Journal of Polymer Research Vol. 7, No. 3, 167-173, September 2000

Synthesis and Characterization of Cholesteric Liquid Crystalline Copolysiloxanes Containing 4-Biphenyl 4-allyloxybenzoate and [S]-1-(2-Naphthyl)ethyl 6-[4-(10-undecen-1-yloxy) biphenyl-4'-carbonyloxy]-2-naphthoate Side Groups

Chih-Hung Lin and Chain-Shu Hsu*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan, R.O.C.

Received April 25, 2000; revised July 10, 2000; accepted July 31, 2000

Abstract: A series of side-chain liquid crystalline copolysiloxanes containing 4-biphenyl 4-allyloxybenzoate and [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yloxy) biphenyl-4'-carbonyloxy]-2-naphthoate side groups was synthesized and characterized. Differential scanning calorimetry and optical polarizing microscopy measurements reveal a cholesteric mesophase for all copolysiloxanes. The effect of the monomer feeding ratio on the mesomorphic temperature range of copolysiloxanes is discussed. These copolysiloxanes were used as stationary phases in gas chromatography capillary columns. They show very unique chiral separating properties for various racemic compounds.

Keywords: Polysiloxane, Liquid crystal, Cholesteric phase, Chiral resolution.

Introduction

Thermotropic side-chain liquid crystalline polysiloxanes were first synthesized by Finkelmann and Rehage [1]. Since then, nematic, smectic and cholesteric liquid crystalline polymers, and elastomeric liquid crystalline networks containing polysiloxane backbone [2-11] have been synthesized. Some of the synthetic works summarized above have been already reviewed [12-15]. Interest in the polysiloxane backbone for the preparation of side-chain liquid crystalline polymers (LCPs), comes from the low glass transition temperature and high thermostability exhibited by this class of polymers.

Recently, high temperature mesomorphic polysiloxane "solvents" have demonstrated excellent potential as stationary phases in gas chromatography (GC) because of their superior properties with regard to chromatographic efficiency and thermal stability [16-29]. Unlike conventional stationary phases that provide separation based on solute vapor pressure and/or different solubility arising from specific energetic interactions, liquid crystal stationary phase yield separation is based upon differences in solute molecular shape. Although the properties exhibited by many monomeric liquid crystals are good from the point of view of GC requirements, polymeric liquid crystals are attracting growing attention because they offer significant improvements in column efficiency as well as thermal stability over monomeric liquid crystals. Many of the side-chain LCP stationary phases tend to form nematic and smectic phases [17-29]. Only a few cholesteric polymeric liquid crystals have been found that exhibit good properties as GC stationary phases. Menster et al. reported on the LC copolysiloxanes containing cholesterol benzoate and biphenyl benzoate side groups [30]. Depending on the concentration of cholesterol

---

*To whom all correspondence should be addressed.
Tel: 886-3-5712121 ext 56523; Fax: 886-3-5710638
E-mail: cshsu@cc.nctu.edu.tw

J. Polym. Res. is covered in ISI (CD, D, MS, Q, RC, S), CA, EI, and Polymer Contents.

benzoate side groups, the copolysiloxanes are able to form nematic, cholesteric and smectic phases, respectively. The copolymer with a broad temperature range in the cholesteric phase was found to offer better performance as a stationary phase than those with nematic and smectic phases. In a previous publication from our laboratory [31], we reported a side-chain LC polysiloxane containing [S]-2-methyl-1-butyl 6-(4-undecanyloxybiphenyl-4'-carbonyloxy)-2-naphthoate side groups. This polysiloxane exhibits a very wide temperature range in the cholesteric phase and shows the excellent separation ability for some polyaromatic hydrocarbons. However, it exhibits no chiral resolution ability.

In this work, we introduce a large chiral end group, i.e., [S]-1-(2-naphthyl)ethanol, so as to increase the chiral resolution ability. A series of new cholesteric liquid crystalline copolysiloxanes containing 4-biphenyl 4-allyloxybenzoate and [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yloxy) biphenyl-4'-carbonyloxy]-2-naphthoate side groups were synthesized and characterized. The copolysiloxanes were used as GC stationary phases. Their chiral separation properties are also demonstrated.

