

Synthesis and Characterization of Chiral Side-Chain Liquid-Crystalline Polymer Containing Menthol Ester

Tong-Ying Jiang, Bao-Yan Zhang, Mei Tian, Ying Wang

Center for Molecular Science and Engineering, Northeastern University, Shenyang 110004, People's Republic of China

Received 16 July 2002; accepted 25 September 2002

ABSTRACT: The synthesis of new chiral side-chain liquid-crystalline polysiloxanes containing *p*-(allyloxy)benzoxy-*p*-chlorophenyl (ABCH) as mesogenic units and undecylenic acid menthol ester (UM) as chiral nonmesogenic units is presented. The chemical structures of monomers and polymers are confirmed by IR spectroscopy. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are used to measure thermal properties of those polymers. Mesogenic properties are characterized by polarized optical microscope (POM), DSC, and small-angle X-ray diffraction. Analytic results revealed that polymers P₀–P₆ are thermotropic liquid-crystalline polymers with low glass

transition; Polymers P₂–P₆ exhibit chiral smectic liquid-crystalline properties with marble texture, optical rotation, and a sharp reflection at low angles in X-ray diffraction; polymers P₀, P₁ only exhibit smectic liquid-crystalline properties without chirality; and P₇ only exhibits chirality without liquid-crystalline properties. All the polymers exhibit good thermal stability with temperature of 5% mass loss over 297°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2845–2851, 2003

Key words: chiral; smectic; liquid-crystalline polymer; *p*-(allyloxy)benzoxy-*p*-chlorophenyl; undecylenic acid menthol ester.

INTRODUCTION

In recent years, chiral side-chain liquid-crystalline polymers have been of more interest in fundamental research and application because of their unique properties, such as selective reflection of light and ferroelectricity. They have potential applications in numerous areas, especially in the field of optical-electro devices, thermoconducting materials, and fast switching.^{1–5} The mesomorphic properties of side-chain liquid-crystalline polymers mainly depend on the nature of polymer backbone, the type of mesogenic unit, the flexibility and length of the spacer, the nature of terminal groups, and so on. In order to obtain a higher mobility of the mesomorphic phase at moderate temperature and display mesomorphic properties at room temperature, the polysiloxane backbone is usually preferred. Recently, some successful investigations on the synthesis and characterization of side-chain liquid-crystalline polysiloxanes have been reported.^{6–10}

Many liquid-crystalline polysiloxanes in which mesogenic units contain halide or nitrile grouping have expressed nematic or twisted-nematic mesophase; moreover, they can give rise to a large number of smectic mesophases.¹¹ These polymers not only possess higher auto-polarizing vector (*P*_s), shorter re-

sponse time, lower viscosity, wider mesogenic region, and lower cost than main-chain and other side-chain liquid-crystalline polymers, but also lack the poor stability and difficulty in membrane-forming exhibited by low molecular weight liquid crystalline.⁵

Preparation of the chiral polymers by introducing a chiral nonmesogenic moiety to the mesogenic polymer has been studied for main-chain liquid-crystalline polymers.^{12,13} In side-chain liquid-crystalline polymers, the mixture of the homopolymers of the mesogenic monomer and chiral nonmesogenic monomer did not exhibit clear chiral mesomorphic phases. But the chiral mesomorphic phases can be induced by the copolymerization of a mesogenic monomer and a chiral nonmesogenic monomer.¹⁴

