Polymer Journal, Vol. 25, No. 2, pp 153—167 (1993)

Synthesis of High Temperature Mesomorphic Polysiloxanes and Their Use as Stationary Phases for High Resolution Gas Chromatography

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(Received August 5, 1992)

ABSTRACT: Two new liquid crystalline polysiloxanes with very wide mesomorphic temperature range have been prepared. One containing 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-hexanyloxybiphenyl-4′-carboxylate side groups displays enantiotropic smectic A, chiral smectic C and smectic B phases. The other containing (*S*)-2-methyl-1-butyl 6-(4-undecanyloxybiphenyl-4′-carbonyloxy)-2-naphthalenecarboxylate side groups exhibits only an enantiotropic cholesteric phase. Both mesomorphic polysiloxanes were used as stationary phases in gas chromatography capillary columns. They show very unique separating properties for various isomeric halogenated naphthalene compounds, methylanthracene compounds, fatty acid methyl esters and polycyclic aromatic compounds.

KEY WORDS Liquid Crystalline Polymers / Mesomorphic Polysiloxanes / Gas Chromatography / Liquid Crystal Stationary Phases /

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 has 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] The use of liquid crystals as stationary phase in GC was first reported by Kelker in 1963.[30,31] This field has been extensively reviewed.[32-34] 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 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.

In this work, the synthesis of a new chiral smectic and a new cholesteric liquid crystalline polysiloxanes which can be used as GC stationary phase over a wide temperature

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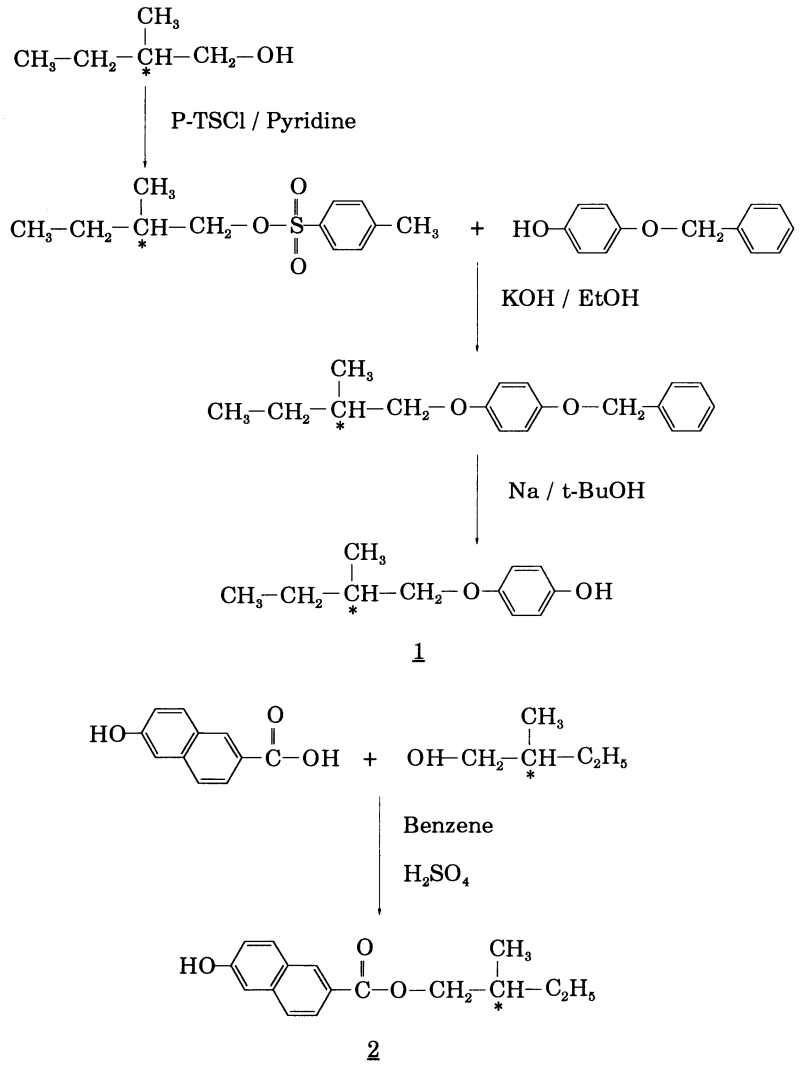

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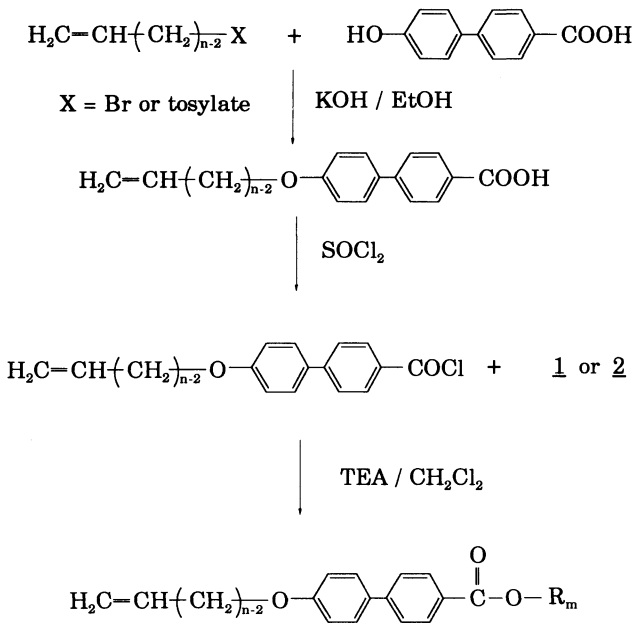
range is presented. The particular examples refer to side chain liquid crystalline polysiloxanes containing either 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-hexanyloxybiphenyl-4′-carboxylate or (*S*)-2-methyl-1-butyl 6-(4-undecanyloxybiphenyl-4′-carbonyloxy)-2-naphthalenecarboxylate side groups. Their selectivity for isomeric halogenated naphthalenes, methylanthracenes, fatty acid methyl esters and polycyclic aromatic compounds, is also demonstrated.