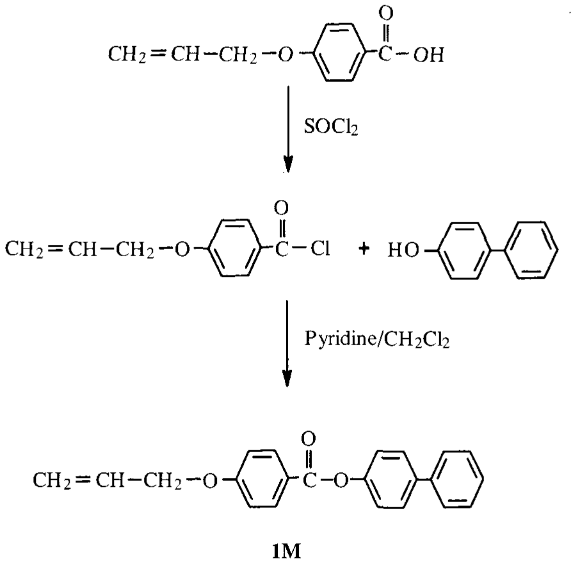
Experimental

1. Materials

Poly(methylhydrogensiloxane) ($\overline{Mn}$ = 2,270) and platinum divinyltetramethyl disiloxane catalyst were obtained from United Chemical Technologies Inc., and used as received. 4-Hydroxybiphenyl-4'-carboxylic acid, 4-hydroxybenzoic acid, (S)-1-(2-naphthyl)ethanol $[\alpha]_{D}^{20\,^{\circ}C} = -40^{\circ}$ (c = 5, C_2H_5OH) and the other reagents were obtained from Aldrich and used as received. The toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under nitrogen.

2. Techniques

^1H NMR spectra were recorded on a Varian VXR-300 or Bruker 300 MHz NMR 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 Ziess 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. The hydrosilylation reaction was traced by using a Nicolet 520 FTIR spectometer. Elemental analysis was performed with a Heraeus CHN-OS Rapid elemental. The specific rotations were measured in methylene chloride using a JASCO DIP-140 digital Polarimeter (Na 589 nm).



