances the decoupling of the motions of mesogenic side groups and polymer backbones and therefore tends to increase the possibility of the formation of an S_C^* phase. Strong polymer effect was achieved by the flexible polysiloxane polybackbone and therefore the obtained polymers tend to give rise to a higher thermal stability of the mesophases, including the chiral smectic C phases.

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