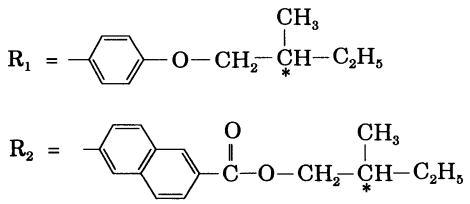
RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers IP and IIP

The synthetic route used for the preparation of 4-[(*S*)-2-methyl-1-butoxy]phenyl 4-(5-hexen-1-yloxy)biphenyl]-4′-carboxylate (IM) and (*S*)-2-methyl-1-butyl 6-[4-(-undecen-1-yloxy)biphenylcarbonyloxy]-2-naphthalenecarboxylate (IIM) is outlined in Scheme 1. The chiral group was inserted into these mesogenic compounds starting with the commer-



m = 1, 2 ; n = 6, 11

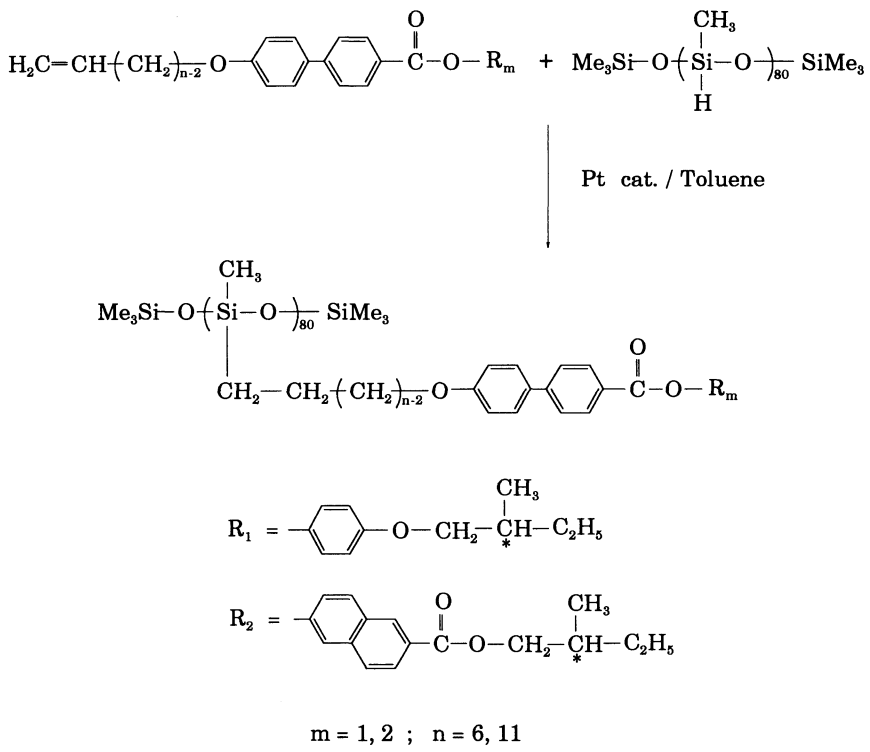


(IM : m = 1, n = 6 ; IIM : m = 2, n = 11)

Scheme 1. Synthesis of monomers IM and IIM.

cial available (−)-2-(*S*)-methyl-1-butanol. This was done by a sequence of reactions which avoided its recemerization. Scheme 2 describes the synthesis of both side-chain liquid crystalline polysiloxanes which contain respectively 4-[(*S*)-2-methyl-1-butoxy]phenyl-4-hexanyloxybiphenyl-4′-carboxylate (IP) and (*S*)-2-methyl-1-butyl 6-(4-undecanyloxybiphenyl-4′-carbonyloxy)-2-naphthalenecarboxylate (IIP) in their side groups. Excess amount of olefinic monomers was usual used to carry the hydrosilation reaction to completion. The unreacted monomers were removed by several reprecipitations from tetrahydrofuran (THF) solution into methanol and by preparative GPC. Therefore the polymers were isolated with high purity.

Table I records the phase transitions and phase transition enthalpies of monomers IM and IIM and polymers IP and IIP. Monomer



(IP : m = 1, n = 6 ; IIP : m = 2, n = 11)

Scheme 2. Synthesis of polymers IP and IIP.

Table I. Phase transitions and phase transition enthalpies of monomers IM and IIM and Polymers IP and IIP

Monomer	n[a]	Phase transition, °C (Corresponding enthalpy change, kcal mol or kcal per mru[b]) Heating / Cooling
IM	6	K 116 (5.25) S_A 193 (1.26) I / I 187 (1.48) S_A 109 (0.71) S_B 86.6 (0.66) K
IIM	11	K 77 (8.06) N* 222 (1.65) I / I219 (1.57) N* 55 (6.83) K
IP	6	G 16 S_B 120 (1.73) S_C* 166 (−)[c] S_A 244 (1.24) I / I 236 (0.98) S_A 164 (−)[c] 109 (1.47) S_B 10 G
IIP	11	G 12 N* 319 (1.02) I / I 306 (0.57) N* −22 G

[a] n according to Schemes 1 and 2.
[b] K = crystalline; N* = cholesteric; S = smectic; G = glassy; I = isotropic; mru = mole repeating unit.
[c] Enthalpy is very small.