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

3. Synthesis of monomers 1M and 2M

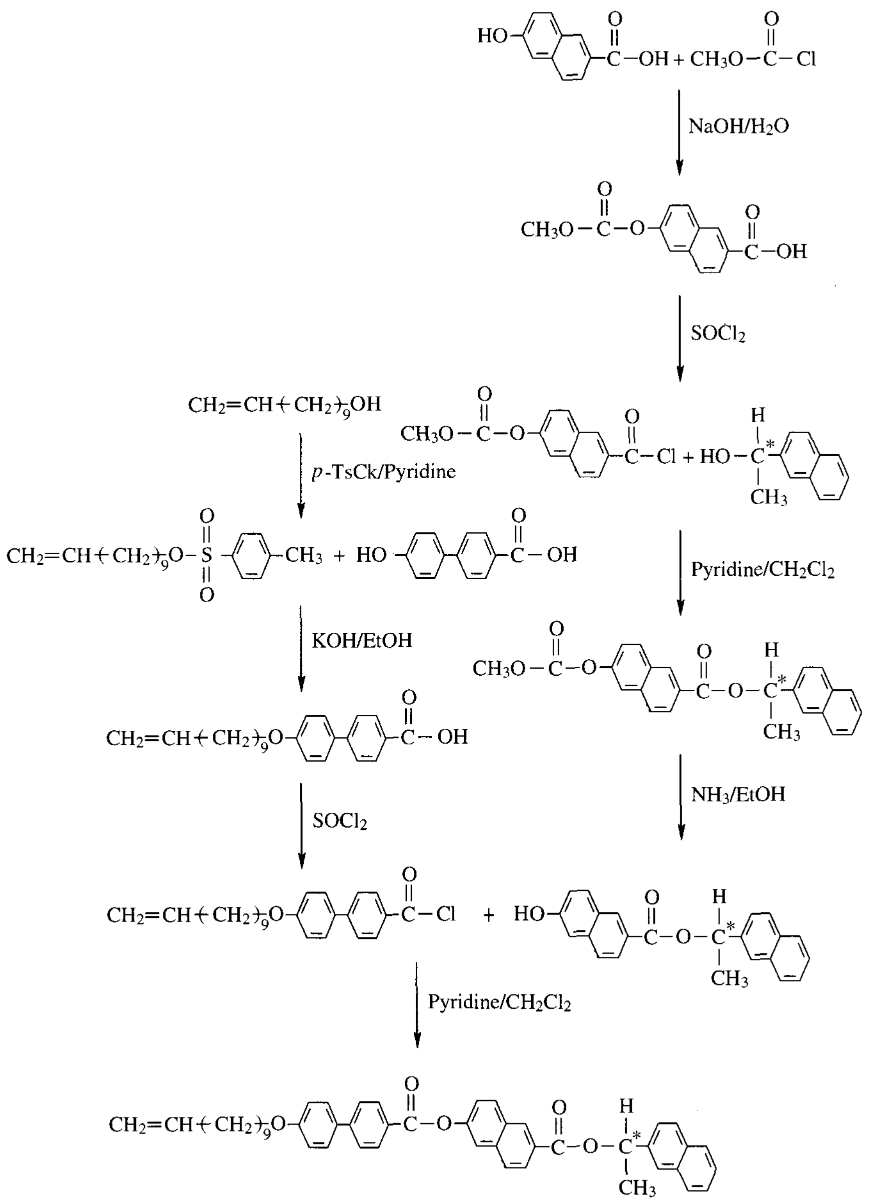
The synthesis of olefinic monomers **1M** and **2M** is outlined in Schemes 1 and 2. 4-Allyloxybenzoic acid and 4-(10-undecen-1-yloxy)biphenyl-4'-carboxylic acid were synthesized according to literature procedures reported by our laboratory [31].

3.1 4-Biphenyl 4-allyloxybenzoate (**1M**)

4-Allyloxybenzoic acid (3.56 g, 0.02 mol) was reacted at room temperature with excess thionyl chloride (10 mL) containing a few frops of diethyl formamide in methylene chloride (20 mL) for 2 h. The solvent and excess thionyl chloride were removed under reduced pressure to give the corresponding acid chloride. The acid chloride was further dissolved in 20 mL of methylene chloride and slowly added to a cold colution of 4-hydroxybiphenyl (3.4 g, 0.02 mol) and triethylamine (5.0 mL) in 100 ml of methylene chloride. The resulting solution was stirred at room temperature overnight. After the solvent was removed on a rotavapor, the crude product was recrystallized from a mixture of diethyl ether and acetone (1/1) to yield 3.21 g (46.8%) of white crystals. m.p. = 136.0 °C; ^1H NMR ($CDCl_3$, δ, ppm): 4.65 (t, 2H, $-O-C\underline{H}_2-$), 5.48 (m, 2H, $C\underline{H}_2=$), 6.07 (m, 1H, $=C\underline{H}-$), and 7.03~8.19 (m, 13 aromatic protons). Anal. Cal. For $C_{22}H_{18}O_3$; C: 80.00% and H: 5.45%; Found C: 79.87% and H: 5.44%.

3.2 6-Methoxycarbonloxy-2-naphthoic acid

To a 150 mL of Sodium hydroxide (5.8 g,



2M

Scheme 2. Synthesis of monomer **2M**.

0.145 mol) aqueous solution which was maintained at -10 °C, 6-hydroxy-2-naphthoic acid (9.4 g, 0.05 mol) was added with vigorous stirring. Methyl chloro-formate (7.7 g, 0.0815 mol) was then added slowly to the resulting supersion which was maintained at -5 °C. The resulting slurry was stirred for a further 4h and brought to pH 5 by the addition of a 1/1 mixture of conc. hydrochloric acid and water. The precipitate was filtered , washed with water and recrystallized from ethanol to yield 11.9 g (96.7%) of white crystal. m.p. = 215.1 °C; ^{1}H NMR (CDCl$_3$, δ, ppm): 3.96 (s, 3H, –O–C$\underline{H}_3$) and 7.24~8.69 (m, 6 aromatic protons).