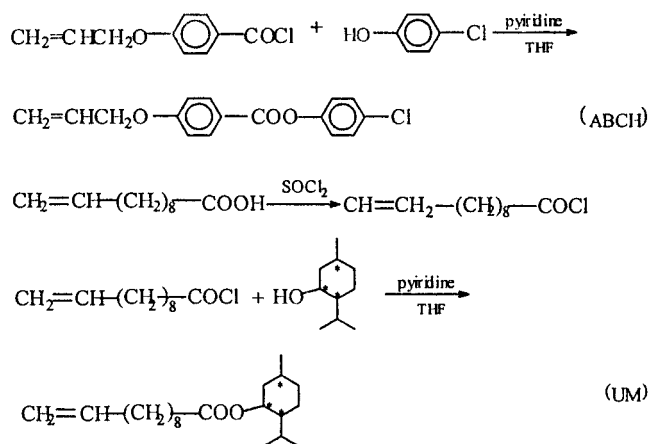
This article describes the synthesis and characterization of a series of side-chain liquid-crystalline polysiloxanes, which contain the mesogenic pendants and chiral nonmesogenic pendants.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS) was obtained from Jilin Chemical Industry Company (Jilin City, P. R. China). Undecylenic acid and menthol were the analytical reagents, obtained from Liaoning Chemical Industry Company (Shenyang City, P. R. China). Toluene used in the polymerization reaction was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard method.

Correspondence to: B. Y. Zhang (baoyanzhang@hotmail.com).



Scheme 1 Routes for monomer synthesis.

Synthesis of monomers

The synthesis of monomers is outlined in Scheme 1.

p-(allyloxy)benzoxy-p-chlorophenyl (ABCH)

4-allyloxy-benzoic acid and 4-allyloxy-benzoxy chloride were prepared according to procedures in the literature.^{15,16} In flask, 0.025 mol of 4-allyloxy-benzoxy chloride was dissolved in 16 mL of tetrahydrofuran. This solution was added dropwise to a solution containing 0.024 mol of 4-chlorophenol (laboratory-synthesized) and 9 mL of pyridine. The mixture was stirred for 6 h under 40°C, and then poured into 400 mL of water and precipitated. The precipitate obtained was recrystallized from ethanol. The white crystals obtained 83–84°C mp with a yield of 75%. IR(KBr)cm⁻¹: 3074(=C—H); 2800–3000(—CH₂—, —CH₃); 1735(C=O); 1605, 1510(Ar—); 1255(—C—O—C—); 600–700(Ar—Cl).

Undecylenic acid menthol ester

The synthesis of undecylenic acid menthol ester (UM) was composed of the following two steps. First, 0.10 mol of undecylenic acid reacted with 0.35 mol of thionyl chloride for 2 h at 20°C, then the solution was heated to 60°C and stirred for 3 h. The excess thionyl chloride was removed and undecylenic acid chloride was collected at 129–131°C/1.33 Kpa, yield: 78%. Second, 0.07 mol of 25 mL of tetrahydrofuran and 2 mL of pyridine were stirred to completely dissolve. Then undecylenic acid chloride was slowly dropped into the solution. The mixture reacted for 6 h at 40°C and was poured into 200 mL of water. After removing the water layer, the oil layer was neutralized with 2% K₂CO₃ to pH = 7 and washed several times with distilled water. The oil layer obtained was dried with anhydrous CaCl₂ for 24 h, with a yield of 85%.

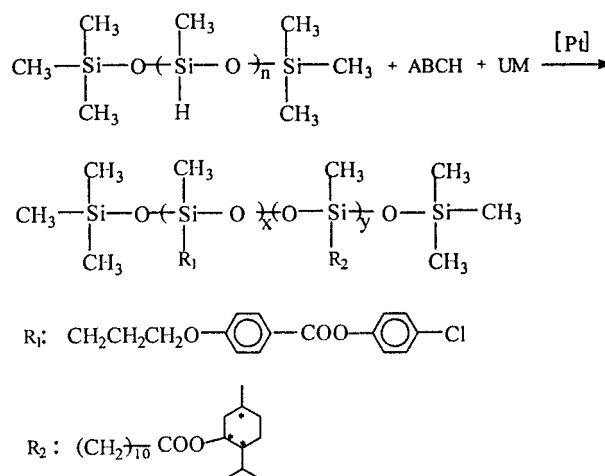
IR (KBr) cm⁻¹: 2800–3000(—CH₂—, —CH₃); 1730 (C=O).

