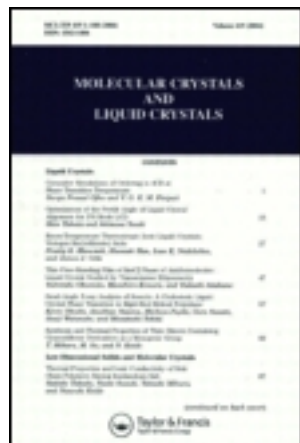


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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Published online: 04 Oct 2006.

To cite this article: Chain-Shu Hsu & Yi-Jing Leu (1997) Synthesis of Liquid Crystalline Polysiloxanes Containing Naphthalene-Based Mesogens and Chiral Side Chains, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 300:1, 83-95, DOI: [10.1080/10587259708042340](https://doi.org/10.1080/10587259708042340)

To link to this article: <http://dx.doi.org/10.1080/10587259708042340>

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Synthesis of Liquid Crystalline Polysiloxanes Containing Naphthalene-Based Mesogens and Chiral Side Chains

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(Received 1 August 1996; In final form 4 October 1996)

The synthesis and characterization of side-chain liquid crystalline polysiloxanes containing (2S)-2-chloro-4-methylpentyl 4-[(6-alkanyloxynaphthyl-2-yl)carbonyloxy]benzoate and (2S,3S)-2-chloro-3-methylpentyl 4-[(6-alkanyloxynaphthyl-2-yl)carbonyloxy]benzoate side groups are presented. All of the obtained polymers reveal respectively an enantiotropic smectic A phase. The phase transition temperatures of the obtained polymers depend on the spacer length. As the spacer length increases the glass transition temperature decreases while the isotropization temperature increases. The thermal stability of the obtained polymers increases as the spacer length increases. All of the obtained polymers present no chiral smectic C phase. The result seems to demonstrate that incorporation of a naphthalene ring in the mesogenic core decreases the tendency to form a chiral smectic C phase.

Keywords: Side-chain liquid crystalline polymer; polysiloxane; naphthalene-based mesogen

1. INTRODUCTION

The potential application of ferroelectric liquid crystals (FLCs) in fast switching, high-resolution electrooptical devices is well documented [1–3]. Besides low molar mass FLCs, a number of ferroelectric liquid crystalline side-chain polymers have been successfully prepared during the past few years [4–30]. These polymers are interesting because of their ferroelectric properties. This

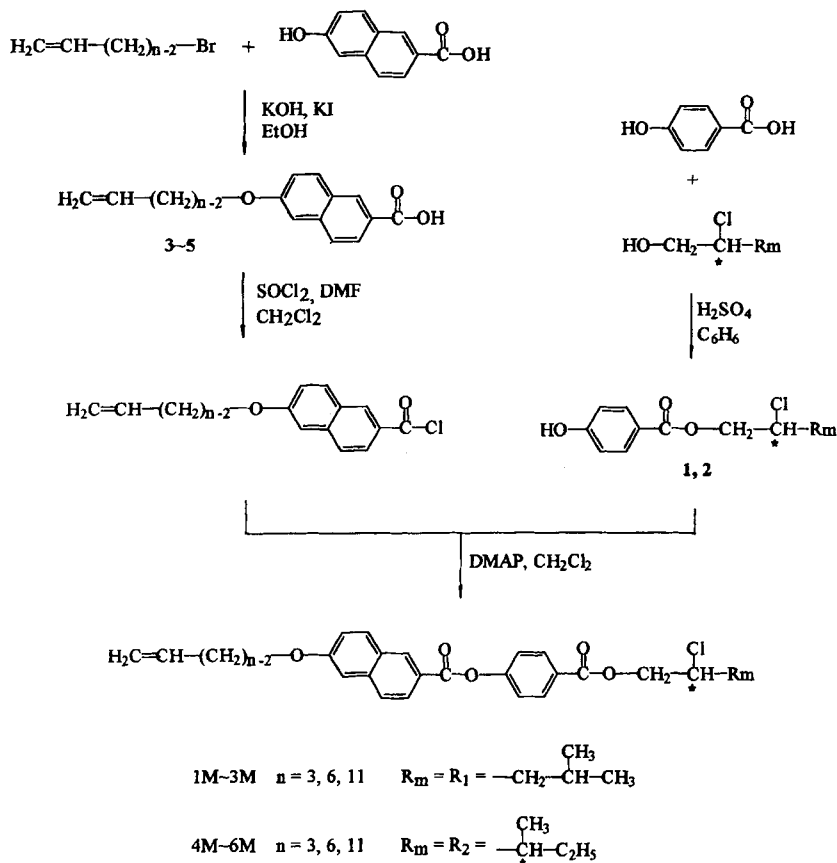
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field has been reviewed by P. LeBarney and J. C. Dubois [31]. However, the detailed structure-property relationship of ferroelectric liquid crystalline polymers (LCPs) has not been very clear up until now. It seems necessary to introduce additional functional groups to the mesogenic units, spacers and polymer backbones of side-chain liquid crystalline polymers to create some new property combinations to achieve these goals.