3.3 [S]-1-(2-Naphthyl)ethyl 6-methoxycarbonyloxy-2-naphthoate

6-Methoxy carbonyloxynaphthoic acid (0.984 g, 0.004 mol) was reacted at room temperature with excess thionyl chloride (3 mL) for 1h in methylene chloride (10 mL) and then added a few drops of dimethyl formamide was added at 60 °C for 3 hr. The solvent and excess thionyl chloride were removed under reduced pressure to give the corresponding acid chloride. The product was further dissolced in 5 mL of THF and slowly added to a cold solution of [S]-1-(2-naphthyl) ethanol (0.688 g, 0.004 mol) and dry pyridine (3.2 mL) in 7 mL of

THF. The resulting solution was stirred at room temperature overnight. Then the solvent was removed on a rotavapor, and the crude product was purified by column chromatography (silica gel, methylene chloride as eluent) to yield 0.6 g (37.5%) of white crystal. $[\alpha]_D^{25\,^{\circ}C}$ = +170.4° (c = 0.01, CH_2Cl_2), m.p. = 100.3 °C; ^1H NMR ($CDCl_3$, δ, ppm): 1.82 (d, 3H, $-C^*-C\underline{H}_3$), 3.97 (s, 3H, $-O-C\underline{H}_3$), 6.37 (q, 1H, $-O-C^*\underline{H}-$) and 7.26~8.65 (m, 13 aromatic protons).

3.4 [S]-1-(2-Naphthyl)ethyl 6-hydroxy-2-naphthoate

[S]-1-(2-Naphthyl)ethyl 6-methoxycarbonyloxy-2-naphthoate (0.6 g, 0.0015 mol) was stirred in a mixture of ethanol (18 mL) and ammonia (10~15%, 9 mL) at room temperature for 1 h. The extent of the reaction was monitored by thin layer chromatography. After the reaction was complete (usually 30 min), the solution was concentrated by rotavapor. The residue was recrystallized from a mixture of acetonitrile and water (1/1) to yield 0.76 g (74.1%) of yellow crystal. $[\alpha]_D^{25\,^{\circ}C}$ = +196.9° (c = 0.01, CH_2Cl_2), m.p. = 166.0 °C; ^1H NMR ($CDCl_3$, δ, ppm): 1.81 (d, 3H, $-C^*-C\underline{H}_3$), 5.25 (s, 1H, $-O\underline{H}$), 6.36 (q, 1H, $-O-C^*\underline{H}-$) and 7.14~8.58 (m, 13 aromatic protons).

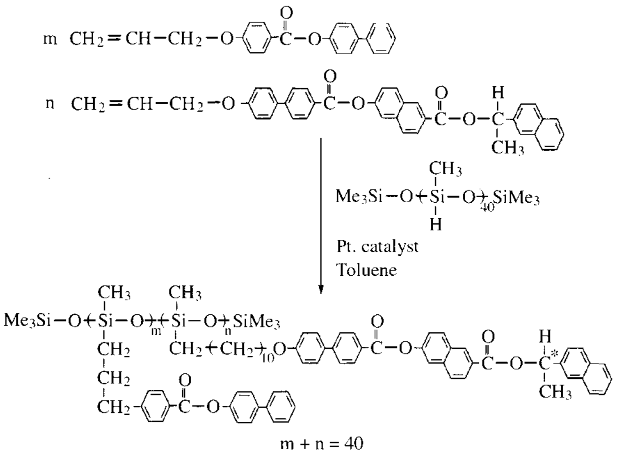
3.5 [S]-1-(2-Naphthyl)ethyl6-[4-(10-indecen-1-yloxy)biphenyl-4'-carbonyloxy]-2-na[hthoate **(2M)**