Synthesis of polymer

The synthetic routes are shown in Scheme 2. All polymers synthesized are listed in Table I. A general procedure is described below. The monomers ABCH, UM, and PMHS were dissolved in dried, freshly distilled toluene. The solution was heated to 50–60°C under nitrogen, and a proper amount of tetrahydrofuran solution of hexachloroplatinate (IV) hydrate was injected to the solution by syringe. The reaction was kept for 60 h under 60–70°C. Then, the polymers were precipitated in methanol. The precipitation was precipitated repeatedly in alcohol and dried in a vacuum oven at room temperature. IR(KBr)cm⁻¹: 2800–3000(—CH₂—, —CH₃); 1730(C=O); 1605,1510(Ar—); 1255(—C—O—C—, Si—CH₃); 1000–1150 (Si—O—Si).

Experimental techniques

The structures of the polymers were determined with a Nicolet 510-PFT IR spectrometer (Madison, WI), using all samples on KBr. Optical activities were measured at 15°C using the spectrofluorophotometer Model 960 with tube length of 100 mm and wavelength of 589.0 nm. Thermal transitions were determined with a Perkin-Elmer DSC-7 (Perkin-Elmer, Foster City, CA), equipped with a PE data station, using nitrogen atmosphere and a 20°C/min heating and cooling rate. Thermal stabilities of the polymers were measured with a Perkin-Elmer TGA-7 thermogravimetric analyzer using nitrogen atmosphere and a 20°C/min heating rate. The textures of the polymers were observed with a Leitz Microphot-FX (Wetzlar, Germany) polarized optical microscope (POM), equipped with a Meltzer FP82 hot stage and an FP80 central processor that was used to observe the thermal transitions and analyze the anisotropic texture.



Scheme 2 Routes for polymer synthesis.

TABLE II
Thermal Analysis Results

Polymers	Feed	Results			
	PMHS:ABCH:UM	T_g^a (°C)	T_m^a (°C)	T_c^b (°C)	$T_{5\%}^c$ (°C)
P ₀	1.00:6.65:0.35	22.9	53.7	135.0	398.5
P ₁	1.00:6.30:0.70	22.0	53.1	124.0	348.9
P ₂	1.00:5.95:1.05	17.4	51.4	115.0	342.2
P ₃	1.00:5.60:1.40	15.1	51.3	92.0	345.3
P ₄	1.00:5.25:1.75	12.0	48.0	81.0	334.6
P ₅	1.00:4.90:2.10	13.8	50.2	76.0	331.3
P ₆	1.00:4.55:2.45	3.6	50.7	55.0	317.3
P ₇	1.00:4.20:2.80	1.6	47.0	—	297.1

$T_{5\%}$: Temperatures of 5% mass loss.

^a determined by DSC.

^b determined by POM.

^c determined by TGA.

The X-ray diffraction measurements were performed by using nickel-filtered Cu—K_α radiation with a Rigaku power diffractometer (Japan) at room temperature.

RESULTS AND DISCUSSION

IR spectra analysis

In the IR spectra of the polymers, the bands of the Si—H bond at 2140 cm⁻¹ disappeared and the bands of carbonyl near 1730 cm⁻¹ coming from the monomers were very strong, which showed that Si—H bands in PMHS had completely reacted with the monomers; meanwhile, the bands of C—H bond in methylene became increasingly strong with an increase in the content of UM from polymer P₀ to P₇.

Optical activity analysis

Optical activity is an important character of chiral materials. In this article, the polymers' optical activity

was confirmed by optical rotation measured by the Spectrofluorophotometer. Optical rotations from the solutions of chiral monomer UM and polymers are listed in Table I. Specific rotatory power and molar-specific rotatory power were respectively calculated by the following formulas:

$$[\alpha]_D^t = \alpha / cL$$

$$[\alpha]_{\text{mol}}^t = [\alpha]_D^t M$$

In the above formulas, $[\alpha]_D^t$ is specific rotatory power, $[\alpha]_{\text{mol}}^t$ is molar-specific rotatory power, t is temperature, c is concentration (g/ml), L is length (dm), and M is molecular weight or average molecular weight. As we can see, optical rotation from menthol did not disappear for esterification, thus chiral monomer UM also had optical rotation of 46.84°. Optical rotations of polymers P₂–P₇ showed that they were chiral compounds, but polymer P₀ and P₁ had no optical rotation because the concentration of UM was too low to exhibit chirality. Molar-specific rotatory power means specific rotatory power per mole of