Recently we have synthesized several series of ferroelectric side-chain LCPs which contain a biphenyl and a phenyl ring in the mesogenic side groups [28–30]. It would be interesting to replace the biphenyl ring with a naphthalene ring in the mesogenic core so as to study the detailed structure–property relationship for the chiral smectic C LCPs. Presenting the synthesis of some liquid crystalline polysiloxanes containing the (2S)-2-chloro-4-methylpentyl 4-[[6-(alkanyloxynaphthyl-2-yl)carbonyloxy]benzoate and (2S, 3S)-2-chloro-3-methylpentyl 4-[[6-(alkanyloxynaphthyl-2-yl)carbonyloxy]benzoate side group is the goal of this study. Their characterizations by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction are presented.

2. RESULTS AND DISCUSSION

The synthetic route used for the preparation of monomers 1M–6M is outlined in Scheme 1. (2S)-2-Chloro-4-methylpentanol and (2S, 3S)-2-chloro-3-methylpentanol were prepared respectively from L-leucine and isoleucine by a Sandmeyer reaction followed by reduction with LiAlH_4 . The reactions were performed with retention of the configuration [32]. The esterification of (2S)-2-chloro-4-methylpentanol and (2S, 3S)-2-chloro-3-methylpentanol with 4-hydroxybenzoic acid was also achieved with retention of the configuration. The obtained monomers 1M–6M were characterized by differential scanning calorimetry and optical polarizing microscopy. Representative DSC traces of monomers 4M are presented in Figure 1. Monomers 4M exhibits a melting transition at 99.4°C on the heating scan. On the cooling scan, it reveals an isotropic to cholesteric phase transition at 83.1°C , a cholesteric to smectic A phase transition at 68.5°C and a crystallization temperature at 55.7°C . Figure 2 shows the typical cholesteric and smectic A textures exhibited by monomer 4M. Table I summarizes the thermal transitions and corresponding enthalpy changes of monomers 1M–6M. Both monomers 1M and 4M which contain three methylene units in the spacers display monotropic cholesteric and smectic A phases, both monomer 2M and 5M which contain six methylene units in the spacers exhibit a monotropic smectic A phase, while monomers 3M and 6M which contain eleven



SCHEME 1 Synthesis of monomers 1M ~ 6M.

methylene units in the spacer show respectively a monotropic smectic A phase and an enantiotropic smectic A phase. The experimental results demonstrate that the type of the mesophases formed by the monomers depend on the spacer length.

The synthesis of polysiloxanes 1P-6P is 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 reprecipitations from THF solution into methanol and by preparative GPC. Therefore the polymers were isolated with high purity. The obtained polymers were characterized by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction. Figure 3 depicts the representative