4-(10-Undecen-1-yloxy) biphenyl-4'-carboxylic acid (1.274 g, 0.0035 mol) was reacted with excess thionyl chloride (2 mL) to from acid chloride. The obtained acid chloride was esterified with [S]-1-(2-naphthyl)ethyl 6-hydroxy-2-naphthoate (0.992 g, 0.0029 mol) to form monomer **2M**. Details of the synthetic procedure are similar to the synthetic procedures of monomer **1M**. The crude product was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane=1/1 as eluent) to yield 0.94 g (47%) of white crystal. $[\alpha]_D^{25\,^{\circ}C}$ = +120.9° (c = 0.01, CH_2Cl_2), m.p. = 154.4 °C; ^1H NMR ($CDCl_3$, δ, ppm): 1.24~1.77 (m, 17H, $-CH_2-$ and $-CH_3$), 1.98 (m, 2H, $=CH-C\underline{H}_2-$), 3.95 (t, 2H, $-O-C-CH_2-C=$), 4.78~4.95 (m, 2H, $=C\underline{H}_2$), 6.32 (q, 1H, $-C^*H-$), and 6.93~8.62 (m, 21 aromatic protons). Anal. Cal. for $C_{47}H_{46}O_5$; C: 81.74%, H: 6.67%, and O: 11.59%; Found C: 81.70%, H: 6.65%, and O: 11.65%.

4. Synthesis of polysiloxanes 1P-4P

The synthesis of liquid crystalline polysiloxanes **1P-4P** is outlined in Scheme 3. A general synthetic procedure is described below.

An olefinic mixture (0.5 g, 10 mol% excess versus the Si-H groups present in polysiloxane) was dissolved in 50 mL dry, freshly distilled toluene together with the proper amount of poly(methylhydrogensiloxane). The reaction mixture was heated to 75 °C under nitrogen and 3~5 drops of platinum divinyltetramethyldisiloxane catalyst was then injected with a syringe. The reaction mixture was stirred at 75 °C for 2 hr. After this reaction time, the FT-IP analysis showed that the hydrosilation reaction was complete. The polymers were separated and purified by several reprecipitations from methylene chloride solution into methanol and then dried under vacuum.



Polymer	1 P	2 P	3 P	4 P
Monomer feeding ratio **1M/2M** (mol %)	100/0	90/10	80/20	70/30

Scheme 3. Synthesis of polymers **1P-4P**.

5. GC column fabrication and testing

A deactivated fused silica column, 30 m by 0.32 mm i.d. (from Restek) was washed with acetone, methylene chloride and water. It was dried at 280 °C under a nitrogen flow and then filled with a solution of 3.125 mg/mL polymer in chloroform, calculated so as to produce a film thickness of ca. 0.25 μm. One end was then sealed and the other end attached to a vacuum pump, and the entire column was placed in a water bath at 40 °C in order to hasten the evaporation of volatile solvent. The stationary phases were crosslinked with dicumyl peroxide. The columns was conditioned at 280 °C overnight under a nitrogen flow until a stable baseline was obtained at the maximum sensitivity of the instrument.

Results and Discussion

The synthetic routes used for the preparation

Table I. Thermal transitions and transition enthalpies for monomers **1M** and **2M**.

Monomers	Phase transitions (°C) heating(a)	Phase transitions (°C) cooling
1M	k 136.0 I	I 133.8 N 106.3 k
2M	k_1 48.8 k_2 154.4 I	I 135.4 k_2 30.0 k_1

(a) K, crystalline; N, nematic; I, isotropic.