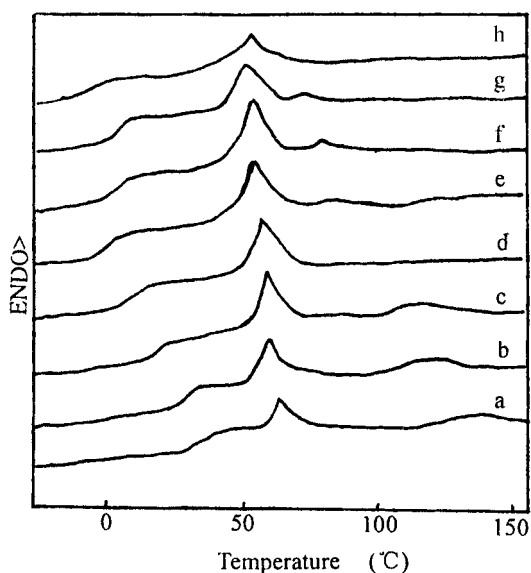


Figure 1 DSC thermographs of P₀–P₇ labeled a–h.

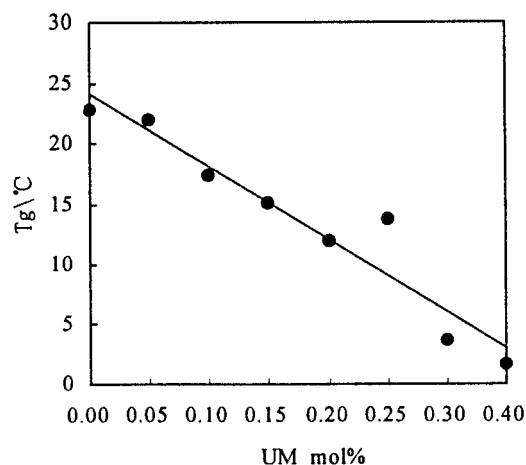


Figure 2 T_g vs UM concentration of polymers P₀–P₇.

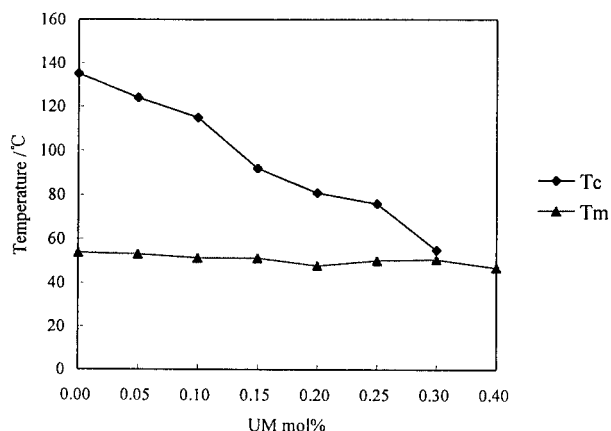


Figure 3 T_m and T_c vs UM concentration of polymers P_0 – P_7 .

chiral compounds. It is usually used to compare the optical activities of compounds. In polymers P_2 – P_7 , molar-specific rotatory powers increased with increasing content of UM, thus showing that optical activities became increasingly stronger. The increasing content of effective spire that was based on the increase in the content of UM and directly affected optical rotation may lead to this result.¹⁷

Thermal analysis

Results of the thermal analyses of the samples are summarized in Table II. Representative DSC traces of the polymers are presented in Figure 1.

The glass-transition temperature T_g is an important parameter in connection with the structures and properties of polymers. Generally, factors including main-chain or side-chain flexibility, molecular weight, and inter-chain interaction will affect T_g . Figure 2 shows that the T_g of the polymers decreased from 22.9°C to 1.6°C with an increase in the concentration of UM. As we know, T_g involves the mobility of chain segments in polymers, decreasing with an increase in the mobility of chain segments. In the comb-like polymers P_0 – P_7 , the flexibility of chain segments increased with an increase in the concentration of UM, whose long flexible hydrocarbon chains can diminish the rigidity of chain segments; thus, the mobility of chain segments increased and T_g decreased. In addition, the better flexibility of the polysiloxanes' backbone resulted in the good flexibility and low T_g of the polymers.