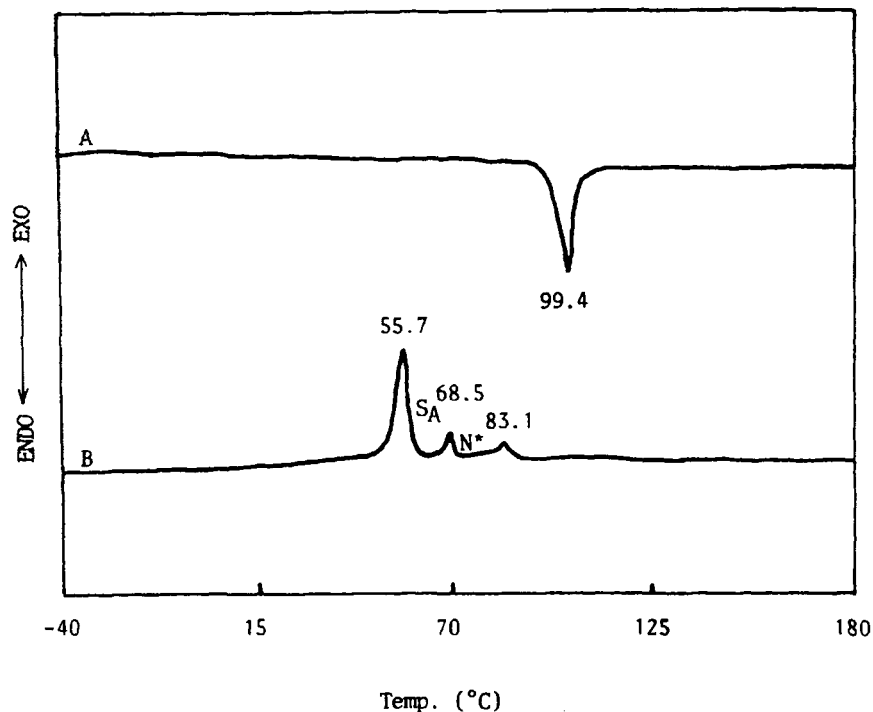
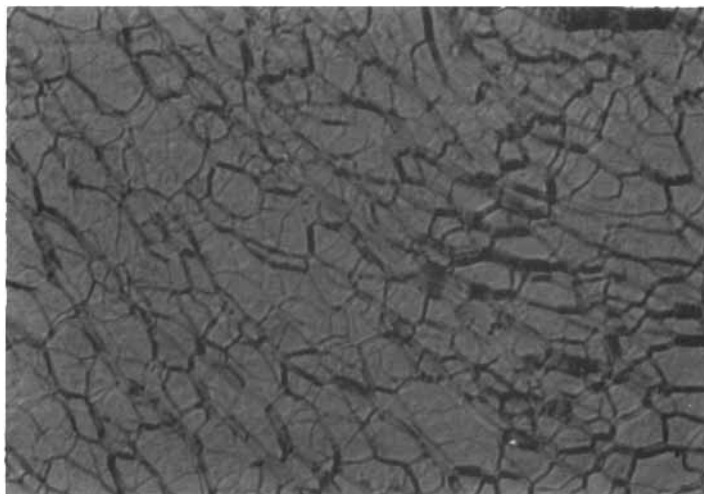
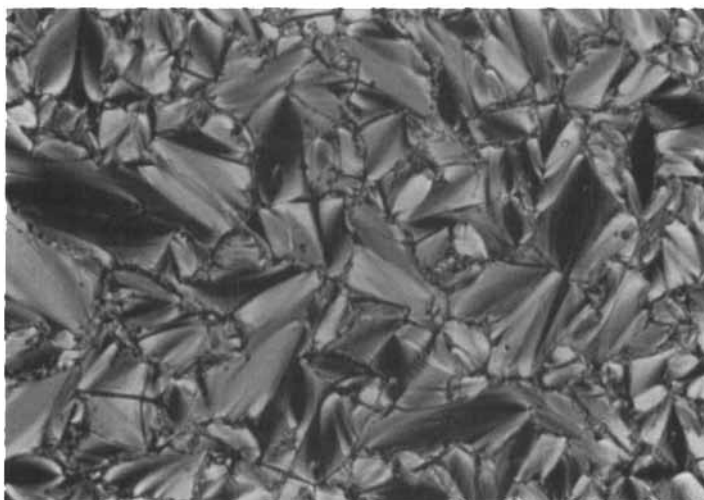


FIGURE 1 DSC thermograms of monomer 4M (10°C/min): (A) heating scan; (B) cooling scan.

DSC heating and cooling traces for polymer 3P. On the heating scan (curve A), it shows a glass transition temperature (T_g) at -2.5°C , followed by a smectic A to isotropic phase transition at 155.3°C . The cooling scan (curve B) looks identical to the heating scan, except that a very small supercooling (less than 5°C) is observed for the isotropic to smectic A phase transition. Figure 4 displays the typical smectic A texture exhibited by polymer 3P. Figure 5 presents the temperature-dependent X-ray diffraction diagrams obtained from the powder sample of 3P at 140, 110, 80, 50 and 25°C . A broad reflection at wide angle (associated with the lateral packings) and a sharp reflection (associated with the smectic layers) are respectively shown by all curves. When the measuring temperature has been lowered from 140°C to 25°C , the smectic layer spacing keeps at about the same value. This result which is in agreement with the optical microscopic observation indicates the formation of a smectic A structure. Table II summarizes the thermal transitions and corresponding enthalpy changes of polymers 1P–6P. All