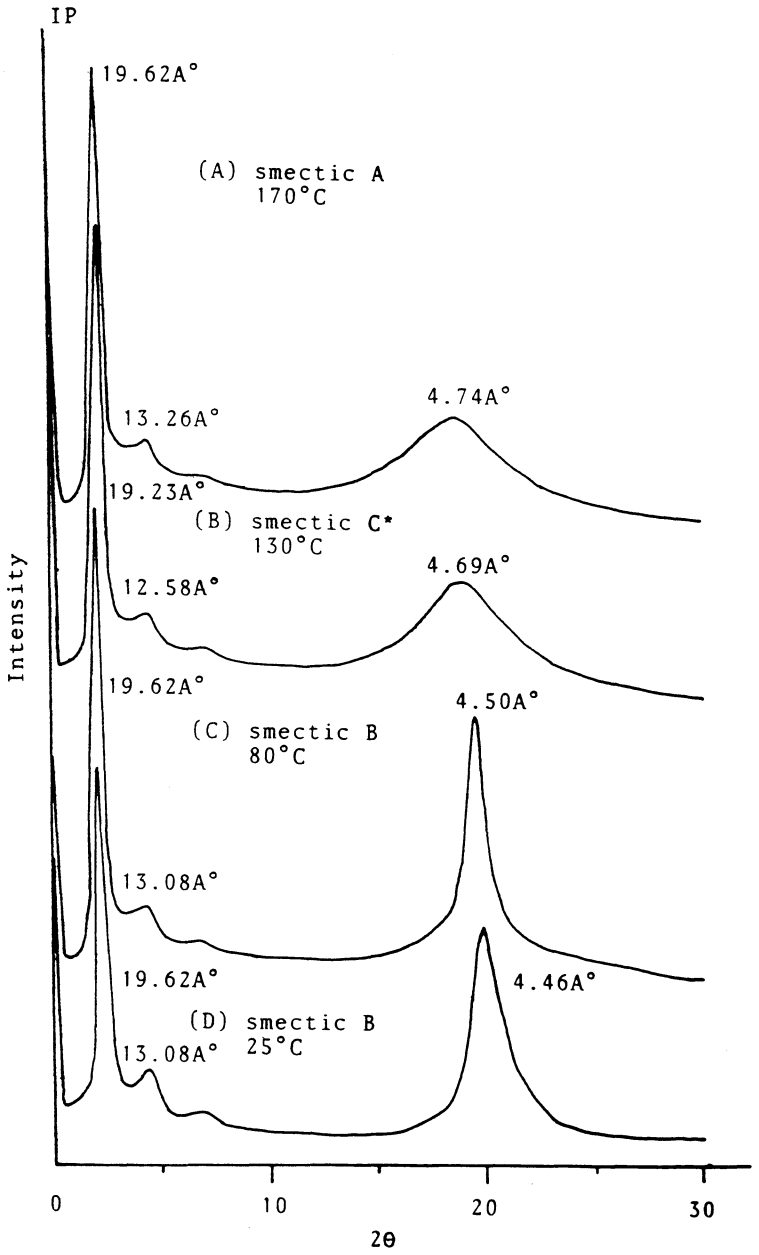
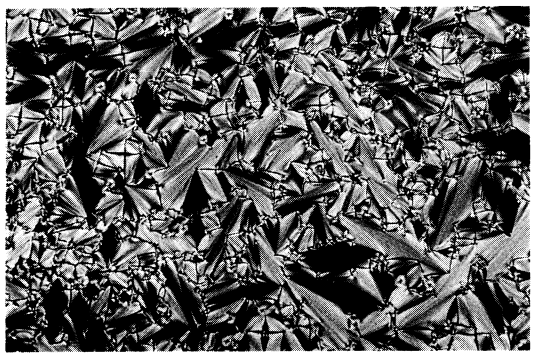


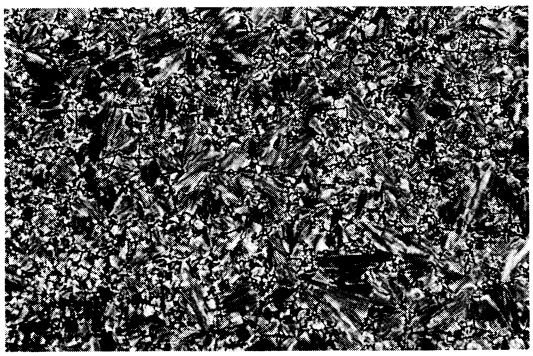
Figure 1. Temperature-dependent X-ray diffraction diagrams obtained from powder sample of IP at 170, 130, 80, and 25°C.

IM presents an enantiotropic S_A phase and a monotropic S_B phase while monomer IIM shows only an enantiotropic cholesteric phase. Polymer IP presents a glass transition at 16°C, a S_B to S_C* phase transition at 120°C, a S_C* to S_A phase transition at 166°C and a S_A to isotropic phase transition at 244°C on DSC heating scan. Upon cooling scan, the phase transitions look identical to those of heating scan except that a few degrees' supercooling is



(A)

(B)



(C)

Figure 2. Optical polarizing micrographs displayed by IP: (A) S_A testure obtained after cooling to 198.2°C; (B) S_C* texture obtained after cooling to 161.8°C; (C) S_B texture obtained after cooling to 98.0°C.

observed for each of the transitions. Polymer IIP show a glass transition at 12°C and a cholesteric to isotropic phase transition at

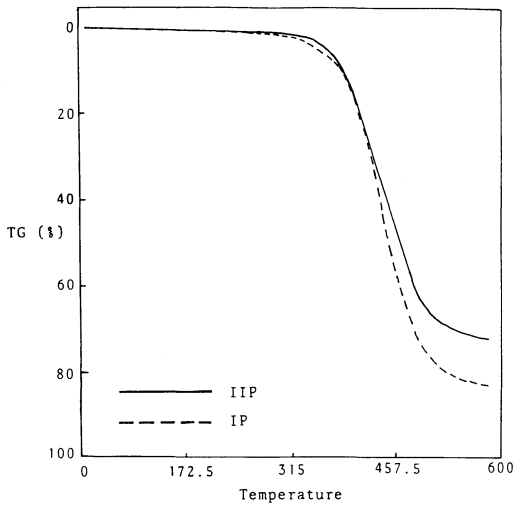


Figure 3. TGA thermograms of polymers IP and IIP.

319°C on DSC heating scan. Upon cooling scan, the isotropic to cholesteric phase transition presents at 306°C. The mesophase identifications have been achieved by optical polarizing microscopic observations and X-ray diffraction measurements. Figure 1 reveals the X-ray diffraction diagrams obtained from powder sample of IP at 170, 130, 80, and 25°C. A broad reflection at wide angle (associated with the lateral packing) and a sharp reflection at low angle (associated with the smectic layers) are respectively shown by all the curves. The d spacings of first-order reflections show respectively a value of 19.62 Å at 170°C, 19.23 Å at 130°C, and 19.62 Å at 80°C and 25°C. The results which are in agreement with the optical microscopic observations, indicate the formation of S_A, S_C*, and S_B phases. Figure 2 shows the representative S_A, S_C*, and S_B textures displayed by polymer IP. Figure 3 shows the TGA thermograms of polymers IP and IIP. Their thermal decomposition temperatures are higher than 370°C. Both polymers show very wide temperature range of mesophases and high thermal stability. Polymer IP presents three chiral smectic phases in the temperature range of about 220 degrees while polymer IIP presents a cholesteric phase

in the temperature range of about 300 degrees. Since both polymers have very different mesomorphic properties, it would be very interesting to compare their chromatographic properties.

Practical Applications of Polymers IP and IIP as GC Stationary Phases

The capillary columns which were coated with polymer IP or IIP are respectively named as LC-1 and LC-2. LC-1 column containing IP yields about 2100 plates/m while LC-2 column containing IIP yields about 2340 plates/m (triphenylene, 230°C). Both columns were found in this work to provide statisfactory column efficiency (see chromatograms presented below).