The strong polarity of the mesogenic units gave the polymers a better ability to crystallize, although the main chain was composed of amorphous material. Therefore, those polymers were semi-crystalline polymers with amorphous regions and crystalline regions. Melting point (T_m) is connected with crystalline regions and usually emerges after T_g in the DSC traces of polymers. When a polymer is heated to its T_m , its entire chain, crossing all regions, begins to move. The melting points of polymers P_0 – P_7 decrease from 53.7°C to 47°C with an increase in the UM content for the increased flexibility. The clearing point (T_c) is the temperature that involves the transition between the

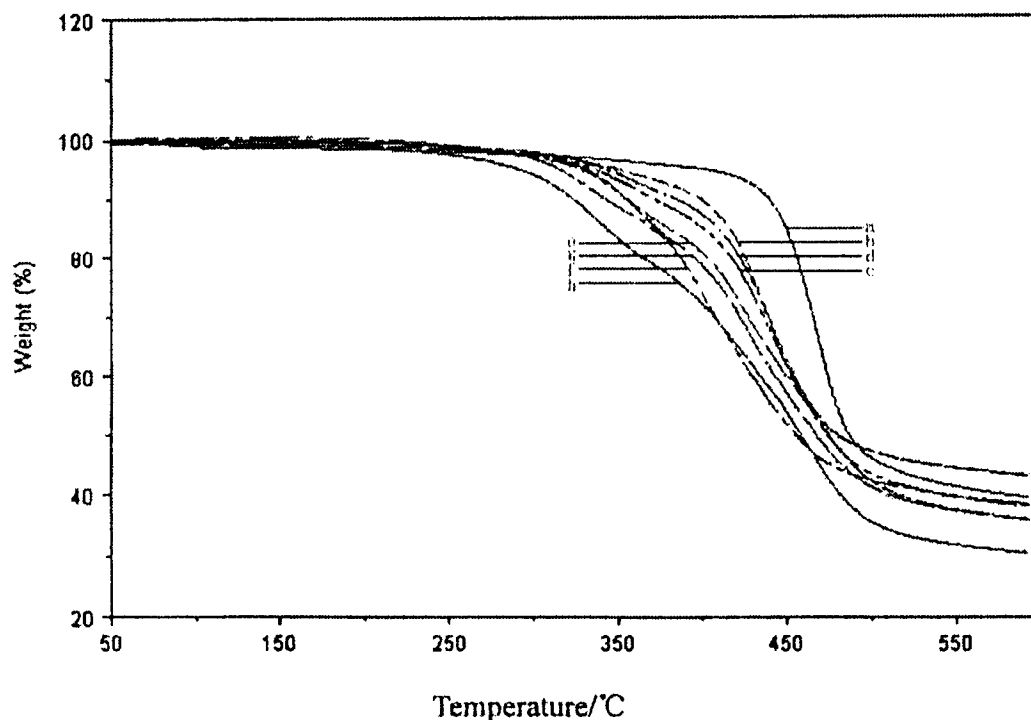


Figure 4 TGA thermographs (20°C/min) of polymers P_0 – P_7 labeled a–h, respectively.