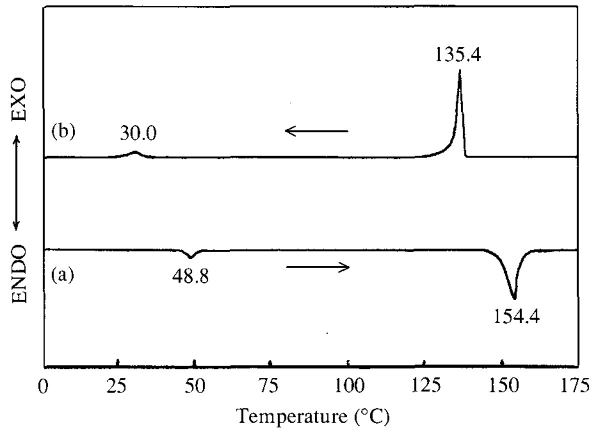


Figure 1. DSC thermograms of monomer **2M** : (a) heating scan and (b) cooling scan.

Table II. Thermal transitions and transition enthalpies for polymers **1P**~**4P**.

Polymer	Mononer feeding ratio **1M/2M** (mol %)	Phase transitions (°C) (corresponding enthalpy change, mJ/mg) heating(a)	Phase transitions (°C) (corresponding enthalpy change, mJ/mg) cooling
1 P	100/0	g 65.9 N 174.5 (2.46) I	I 169.0 (0.94) N
2 P	90/10	g 66.0 N^* 196.6 (0.54) I	I 185.8 (0.57) N^*
3 P	80/20	g 54.1 N^* 213.2 (1.19) I	I 209.4 (0.41) N^*
4 P	70/30	g 53.2 N^* 234.8 (1.55) I	I 225.4 (0.77) N^*

(a) g, glassy; N, nematic; N^*, cholesteric; I, isotropic.

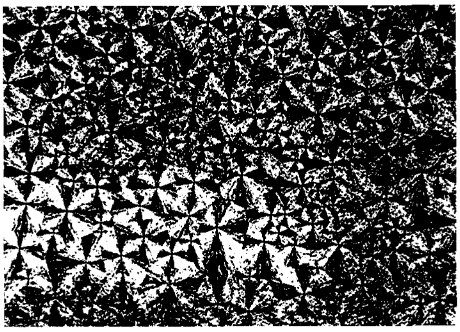


Figure 2. Optical micrograph of monomer **2M** (200×).

of 4-biphenyl 4-allyloxybenzoate (**1M**) and [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yloxy)biphenyl-4'-carbonyl oxy]-2-naphthoate (**2M**) are outlined in Schemes 1 and 2. The chiral group was inserted into monomer **2M** starting with the commercial available [S]-(-)-1-(2-naphthyl)ethanol. This was done by a sequence of reactions which avoided its recemerization. Table I summarizes the thermal transitions of both monomers **1M** and **2M**. Monomer **1M** exhibits a monotropic nematic phase while monomer **2M** displays only two crystalline transitions on both DSC heating and cooling scans. Figure 1 presents the DSC thermograms of monomer **2M**. When monomer **2M** was cooled from the isotropic phase to 135 °C, it formed a spherulite texture (see Figure 2). The spherulite texture was maintained when it was cooled to 25 °C. The result demonstrated that monomer **2M** formed two very ordered smectic phases which could be viewed as crystalline phases.

The synthesis of polymer **1P**~**4P** is described in Scheme 3. 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 methylene chloride solution into methanol and then dried under vacuum. Table II summarizes the thermal transitions and thermodynamic parameters of the obtained polymers **1P**-**4P**. Polymer **1P**, which contains only monomer **1M** as mesogenic side groups, reveals an enantiotropic nematic phase. As can be seen from Table I, monomer **1M** presents only a monotropic nematic phase and exhibits a much narrower temperature range of the nematic phase than polymer **1P**. It is well documented that in many cases the mesophase formed by a side-chain liquid crystalline polymer is more organized than the one exhibited by the corresponding monomer. This is the so-called polymer effect. Figure 3 presents the nematic schelieren texture exhibited by polymer **1P**. Polymers **2P**~**4P** which contain both monomers **1M** and **2M** as mesogenic side groups, display respectively an enantiotropic cholesteric phase. Figure 4 shows the representative finger printed cholesteric texture exhibited by polymer **2P**. On going from **2P** to **4P**, the monomer **2M** content increases from 10 to 30 mol%. All three polymers reveal very wide