The separations of two pairs of halogenated naphthalene isomers on SE-54, LC-1, and LC-2 columns are illustrated in Figures 4A—4C. Table II summarizes the capacity factor, relative retention time data and length-to-breath ratios (L/B)[35-37] for the isomers on SE-54, LC-1, and LC-2 columns. Both LC-1 and LC-2 columns show much better selectivity for two pairs of halogenated naphthalene isomers than SE-54 column. As can be seen from Table II, the more rod-like 2-chloro and 2-bromonaphthanes which have higher L/B ratios were retained longer than the other isomers in both liquid crystalline polymer stationary phases. Figures 5A—5C show

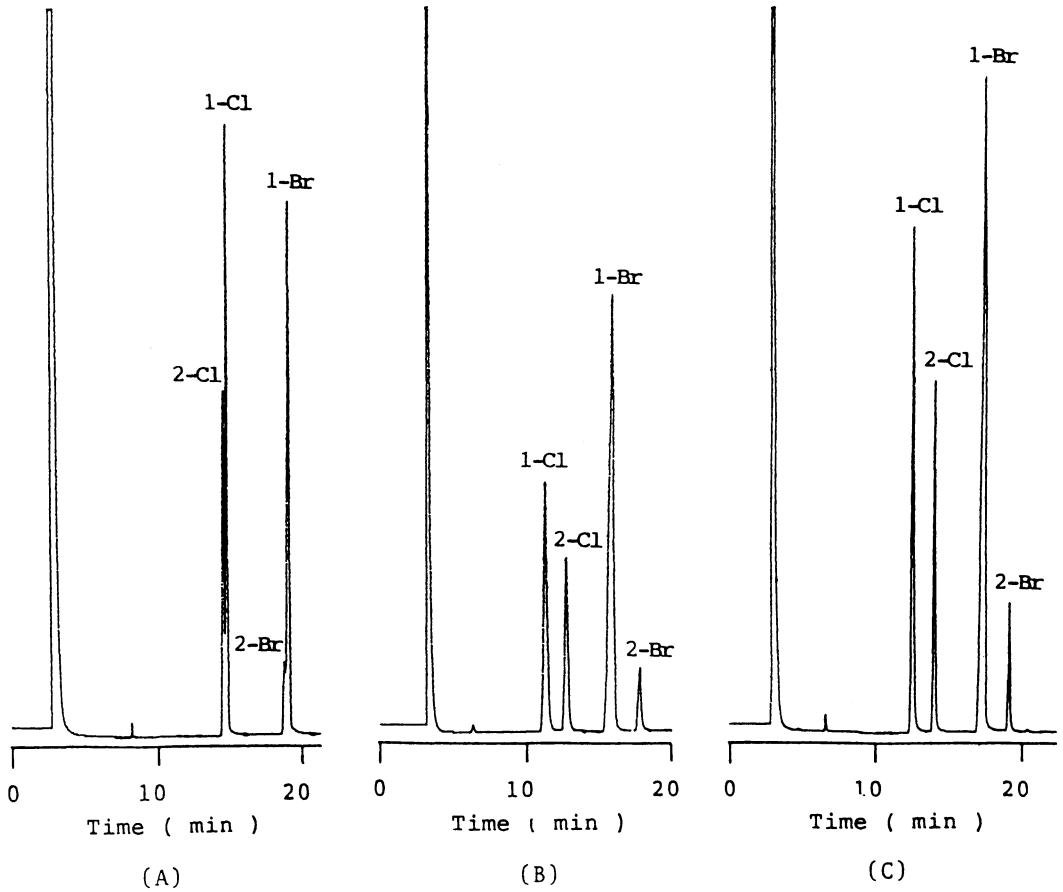


Figure 4. Chromatograms of 1- and 2-chloronaphthalenes and 1- and 2-bromonaphthalenes on (A) SE-54, (B) LC-1, and (C) LC-2. Temperature was programmed from 130°C to 200°C at 2°C min^{-1}.

Table II. Capacity factor and relative retention time and calculated length-to-breadth data for halogenated naphthalene compounds on SE-54, LC-1, and LC-2 columns

Compound	Boiling point	L[a]/B	Capacity factors (k')			Relative retention time (α)[b]		
			SE-54	LC-1	LC-2	SE-54	LC-1	LC-2
1-Chloronaphthalene	259°C	1.16	9.01	6.59	7.47	1.02	0.87	0.89
2-Chloronaphthalene	261°C	1.40	8.83	7.55	8.44	1.00	1.00	1.00
1-Bromonaphthalene	279—281°C	1.17	11.92	9.65	10.80	1.02	0.89	0.91
2-Bromonaphthalene	281—283°C	1.40	11.65	10.89	11.93	1.00	1.00	1.00

[a] L/B, length/breadth (see ref 35—37).
[b] Retention time relatives to 2-chloronaphthalene or 2-bromonaphthalene $\alpha = k'_2/k'_1$.

Table III. Capacity factor and relative tetention time and calculated length to breadth data for 1-, 2-, and 9-methylanthracenes on SE-54, LC-1, and LC-2 columns

Compound	bp or mp	L[a]/B	Capacity factor (k')			Relative retention time (α)[b]		
			SE-54	LC-1	LC-2	SE-54	LC-1	LC-2
1-Methylanthracene	bp 363°C	1.41	9.79	11.07	11.32	1.03	0.84	0.89
2-Methylanthracene	mp 204—206°	1.74	9.49	13.17	12.78	1.00	1.00	1.00
9-Methylanthracene	bp 196—197°C/12 mm	1.38	10.60	12.38	12.55	1.12	0.94	0.98

[a] L/B: length/breadth (see ref 35—37).
[b] Retention time relatives to 2-methylanthracene, $\alpha = k'_2/k'_1$.

chromatograms of three methylanthracene isomers separated by SE-54, LC-1, and LC-2 columns. The GC retention data and the L/B ratios for these isomers are summarized in Table III. All three isomers exhibit longer retention time with LC-1 and LC-2 columns than with SE-54 column. This could be due to the fairly large L/B values exhibited by the isomers. Among three isomers, 2-methylanthracene presents a longest retention time on LC-1 and LC-2 columns due to its largest L/B value. However, it shows shortest retention time on SE-54 column due to its highest boiling point. Comparing the retention time of 1-methylanthracene and 9-methylanthracene, 9-methylanthracene has a higher value on all three columns although the L/B value of 9-methylanthracene is smaller than that of 1-methylanthracene. The reason could be due to much lower boiling point of 1-methylanthracene. Among three columns, LC-1 demonstrates the best selectivity for these isomers. Upon comparison of the data reported in both Tables II and III, it can be concluded that the order of elution of these isomers on liquid crystalline stationary phase in this study strictly adheres to their L/B ratios. The isomer with higher L/B value retains longer in the liquid crystalline stationary phase.