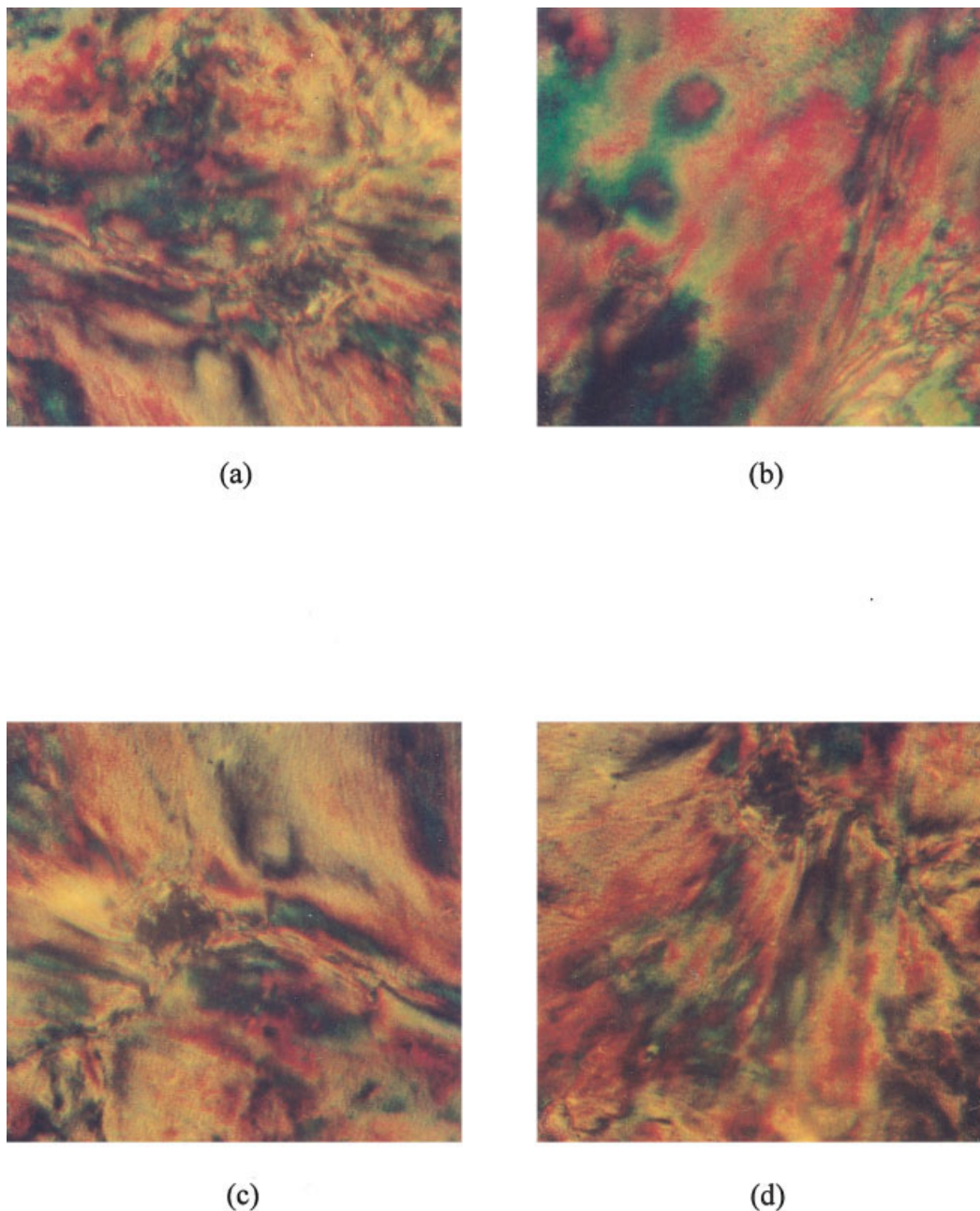


Figure 5 Polarized optical micrographs of four samples ($\times 320$) at different temperatures: (a) polymer P_0 at 100°C , (b) polymer P_1 at 90°C , (c) polymer P_3 at 65°C , and (d) polymer P_6 at 52°C .

mesomorphous and isotropic phases. Although the T_c values of polymers were not very obvious in the DSC traces, yet they were basically accordant with the results observed by POM, except that polymer P_7 had no T_c . The reason for this was that the concentration of ABCH was too low to form mesomorphous phases. The mesomorphous phase existed between T_m and T_c , and the range became narrow from 81.7°C to 8°C with an increase in the content of UM (see Fig. 3). As we can see, T_c declined faster than T_m . The most likely reason is as follows. In liquid-crystalline polymers, the mobility of chains after T_c was free and disorderly within

a larger range, whereas the mobility of chains between T_m and T_c was orderly within a smaller range. The effect of space-steric hindrance and the flexibility of the side group on the former is more evident, thus T_c declined faster.