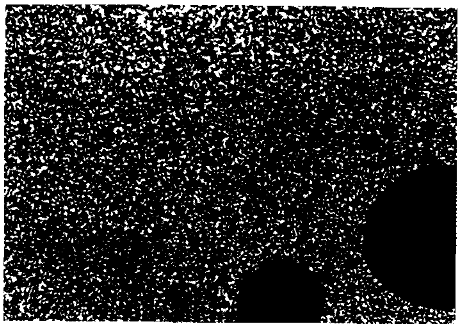


Figure 3. Typical optical micrograph of polymer **1P**: Nematic texture (200×).

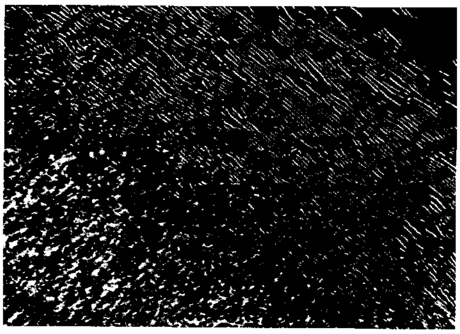


Figure 4. Typical optical micrograph of polymer **2P**: Cholesteric texture (200×).

temperature ranges of the cholesteric phase. As the monomer **2M** content increases, the glass transition temperature of the polymer decreases and the isotropization temperature increases. Polymer **4P**, which contains the highest mole percent of monomer **2M** in its mesogenic side groups, presents the widest cholesteric temperature range. Therefore, polymer **4P** was chosen as the stationary phase used in the gas chromatography capillary column. The separation of three kinds of enantiomers, i.e., α-pallandrene, limonene and menthol, on a capillary column which was coated with polymer **4P** are illustrated in Figures 5-7. As can be seen from these figures, three kinds of enantiomers can be easily separated by this cholesteric stationary phase. Their separation factors are 1.171, 2.044 and 1.158 for the α-pallandrene, limonene and menthol respectively. As far as we know, this is the first study to demonstrate that cholesteric liquid crystalline polymer has a chiral resolution ability.

In conclusion, a series of new cholesteric liquid crystalline polysiloxanes containing 4-biphenyl 4-allyloxybenzoate and [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yloxy) biphenyl-4'-carbonyloxy]-2-naphthoate side groups was synthesized and characterized. All of the obtained copolysiloxanes

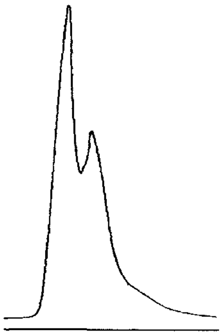


Figure 5. Separation of α-pallandrene by a polymer **4P** capillary column.

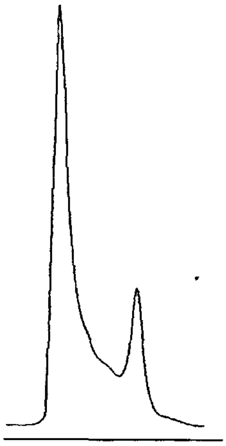


Figure 6. Separation of limonene by a polymer **4P** capillary column.

Figure 7. Separation of menthol by a polymer **4P** capillary column.

reveal a very wide temperature range in the cholesteric phase. The copolysiloxane containing the highest mol percent of [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yloxy) biphenyl-4'-carbonyloxy]-2-naphthoate side group shows the widest temperature range in the cholesteric phase. This copolysiloxane presents an excellent chiral resolution ability when it is used as a GC stationary phase of a capillary column.

