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Research Article

Cholesteric Liquid Crystalline Copolymers for Gas Chromatographic Separation of Polycyclic Aromatic Compounds

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A novel series of side-chain liquid crystalline copolysiloxanes containing [S]-1-(2-naphthyl) ethyl 6-[4-(10-undecen-1-yloxy) biphenyl-4′-carbonyloxy]-2-naphthoate mesogenic and 4-biphenyl 4′-allyloxybenzoate mesogenic side groups in the backbone and side chains liquid crystalline copolymers were prepared and evaluated as possible stationary phases for gas chromatography capillary columns. All copolymers display enantiotropic cholesteric phases. These mesomorphic polysiloxanes specimens with the widest temperature range were used as the stationary phase in a gas chromatography capillary column, and it showed good thermal and physical stability, excellent chemical inertness, and unique separation properties for polycyclic aromatic compounds. These cholesteric LC copolysiloxane stationary phases show much better separation effect for the polycyclic aromatic compound than those of the nematic and smectic LC copolysiloxanes.

1. Introduction

Increasing requirements on analyses of isomeric compounds and the problems encountered in their separation necessitate a study of more efficient systems which exhibit a high selectivity. In gas chromatography (GC) new selective stationary phases are studied. Attention is also focused on the use of substances with oriented molecules that permit selective separations; these properties are exhibited by, for example, inclusion of some compounds and liquid crystals. Although the interaction mechanisms are different with liquid crystals, the stereoselective properties are so important that it is desirable to deal with their potential use in GC. The interaction mechanism with inclusion of some compounds is based on a specific interaction during which a molecule (the guest) is inserted, the whole molecule or part of it, into a cavity in another molecule (the host) in order to attain a state with a minimum energy.

Liquid crystals represent a mesomorphic material between solid crystalline substances and isotropic liquids. On heating, mesophases are formed that have ordered structures which can be nematic, smectic, or cholesteric. On further heating, the orientation is disturbed and the phases are converted into an isotropic liquid. The long structure of liquid crystals causes isomers with more drawn-out shapes to be readily dissolved in the ordered liquid crystal substrate (mesophase) thus yielding stronger sorbate-sorbent interactions.

Kelker and Fresenius [1, 2] first used liquid crystals as stereospecific stationary phases in GC. Since then, a great deal of attention has been paid to the separation properties of this relatively wide group of substances [3, 4], used mainly as stationary phases in packed columns. Liquid crystals have been used as stationary phase [5–16] in GC to separate a variety of compounds including isomeric mixtures which cannot be separated on conventional stationary phases. Conventional stationary phase separation of analytes is based on differences in vapor pressures of the solutes and/or differences in solubility arising from specific energetic interactions. A liquid crystal stationary phase separates analytes based upon differences in solute molecular shape, with the anisotropic packing behavior of liquid crystalline materials permitting the separation of isomers based on their individual molecular geometries (length-to-breadth) [6].

Polysiloxane has been used as the backbone for the side-chain liquid crystalline polymers because of its properties of low glass transition temperature and high thermostability. Stationary phases based on low molecular weight liquid crystals gain substantial efficiency when they are attached onto flexible polymer backbones. A flexible spacer between the backbone and mesogenic unit allows the resulting polymers to retain liquid crystalline properties. Polymeric stationary phases containing liquid crystalline substituents are desirable for their high thermal stability.

Many nematic and smectic liquid crystal polymers have been reported as stationary phase [7, 8]. Cholesteric liquid crystals have also attracted particular interest on due to their unusual helical supermolecular structure, which can be used as a stationary phase in GC [9]. In order to take advantage of all these properties, we selected polysiloxane as the polymer backbone and 11 methylene units as the spacer, and [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yl-oxy) biphenyl-4-carbonyloxy]-2-naphthoate as the mesogen.

Cholesteric polymers can be obtained by copolymerization of a nematogenic monomer (4-biphenyl 4-allyloxybenzoate) with a chiral commoner ([S]-1-(2-naphthyl) ethyl 6-[4-(10-undecen-1-yl-oxy) biphenyl-4-carbonyloxy]-2-naphthoate). A cholesteric mesophase can be realized by changing the composition of mesogens attached onto a polysiloxane backbone. These materials tend to form cholesteric mesophases over a broad temperature range. Among these polymers, we selected P3, which shows the widest temperature range of cholesteric phase, to fabricate the capillary column stationary phase.