The separations of some fatty acid methyl esters on LC-1 and LC-2 columns are presented in Figures 6B and 6C. The order of elution is remarkable when compare with that generally observed with OV-210 column (see Figure 6A). First, the *cis* and *trans* isomers are better resolved on both LC-1 and LC-2 columns. Second, the *trans* isomers are retained longer than the corresponding *cis* isomers of the same carbon number, which is the reverse of that observed with OV-210 column. Furthermore, the compounds are eluted in order of increasing carbon number and for each group of compounds having the same carbon number, the elution time increases with increasing

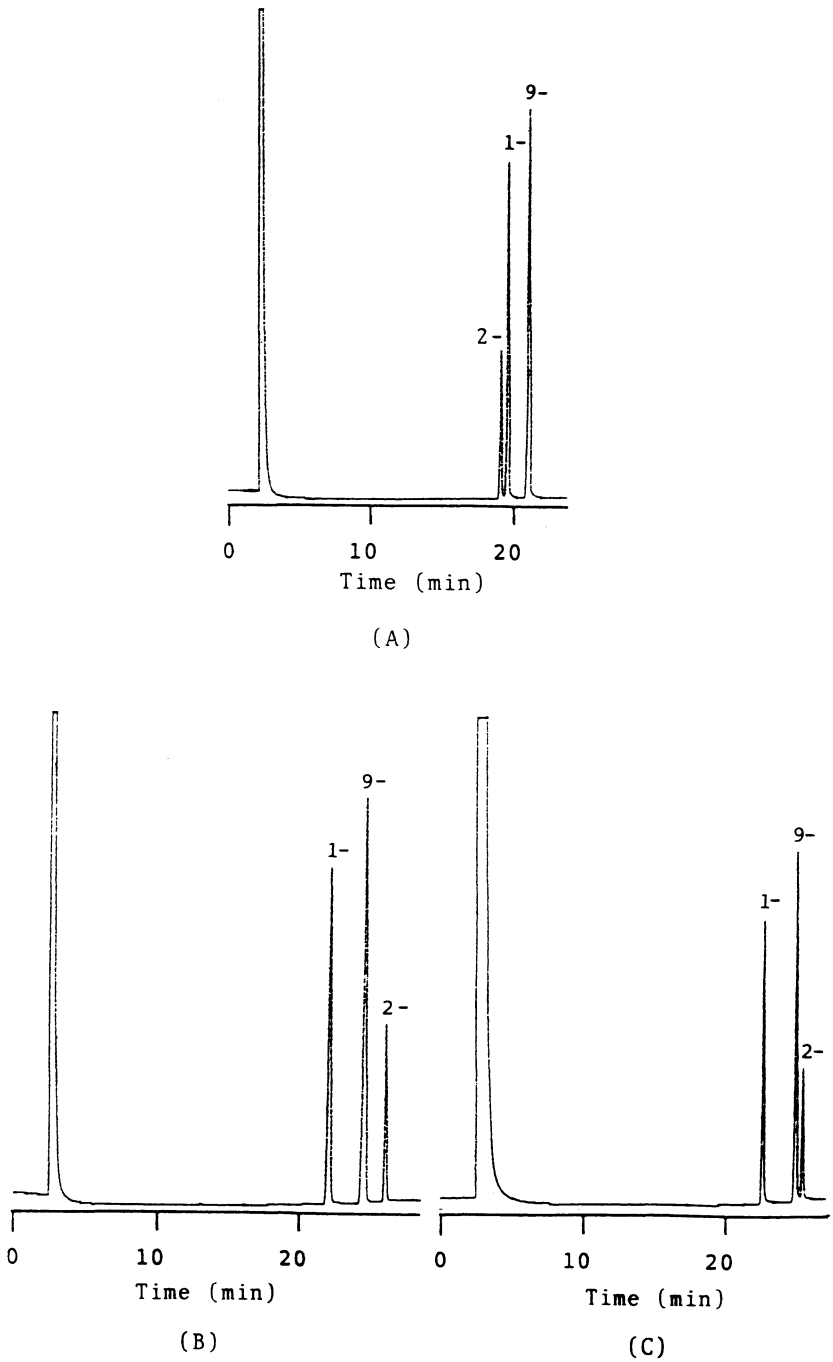


Figure 5. Chromatograms of 1-, 2-, and 9-methylanthracenes on (A) SE-54, (B) LC-1, and (C) LC-2. Temperature was programmed from 150°C to 210°C at 2°C min^{-1} for (A) and from 150°C to 240°C at 3°C min^{-1} for (B) and (C).