A



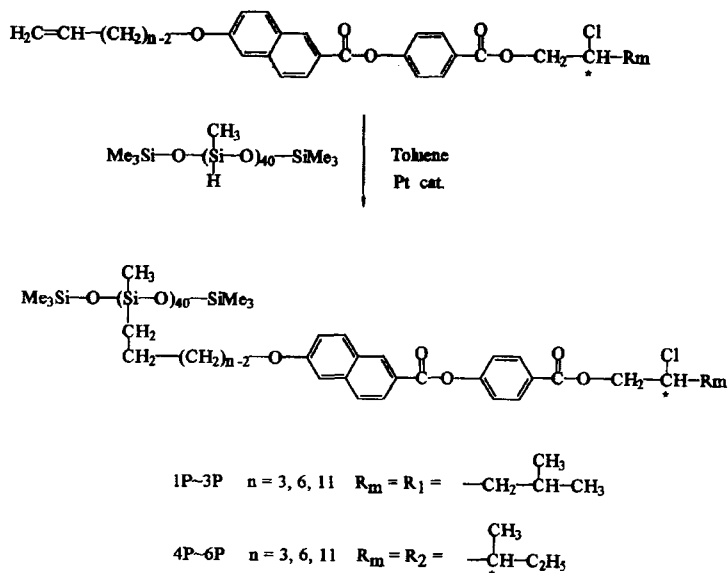
B

FIGURE 2 Optical polarizing micrographs displayed by monomer 4M: (A) cholesteric texture obtained after cooling from isotropic phase to 76.7°C; (B) S_A texture obtained after cooling to 67.3°C. (See Color Plate V).

polymers present respectively an enantiotropic smectic A phase. As can be seen from the data listed in Table II, the glass transition temperatures decrease with increasing the spacer length and the thermal stability of the mesophase increases with increasing the spacer length.

TABLE I Phase transitions and phase transition enthalpies for monomers 1M–6M

Monomer	n^a	R_m^a	Phase Transition, °C (Corresponding enthalpy changes Kcal/mol) ^b	
			heating	cooling
1M	3	R_1	K 78.7 (23.2) I	I 63.0 (0.27) N^* 52.5 (0.36) S_A 16.5 (12.4) K
2M	6	R_1	K 67.5 (30.2) I	I 65.1 (3.7) S_A 19.3 (17.6) K
3M	11	R_1	K 80.3 (55.2)	I 77.7 (5.31) S_A 13.2 (24.1) K
4M	3	R_2	K 99.4 (27.6) I	I 83.1 (0.23) N^* 68.5 (0.9) S_A 55.7 (20.5) K
5M	6	R_2	K 81.9 (13.5)	I 70.9 (1.3) S_A 45.8 (8.1) K
6M	11	R_3	K 71.4 (36.7) S_A 86.5 (4.4) I	I 84.7 (4.91) S_A 3.7 (15.4) K

^a n, R_m according to Scheme 1.^b K = crystalline, N^* = chloestic, S_A = smectic A, I = isotropic.

SCHEME 2 Synthesis of side-chain LC polysiloxanes 1P ~ 6P.