The TGA thermograms of polymers P_0 – P_7 measured under nitrogen atmosphere are respectively presented in Figure 4. The temperatures of 5% mass loss ($T_{5\%}$) listed in Table II are defined as the initial decomposition temperature of the polymers. From these TGA thermograms, we can see that the rapid mass loss of the polymers generally took place between

TABLE I
Optical Activity of the Chiral Monomer And Polymers

Comp.	SC ^a (g/ml)	OR ^b (°, -)	SRP ^c (deg dm ⁻¹ g ⁻¹ cm ³)	MSRP ^d (deg dm ⁻¹ mol ⁻¹ cm ³ 10 ⁻²)
UM	0.95	46.84	49.30	150.82
P ₀	—	—	—	—
P ₁	0.00	0.00	0.00	0.00
P ₂	0.96	0.25	2.58	67.72
P ₃	0.97	0.30	3.07	80.95
P ₄	0.89	0.33	3.73	98.79
P ₅	0.95	0.53	5.54	147.37
P ₆	0.81	0.57	7.04	188.10
P ₇	0.87	0.88	10.13	273.03

^a Solution concentration.

^b optical rotation.

^c specific rotatory power.

^d molar-specific rotatory power.

400–450°C; The mass loss of all the polymers was nearly identical in this region. In the region of 470–600°C, the polymers nearly lost all their mass. The temperatures of the 5% mass loss of polymers were almost over 300°C, which proved that the series of polymers exhibited good thermal stability. Meanwhile, decreasing T_{5%} with increasing content of UM may be attributed to weaker and weaker association and the junction of silicone with the side groups.¹⁶

TEXTURE ANALYSIS

The textures of polymers observed with POM under nitrogen atmosphere are shown in Figure 5. The polymer P₀ exhibited a marble texture that is one of the smectic textures.¹¹ During heating, a marble texture with fluidity and bright colors as in Figure 5(a) was observed and did not change until 130°C, at which green became dark and yellow began to be preponderant. Finally, only yellow was left before the clearing point at 135°C. During cooling, the same marble texture was also observed. The textures of polymers P₁–P₆ were identical with that of P₀ at their respective temperatures. The textures of polymers P₁, P₃, and P₆ are presented in Figure 5(b)–(d), respectively. The same textures of polymers P₁–P₆ showed that the introduction of monomer UM did not change the polymers' textures. Polymer P₇ did not exhibit any textures. On the basis of the marble textures, polymers P₀–P₆ may be smectic liquid crystalline polymers. However, an accurate conclusion needs to be further established with the results of X-ray diffraction analysis.

Figure 6 shows typical small-angle X-ray diffraction patterns of quenched samples of polymers P₀ and P₃. Polymer P₀ was quenched at 100°C, and polymer P₃ was quenched at 67°C. Quenched samples were measured by small-angle X-ray diffraction. Both of them gave sharp peaks at angles no higher than 3°. This

evidence indicated that they both exhibited smectic mesomorphous phase. Moreover, the angle of P₀ was under that of P₃. The cause for this may be that chiral nonmesogenic units slanted the molecular axis of mesogenic units of polymer P₃ compared with that of polymer P₀, which diminished the distance between layers. This explanation coincided with the Bragg equation, based upon which bigger angle of polymer P₃ should correspond to less distance between the layers. Considering the results of X-ray diffraction analysis, texture analysis, and DSC analysis together, we may conclude that polymers P₀–P₆ all exhibited smectic mesomorphism, and that polymers P₂–P₆ were chiral smectic liquid crystalline polymers.