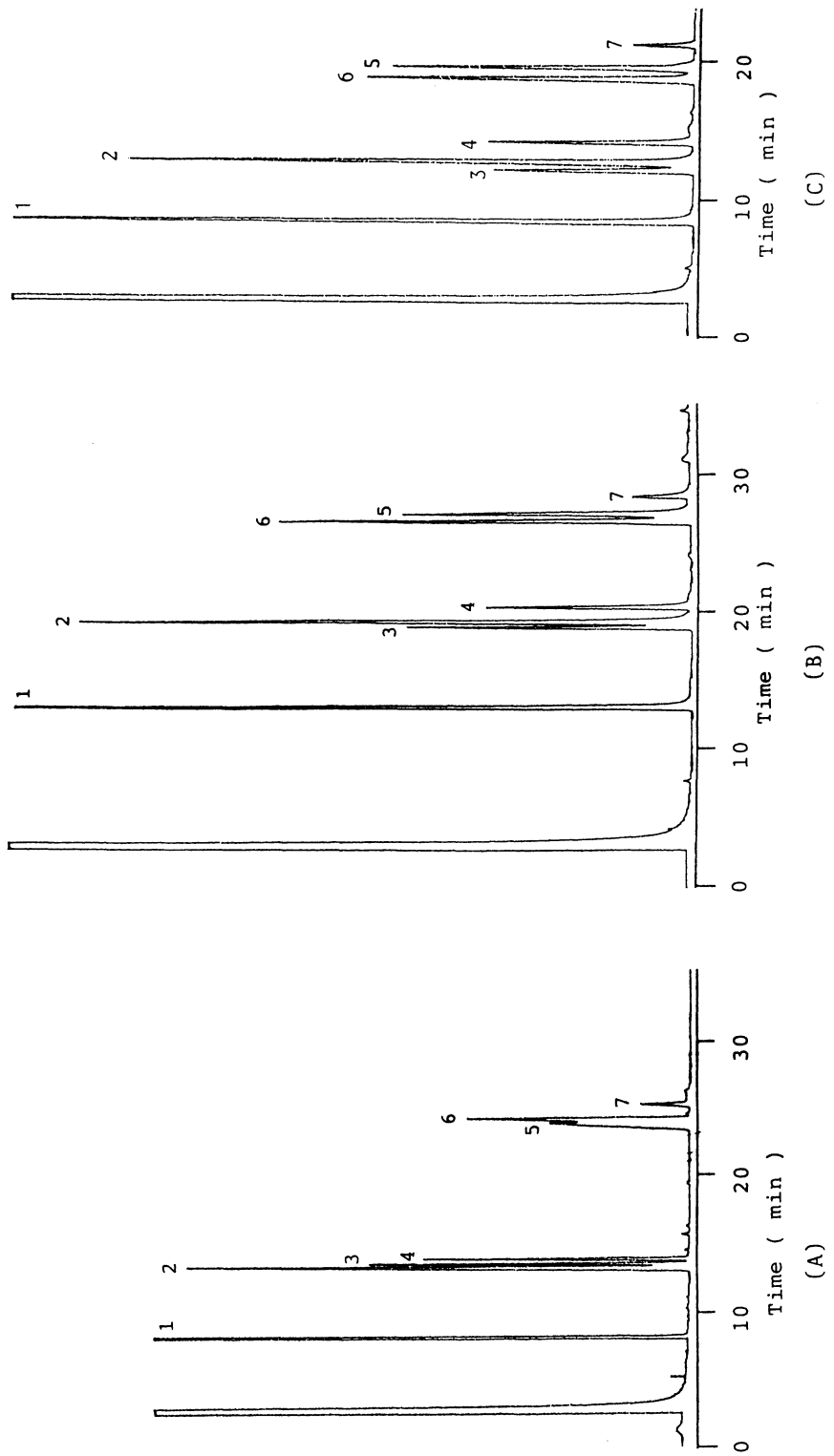


Figure 6. Chromatograms of fatty methyl esters on (A) OV-210; column temperature, 160°C; isothermal, (B) LC-1; (C) LC-2. Temperature was programmed from 130°C to 200°C at 2°C min^{-1} for (B) and (C). 1, myristic; 2,palmitelaidic; 3, palmitoleic; 4, palmitic; 5, elaidic; 6, oleic; 7, steric.

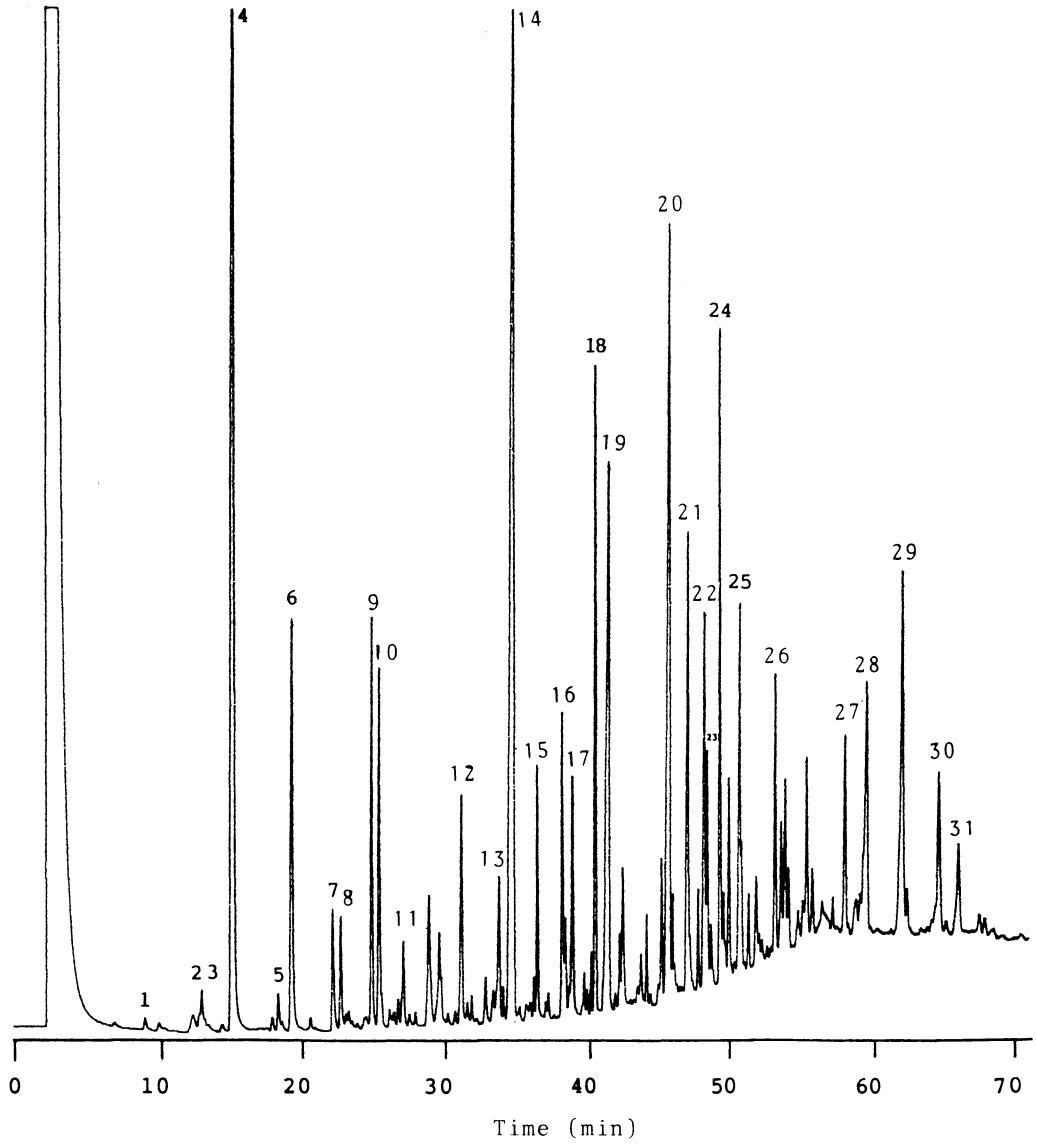


Figure 7. Chromatograms of 31 kinds of PAH compounds on LC-2. Temperature was programmed from 110°C to 280°C at 3.5°C min^{-1}.

saturation.