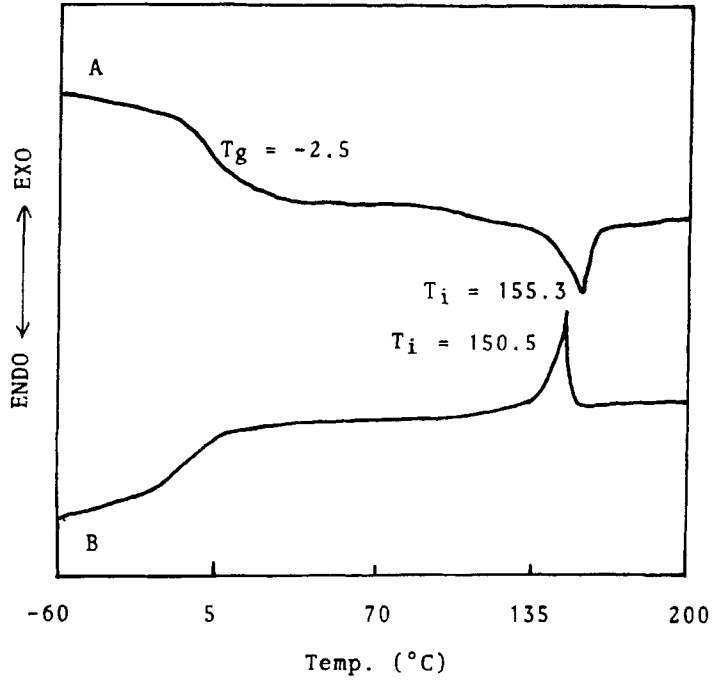


FIGURE 3 DSC thermograms of 3P (10°C/min): (A) heating scan; (B) cooling scan.

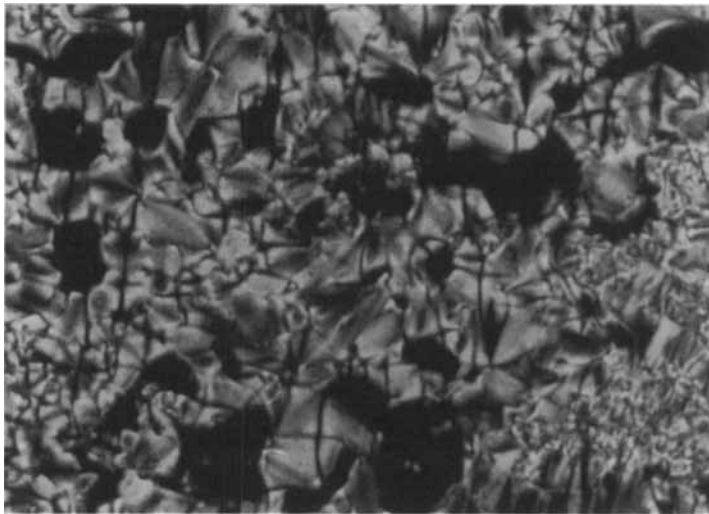


FIGURE 4 Optical polarizing micrograph displayed by 3P: Smectic A texture obtained after cooling from isotropic phase to 140°C. (See Color Plate VI).

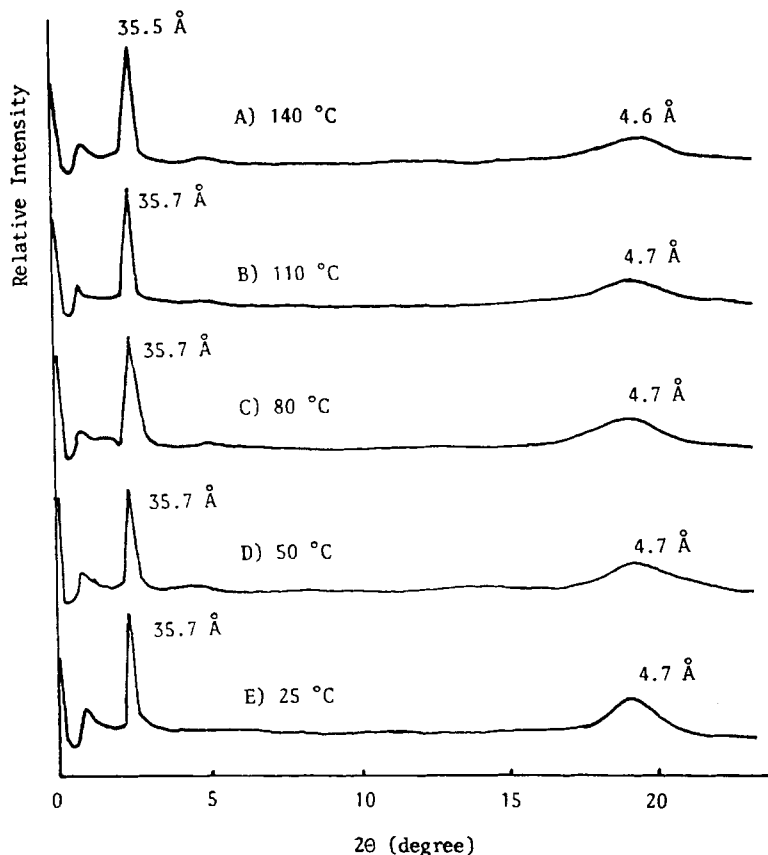


FIGURE 5 Temperature-dependent X-ray measurement for polymer 3P at (A) 140, (B) 110, (C) 80, (D) 50, (E) 25°C.