CONCLUSION

A series of chiral side-chain liquid crystalline polymers containing chiral nonmesogenic side groups (undecylenic acid menthol ester, UM) and mesogenic side groups (p-(allyloxy)-benzoxy-p-chlorophenyl, ABCH)

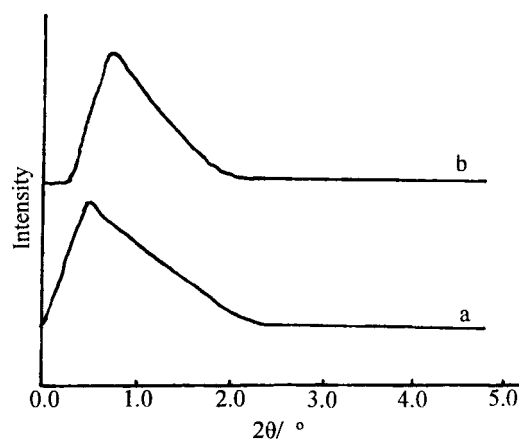


Figure 6 X-ray diffraction patterns of polymers P₀ and P₃ labeled a and b, respectively.

were prepared and characterized. Mesogenic textures and types of polymers did not change when the chiral nonmesogenic units were introduced. When the nonmesogenic units were no more than 30% (mole ratio) the polymers exhibited smectic mesomorphism with marble texture and sharp peak under 3° in X-ray diffraction patterns. Meanwhile, Polymers P₂–P₆ that respectively contained 10–30% (mole ratio) UM were chiral smectic liquid-crystalline polysiloxanes. The polymers P₀–P₇ obtained had a higher thermal stability with temperature of 5% mass loss above 300°C.

The authors are grateful to the National Natural Scientific Foundation Committee of China and the Ministry of Science and Technology of China, Liaoning Provincial Department of Science and Technology, and the Science Committee of Shenyang for their financial support of this work.

References

1. Vallerien, S. U.; Zentel, R.; Kremer, F.; Fischer, E. W. *Makromol Chem Rapid Commun* 1989, 10, 33.
2. Dumon, M.; Nguyen, H. T.; Mauzac, M.; Destrade, C.; Achard, M. F.; Gasparou, H. *Macromolecules* 1990, 23, 355.
3. Lewin, M.; Jaffe, M.; Wendorff, J. H.; Tsuchida, E., Eds. *Polymers for Advanced Technologies*; Wiley: New York, 1992.
4. Mihara, T.; Nomura, K.; Funaki, K.; Koide, N. *Polym J* 1997, 29, 309.
5. Hu, J. S.; Zhang, B. Y.; Feng, Z. L.; Wang, H. G.; Zhou, A. J. *J Appl Polym Sci* 2001, 80, 2335.
6. Hsu, C. S.; Lin, J. H.; Chou, L. R. *Macromolecules* 1992, 25, 7126.
7. Zhi, J. G.; Zhang, B. Y.; Wu, Y. Y.; Feng, Z. L. *J Appl Polym Sci* 2001, 81, 2210.
8. Hsiue, G. H.; Hsieh, P. J.; Wu, S. L.; Hsu, C. S. *Polym Bull* 1994, 33, 159.
9. Hsu, C. S.; Chu, P. H.; Chang, H. L.; Hsieh, T. H. *J Polym Sci Polym Chem* 1997, 35, 2793.
10. Chiang, Y.; Hong, L. D. *J Polym Sci Polym Chem* 2000, 38, 1609.
11. Subramaniam, G.; Gilpin, R. K. *Macromolecules* 1992, 23, 693.
12. Blumstein, A.; Vilasagar, S. *Mol Cryst Liq Cryst Lett* 1981, 1, 72.
13. Krigbaum, W. R. *Mol Cryst Liq Cryst Lett* 1981, 78, 79.
14. Mihara, T.; Nomura, K.; Funaki, K.; Koide, N. *Polym J* 1997, 29, 309.
15. Cer, F.; Griffin, A.; Johnson, J. F., Eds. *Liquid Crystals and Ordered Fluids*; Plenum: New York, 1984.
16. Zhang, B. Y.; Guo, S. M.; Shao, B. *J Appl Polym Sci* 1998, 68, 1555.
17. Yin, Y. Y.; Liu, Y. C. *Organic Chemical Molecular Spiral Theory*; Press of Chemical Industry: Beijing, 2000.