Acknowledgement

The support of this work by the National Science Council of the Republic of China is gratefully acknowledged.(NSC 88-2216-E-255-001)

References

1. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 31 (1980).
2. H. Ringsdorf and A. Schneller, *Br. Polym. J.*, **13**, 43 (1981).
3. H. Ringsdorf and A. Schneller, *Makromol. Chem., Rapid Commun.*, **3**, 557 (1982).
4. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 733 (1980).
5. H. Stevens, G. Rehage and H. Finkelmann, *Macromolecules*, **17**, 851 (1984).
6. P. A. Gemmell, G. W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **122**, 205 (1985).
7. G. W. Gray, D. Lacey, G. Nestor and M. S. White, *Makromol. Chem., Rapid Commun.*, **7**, 71 (1986).
8. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **3**, 859 (1980).
9. H. Finkelmann, H. J. Kock and G. Rehage, *Makromol. Chem., Rapid Commun.*, **2**, 317 (1981).
10. H. Finkelmann, H. J. Kock, W. Gleim and G. Rehage, *Makromol. Chem., Rapid Commun.*, **5**, 287 (1984).
11. H. J. Kock, H. Finkelmann,W. Glein and G. Rehage, *Polymeric Liquid Crystals*, A. Blumstein, Ed., Plenum, New York, 1985, p 275.
12. H. Finkelmann and G. *Rehage, Adv. Polym. Sci.*, **60/61**, 99 (1984).
13. V. P. Shibaev and N. A. Plate, *Adv Polym. Sci.*, **60/61**, 173 (1984).
14. H. Finkelmann, *Phil. Trans. R. Soc., London, Ser. A*, **309**, 105 (1983).
15. G. W. Gray, *Side Chain Liquid Crystal Polymers*, C. B. McArdle Ed., Blackie, Glasgow and London, 1988, p 106.
16. R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao and R. N. Castle, *Anal. Chem.*, **54**, 1802 (1982).
17. B. A. Jones, J. S. Bradshaw, M. Nishioka and M. L. Lee, *J. Org. Chem.*, **49**, 494 (1984).
18. G. M. Janini, R. J. Laub and T. J. Shaw, *Makromol. Chem., Rapid Commun.*, **6**, 57 (1985).
19. M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laub, B. H. Luhmann, A. Price, W. L. Roberts, T. J. Shaw and C. A. Smith, *Anal. Chem.*, **57**, 651 (1985).
20. K. E. Markides, H. C. Chang, C. M. Schregenberger, B. J. Tarbet, J. S. Bradshaw and M. L. Lee, *J. High Result. Chromatogr. Chromatogr. Commun.*, **8**, 516 (1985).
21. K. E. Markides, M. Nishioka, B. J. Tarbet, J. S. Bradshaw and M. L. Lee, *Anal. Chem.*, **57**, 1296 (1985).
22. M. Nishioka, B. A. Jones, B. J. Tarbet, J. S. Bradshaw and M. L. Lee, *J. Chromatogr.*, **357**, 79 (1986).
23. K. P. Naikwadi, A. J. Jadhav, S. Rokushika and H. *Hatano, Makromol. Chem.*, **187**, 1407 (1986).
24. A. L. Jadhav, K. P. Naikwadi, S. Rokushika, H. Hatano, and M. Oshima, J. High Resolut. *Chromatogr. Chromatogr. Commun.*, **10**, 17 (1987).
25. K. P. Naikwadi, A. M. McGovern and F. W. Karasek, *Can. J. Chem.*, **65**, 970 (1987).
26. M. Swerev and K. Ballschmiter, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **10**, 544 (1987).
27. U. Riehle, J. Ehmann, M. Swerev and K. Ballschmiter and Z. Fresenius, *Anal. Chem.*, **331**, 821 (1988).
28. G. M. Janini, G. M. Muschik, H. R. Issaq and R. B. Laub, *Anal. Chem.*, **60**, 1119 (1988).
29. G. M. Janini, G. M. Muschik and S. D. Fox, *Chromatographia*, **27**, 436 (1989).
30. M. K. Menster, D. D. Bombick, D. B. Flora, T. J. Bunning, H. E. Klei and R. L. Crane, *Polym. Prepr.* **33**., 1150 (1992).
31. J. L. Lin and C. S. Hsu, *Polym. J.*, **25**, 153 (1993).
32. C. S. Hsu and L. J. Shih, *J. Polym. Res.*, **3**, 185 (1996).