In conclusion, two series of new side-chain liquid crystalline polysiloxanes containing (2*S*)-2-chloro-4-methylpentyl 4-[(6-alkenyloxy)naphthyl-2-yl]carbonyloxy]benzoate and (2*S*, 3*S*)-2-chloro-3-methylpentyl 4-[(6-alkenyloxy)naphthyl-2-yl]carbonyloxy]benzoate side groups has been prepared. All the obtained polymers have exhibited respectively only an enantiotropic smectic A phase and no chiral smectic C phase. In comparison with our previous results reported in the literature [28–30], it demonstrates that the replacement of the biphenyl ring by a naphthalene ring in the mesogenic core will decrease the tendency to form a chiral smectic C phase.

TABLE II Phase transitions and phase transition enthalpies for polymers 1P–6P

Polymer	n^a	R_m^a	Phase Transition, °C (Corresponding enthalpy changes Kcal/mru) ^b	
			heating	cooling
1P	3	R_1	$G \ 20.4 \ S_A \ 72.0 \ (0.07) \ I$ $I \ 69.1 \ (0.1) \ S_A$	
2P	6	R_1	$G \ 3.0 \ S_A \ 78.5 \ (0.73) \ I$ $I \ 76.1 \ (0.51) \ S_A$	
3P	11	R_1	$G \ -2.5 \ S_A \ 155.3 \ (0.91) \ I$ $I \ 150.5 \ (0.94) \ S_A$	
4P	3	R_2	$G \ 26.0 \ S_A \ 87.2 \ (0.94) \ I$ $I \ 59.8 \ (0.32) \ S_A$	
5P	6	R_2	$G \ -0.2 \ S_A \ 62.2 \ (0.48) \ I$ $I \ 62.4 \ (0.46) \ S_A$	
6P	11	R_3	$G \ -2.7 \ S_A \ 156.4 \ I$ $I \ 155.7 \ (0.86) \ S_A$	

^a m , R_m according to Scheme 2.^bmru = mole repeating unit; G = glassy, S_A = smectic A, I = isotropic.

3. EXPERIMENTAL

3.1. Materials

Poly(methylhydrogensiloxane) ($\overline{M}_n = 2270$) and divinyltetramethyl-disiloxane platinum catalyst were obtained from Patrarch System Inc., and used as received. 6-Hydroxy-2-naphthoic acid and all other reagents (from Aldrich) were used as received. The toluene which was used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen. (2S)-2-Chloro-4-methylpentanol and (2S,3S)-2-chloro-3-methylpentanol were prepared respectively from L-leucine and isoleucine according to literature procedure [32].

3.2. Techniques

¹H NMR spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. FT-IR spectra were measured on a Nicolet 520 FT-IR spectrometer. Polymer samples were casted film onto a KBr tablet for the

IR measurements. 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 scan. A Carl-Zeiss Axiophot optical polarized microscope equipped with a Mettler FP 82 hot stage and an 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. Optical rotations were measured at 25°C on a Jasco DIP-140 polarimeter with chloroform as solvent for all compounds.

3.3. Synthesis of Monomers

The synthesis of the olefinic derivatives 1M~6M is outlined in Scheme 1.

(2S)-2-Chloro-4-methylpentyl-4-hydroxybenzoate (1)

(2S, 3S)-2-Chloro-3-methylpentyl-4-hydroxybenzoate (2)

Both compounds were prepared by esterification of (2S)-2-chloro-4-methylpentanol with 4-hydroxybenzoic acid. The synthesis of compound 1 is described below.

4-Hydroxybenzoic acid (9.66 g, 0.07 mol) and (2S)-2-chloro-4-methylpentanol (20.5 g, 0.15 mol) and concentrated sulfuric acid (0.2 mL) were added to 20 mL of dried benzene. The reaction mixture was refluxed until 4-hydroxybenzoic acid was completely dissolved and 1.26 mL of water was collected on a Dean-Stark trap. After cooling to room temperature, the solution was washed with a 2% aqueous solution of NaHCO₃ and water, and dried over anhydrous MgSO₄. The solvent was removed in a rotavapor. The obtained solid was purified with column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/4 as eluent) to yield 16.5 g (86%) of white crystals. $[\alpha]_D^{25}$ (chloroform, *c* = 1.6 g/dl) = -3.12.