Programed-temperature separation of two-, three-, four-, and five ring polycyclic aromatic hydrocarbons (PAHs) with LC-2 column is presented in Figure 7. More than 31 kinds of PAH compounds which are summarized in Table IV, have been eluted. The elution pattern of these solutes with mesomorphic polysiloxane is consistent with the degree of their rodlike geometry, the more redlike being retained longer. For example, phenanthrene (L/B = 1.46) elutes earlier than anthracene (L/B = 1.56) benz[*a*]anthracene (L/B = 1.58) elutes earlier than chrysene (L/B = 1.72). Among *o*-, *m*-, and *p*-terphenyls, *o*-terphenyl (L/B = 1.10) elutes first, followed by *m*-terphenyl (L/B = 1.47) and

Table IV. Peak assignments for PAH compounds and their identification methods[a]

Peak No.	Compound	mol wt	Identification method[b]
1	Naphthalene	128	a, b
2	2-Methylnaphthalene	142	a, b
3	1-Methylnaphthalene	142	a, b
4	Biphenyl	154	a, b
5	Biphenylene	152	a, c
6	Acenaphthylene	152	a, b
7	Dibenzofuran	168	a
8	9-Methylene-9*H*-fluorene or 1,1′-(1,2-ethynediyl)-bis benzene or 2,3-diphenyl-2-cyclopropen-1-one	178	a
9	the same as 8	178	a
10	Fluorene	166	a, b
11	*o*-Terphenyl	230	a, c
12	1-Phenylnaphthalene	204	a, b
13	the same as 8	178	a
14	Phenanthrene	178	a, b
15	Anthracene	178	a, b
16	4*H*-Cyclopenta[def]-phenanthrene	190	a
17	1-Methylanthracene	192	a
18	2-Phenylnaphthalene	204	a, b
19	*m*-Terphenyl	230	a, c
20	Fluoranthene	202	a, b
21	Acephenanthrylene	202	a, b
22	Pyrene	202	a, b
23	Benzo[*c*]phenanthrene	228	a
24	*p*-Terphenyl	230	a, c
25	11*H*-Benzo[*a*]fluorene or 11*H*-Benzo[*b*]fluorene	216	a
26	1,2′-Binaphthalene or 1,1′-binaphthalene or 9-(phenylmethylene)-9*H*-fluorene	254	a
27	Benzo[ghi]fluoranthene	226	a, c
28	Triphenylene or Naphthacene	228	a
29	Benzo[*a*]anthracene	228	a, b
30	Chrysene 448°	228	a, b
31	1,2′-Binaphthalene or 1,1′-binaphthalene or 2,2′-binaphthalene	254	a

[a] Reference 43.

[b] a, identified by sample mass spectra; b, identified by retention index and standard injected into GC; c, identified by retention index published in ref 57, 58, and 59.

then *p*-terphenyl (L/B = 2.34).

In conclusion, the side-chain liquid crystalline polysiloxanes with wide temperature range of chiral smectic or cholesteric phases have been proven to be useful in separating many classes of compounds. The obtained polymers show very high thermal stability. Because the separation is based on molecular shape, isomers that have very similar intrinsic properties can be separated by these kinds of mesomorphic polymer stationary phases. Both prepared columns show very high column efficiency for all four separation systems. The results may be due to the twisted packing structure of chiral smectic or cholesteric mesophase exhibited by the stationary phases. However, both mesomorphic stationary phases which show no much difference in selectivity of the separation systems used in this study.

EXPERIMENTAL

Materials

Poly(methylhydrognesiloxane) ($\bar{M}_n = 4500$) and divinyltetramethylsiloxane platinum catalyst were obtained from Patrarch System Inc., and used as received. (*S*)-(−)-2-methyl-1-butanol, $[\alpha]_D^{25} = -6.5°$ (from Merck), 4-hydroxybiphenyl-4′-carboxylate (from Tokyo Kasei Co.) and all other reagents (from Aldrich) were used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under nitrogen.

Techniques

^{1}H NMR spectra (300 MHz) were recorded on a varian VXR-300 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were 10°C min^{-1}. Thermal transitions reported were collected during the second heating and cooling scans. Thermal decomposition temper-

atures were determined by a Seiko TG/DTA 200 thermogravimetric analyzer (TG). A Nikon Microphot-FX 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 power diffractometer. The gas chromatograph used throughout was a Varian Model 3300 instrument, equipped with a capillary-column split-injection system and an FID detector. Helium was the carrier, the linear velocity being 1.2—1.4 ml min^{-1}. The SE-54 column (commercial name DB-5) and OV-210 column (commercial name DB-210) which were 30 m by 0.32 mm i.d. and contained a stationary phase film thickness of *ca.* 0.25 μm, were purchased from J & W Scientific Co., U.S.A. The GC-MS spectra were run on a Finnigan Mat ITD-800 GC-MS spectrometer.

Synthesis of Monomers

The synthesis of olefinic monomers IM and IIM for hydrosilation reaction is outlined in Scheme 1. 4-[(*S*)-2-Methyl-1-butoxy]phenol, 6-bromo-1-hexene and 10-undecen-1-yl tosylate, were synthesized according to literature procedures reported by our laboratory.[38,39]

4-(5-Hexene-1-yloxy)biphenyl-4′-carboxylic Acid (IA) and 4-(10-Undecen-1-yloxy)-biphenyl-4′-carboxylic Acid (IIA)

Both compounds were prepared by the etherification of 6-bromo-1-hexene or undecenyl tosylate with 4-hydroxybiphenyl-4′-carboxylic acid. The synthesis of 4-(10-undecen-1-yloxy)biphenyl-4′-carboxylic acid has been described below.

4-Hydroxybiphenyl-4′-carboxylic acid (6 g, 0.028 mol) was added to a solution of KOH (3.76 g, 0.067 mol) and KI (0.2 g) in 90% ethanol (150 ml). The solution was refluxed for 1 h and 10-undecen-1-yl tosylate (4.56 g, 0.034 mol) was added dropwise. The resulting solution was refluxed for 20 h, cooled to room temperature and 100 ml of water was then added. The solution was acidified with dilute hydrochloric acid. The precipitate was filtered and recrystallized from acetic acid to yield 8.26 g (80.6%) of white crystals.

Compound IA: mp = 202.8°C; ^{1}H NMR (acetone-d_6, δ, ppm): 1.82 [m, 4H, –(C$\underline{\text{H}}_2$)$_2$–]; 2.15 (m, 2H, –C$\underline{\text{H}}_2$–CH=); 3.95 (t, 2H, –C$\underline{\text{H}}_2$O–); 4.95 (m, 2H, C$\underline{\text{H}}_2$=); 5.81 (m, 1H, =C$\underline{\text{H}}$–); 7.04—8.09 (m, 8 aromatic protons).

Compound IIA: mp = 162.9°C; ^{1}H NMR ($CDCl_3$, δ, ppm): 1.20—2.21 [m, 16H, –(C$\underline{\text{H}}_2$)$_8$–]; 4.01 (t, 2H, –C$\underline{\text{H}}_2$O–); 4.97 (m, 2H, C$\underline{\text{H}}_2$=); 5.80 (m, 1H, =C$\underline{\text{H}}$–), 6.93—8.18 (m, 8 aromatic protons).