¹H NMR (CDCl₃, TMS, ppm): δ 0.90–1.0 (*m*, 6H, —CH₃), 1.56–1.90 (*m*, 3H, —CH(CH₃)—CH₂—), 4.20 (*m*, 1H, —CH(Cl)—), 4.38–4.51 (*q*, 2H, —CH₂O—) 6.65 (*s*, 1H, —OH), 6.90–8.00 (*m*, 4 aromatic protons).

6-Allyloxy-2-naphthoic acid (3)**6-(5-Hexen-1-yloxy)2-naphthoic acid (4)****6-(10-Undecen-1-yloxy)2-naphthoic acid (5)**

All three compounds were prepared by the esterification of alkenyl bromide or undecenyl tosylate with 6-hydroxy-2-naphthoic acid. The synthesis of compound 3 is described below.

Allylbromide (1.06 g, 8.8 mmol) and 6-hydroxy-2-naphthoic acid (1.50 g, 8 mmol) was added to a solution of KOH (1.07 g, 19 mmol) in 90% ethanol (250 mL). The solution was refluxed overnight, and then was cooled to room temperature, poured into 400 mL of water, and acidified with dilute hydrochloric acid. The solid carboxylic acid was removed by filtration and recrystallized from acetic acid to yield 1.62 g (89%) of white crystals.

$^1\text{H NMR}$ (CDCl_3 , TMS, ppm): δ 4.60 (*d*, 2H, $-\text{CH}_2\text{O}-$), 5.32–5.53 (*m*, 2H $\text{CH}_2=$), 6.09–6.20 (*m*, 1H, $=\text{CH}-$), 7.20–8.70 (*m*, 6 aromatic protons).

Synthesis of Monomers 1M–6M

All six monomers were prepared by esterification of 6-alkenyloxy-2-naphthoic acid (3–5) with corresponding compounds 1 or 2. An example for the synthesis of monomer 1M is described below.

6-Allyloxy-2-naphthoic acid (0.6 g, 2.63 mmol) was reacted at room temperature with excess thionyl chloride (2 mL) containing a drop of dimethyl formamide in 20 mL of methylene chloride for 2 hrs. The solvent and excess thionyl chloride were removed under reduced pressure to give the crude acid chloride. The acid chloride which was dissolved in 10 mL of methylene chloride was added slowly to a cold solution (0°C) of (2S)-2-chloro-4-methylpentyl 4-hydroxybenzoate (0.67 g, 2.63 mmol) and 4-dimethylaminopyridine (0.43 mL, 3.16 mmol) in 20 mL of methylene chloride. The resulting solution was stirred for 2 hrs and extracted with water and dried over anhydrous MgSO_4 . After the solvent was removed in a rotavapor, the crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1.25 as eluent) to yield 0.92 g (75%) of white crystals. $[\alpha]_D^{25}$ (chloroform, *c* = 6.52 g/dl) = -5.96 $^1\text{H NMR}$ (CDCl_3 , TMS, ppm): δ 0.9–1.1 (*q*, 6H, $-\text{CH}_3$), 1.5–1.8 (*m*, 2H $-\text{CH}(\text{Cl})-\text{CH}_2-$), 1.9–2.1 (*m*, 1H, $-\text{CH}(\text{CH}_3)-\text{CH}_3$), 4.2–4.3 (*m*, 1H, $-\text{CH}(\text{Cl})$), 4.4–4.6 (*m*, 2H, $-\text{OCH}_2-$) 4.7 (*d*, 2H, $=\text{CH}-\text{CH}_2-$) 5.3–5.6 (*m*, 2H, $\text{CH}_2=$), 6.1–6.2 (*m*, 1H, $=\text{CH}-$), 7.2–8.7 (*m*, 10 aromatic protons).

3.4. Synthesis of Polysiloxanes 1P–6P

The synthesis of liquid crystalline polysiloxanes is outlined in Scheme 2. A general synthetic procedure is described below.

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(methylhydrogen-siloxane). 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 the FT-IR analysis showed that the hydrosilation reaction was 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.

Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for financial support of this work (Grants NSC-84-2216-E-009-011).

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