(S)-2-Methyl-1-butyl 6-hydroxy-2-naphthalene-carboxylate

6-Hydroxy-2-naphthanoic acid (6.775 g, 0.036 mol) and (*S*)-(−)-2-methyl-1-butanol (4.76 g, 0.054 mol) and sulfuric acid (0.178 ml) were dissolved in dried benzene (15 ml). The resulting solution was refluxed until 6-hydroxy-2-naphthanoic acid was completely dissolved and 0.65 ml of water was collected in a Dean-Stark trap. After cooling, the reaction mixture was extracted with ether. The collected ether solution was washed with an aqueous solution of sodium bicarbonate (5%) and water. Then, it was dried over magnesium sulfate and the solvent was evaporated in a rotavapor. The remaining solid was purified by column chromatography (silica gel, ethyl acetate–*n*-hexane = 1 : 3 as eluent) to yield 7.54 g (81.2%) of crystals. mp = 88.6; $[\alpha]_D^{25}$ = 2.97; ^{1}H NMR ($CDCl_3$, δ, ppm): 0.90—1.10 (m, 6H, –C$\underline{\text{H}}_3$), 1.30—2.10 [m, 3H, –C$\underline{\text{H}}$(CH$_3$)–C$\underline{\text{H}}_2$–], 4.30 (d, 2H, –COO–C$\underline{\text{H}}_2$), 7.30—8.20 (m, 6 aromatic protons).

4-[(S)-2-Methyl-1-butoxy]phenyl 4-(5-hexen-1-yloxy)bipheny]-4'-carboxylate (IM) and (S)-2-methyl-1-butyl 6-[4-(10-undecen-1-yloxy)biphenylcarboxyloxy]-2-naphthalene-carboxylate (IIM)

Both olefinic monomers IM and IIM were prepared by the same method. The synthesis of monomer IM has been described below.

4-(5-Hexene-1-yloxy)biphenyl-4'-carboxylic acid (1.776 g, 0.006 mol) was reacted at room temperature with excess thionyl chloride (4 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 (1.08 g, 0.006 mol) and triethylamine (1.67 ml) in 100 ml of methylene chloride. The solution was stirred at room temperature. The solvent was then removed by heating over a boiling water bath. The obtained crude product was dissolved in methylene chloride and passed through silica gel. The solvent was removed in a rotavapor. The product was recrystallized from a mixed solvent of methanol and benzene to yield 1.95 g (71%) of white crystals.

IM: $[\alpha]_D^{25} = +4.967$; ^{1}H NMR ($CDCl_3$, δ, ppm): 0.87—1.10 (m, 6H, $-CH_3$); 1.14—1.81 [m, 7H, $-(CH_2)_2-$ and $-CH(CH_3)-CH_2$]; 2.07 (m, 2H, $-CH_2-CH=$); 3.72 (m, 2H, $-OCH_2-$); 3.81 (t, $-CH_2-OPh-$); 5.10 (m, 2H, $CH_2=$); 5.86 (m, 1H, $=CH-$); 6.86—8.16 (m, 12 aromatic protons).

IIM: Yield 82.9%; $[\alpha]_D^{25} = +2.85$; ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.95—1.10 (m, 6H, $-CH_3$); 1.20—2.20 [m, 17H, $-(CH_2)_7-$ and $-CH(CH_3)-CH_2-$]; 2.05 (m, 2H, $CH_2-CH=$); 4.00 (t, 2H, $-CH_2-OPh-$); 4.20 (dd, 2H, $-COO-CH_2-$); 4.95 (m, 2H, $CH_2=$); 5.80 (m, 1H, $=CH-$); 6.90—8.60 (m, 14 aromatic protons).

Synthesis of Polysiloxanes IP and IIP

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

1.0 g (10 mol% excess *versus* the Si–H groups present in polysiloxane) of the olefinic derivative 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 divinyltetramethyldisiloxane platinum catalyst was then injected with a syringe as a solution in toluene (1 mg ml^{-1}). The reaction mixture was refluxed (10°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 and further purified by preparative GPC, and then dried under vacuum.

GC Column Fabrication and Testing

Deactivated fused silica columns, 30 m by 0.32 mm i.d (J & W Scientific Inc.) were washed with acetone, dichloromethane and water. They were dried at 280°C under a nitrogen flow, and then filled with a solution of 3.125 mg ml^{-1} IP or IIP in chloroform, calculated so as to produced 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 35°C in order to hasten the evaporation of volatile solvent.[40] The stationary phases were cross-linked with dicumyl peroxide.[41] Both columns were conditioned at 300°C overnight under a nitrogen flow until a stable baseline was obtained at the maximum sensitivity of the instrument.

Acknowledgement. The authors are grateful to the National Science Council of the Republic of China for financial support of this work, (NSC 79-0405E-009-05).

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 (1982).
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, in "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, in "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. H. Kelker and Z. Fresenius, *Anal. Chem.*, **198**, 254 (1963).
31. H. Kelker, *Ber. Bunsenges. Phys. Chem.*, **67**, 698 (1963).
32. H. Kelker, *Adv. Liq. Cryst.*, **3**, 237 (1978).
33. G. M. Janin, *Adv. Chromatogr.*, **17**, 231 (1979).
34. Z. Witkiewicz, *J. Chromatogr.*, **251**, 311 (1982).
35. A. Radecki, H. Lamparczyk, and Kaliszen, *Chromatographia*, **12**, 595 (1979).
36. S. A. Wise, W. J. Bonnett, F. R. Guenther, and W. E. May, *J. Chromatogr. Sci.*, **19**, 457 (1981).
37. S. A. Wise, L. C. Sander, H. Ch. K. Chang, K. E. Markides, and M. L. Lee *Chromatographia*, **25**, 473 (1988).
38. V. Percec, C. S. Hsu, and D. Tomazos, *J. Polym. Sci., Polym. Chem.*, **26**, 2047 (1988).
39. C. S. Hsu, J. H. Lin, L. R. Chou and G. H. Hsiue, *Macromolecules*, in press.
40. J. C. Kuei, J. I. Shelton, L. W. Castle, R. C. Kong, B. E. Richter, J. S. Bradshaw, and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, **7**, 13 (1984).
41. B. E. Richter, J. C. Kuei, N. J. Park, J. J. Crowley, J. S. Bradshaw, and M. L. Lee, *J. High Resolut., Chromatogr. Chromatogr. Commun.*, **6**, 371 (1983).