Polycyclic aromatic hydrocarbons (PAHs) are well suited for analysis by GC using liquid crystalline stationary phases because their molecular geometries have some distinct differences. The cholesteric polysiloxane described herein has merit and has been used to successfully separate PAH compounds.

2. Experimental

2.1. Apparatus and Equipment. ^{1}H-NMR spectra were recorded on a Varian VXR-300 or Bruker 300 MHz 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. Thermal transition reports were collected during the second heating and cooling scans. A SEIKO TG/DTA 200 thermogravimetric analyzer (TGA) determined thermal decomposition temperatures. 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. Polymerization reactions were traced by using a Nicolet 520 FTIR.

2.2. Gas Chromatography. The gas chromatograph used throughout was a Hewlett Packard 5890 Series II instrument equipped with a capillary column, split injection system, and a FID detector. The carrier gas was N_2.

3. Synthesis of Monomers

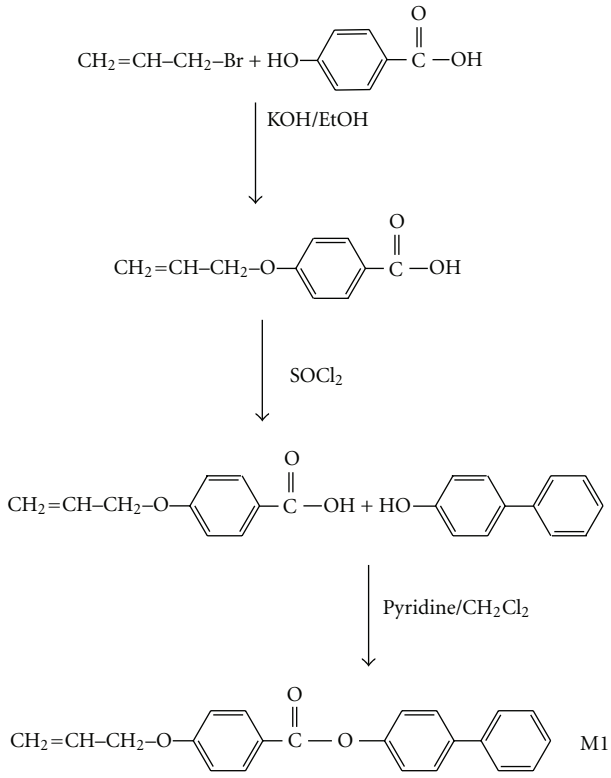
The synthesis of monomers 4-biphenyl 4′-allyloxybenzoate (**M1**) and [S]-1-(2-naphthyl)ethyl 6-[4-(10-undecen-1-yl-oxy) biphenyl-4′-carbonyl oxy]-2-naphthoate (**M2**) was outlined in Schemes 1 and 2. The intermediary compounds were synthesized according to literature procedures reported by Lin and Hsu [11].

4. Biphenyl 4-Allyloxybenzoate (M1)

4-Allyloxybenzoic acid (3.56 g, 0.02 mol) was reacted at room temperature with excess thionyl chloride (30 mL) containing a few drops of DMF in dry methylene chloride (25 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 10 mL of dry methylene chloride and slowly added to a cold solution of 4-hydroxybiphenyl (3.4 g, 0.02 mol) and pyridine (8.2 mL) in 50 mL of dry methylene chloride. The resulting solution was stirred at room temperature overnight. The solution was then extracted by 200 mL of diethyl ether. The extraction solution was washed with 100 mL of 10% sodium bicarbonate then washed with saturated sodium chloride and dried over anhydrous magnesium sulfate. After removal of the solvent by evaporation under reduced pressure, 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; ^{1}H-NMR chemical shifts: 4.65 (t, 2H, –O–CH_2–), 5.48 (m, 2H, =CH_2), 6.07 (m, 1H, =CH–), 7.03∼8.19 (m, 13 aromatic protons). Anal. Cal. For $C_{22}H_{18}O_3$; C: 80.00%, H: 5.45% and O: 14.55%; Found C: 79.87%, H: 5.44% and O: 14.69%.

5. [S]-1-(2-Naphthyl) Ethyl-6-[4-(10-Undecen-1-Yloxy) Biphenyl-4′-Carbonyloxy]-2-Nnaphthoate (M2)

4-(10-Undecen-1-yloxy) bipheny1-4′-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 M2. Details of the synthetic procedure are similar to the synthetic procedures of monomer M1. 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. m.p. = 154.4°C; $[\alpha_D^{25^\circ C}]$ = +196.9 (c = 0.01, CH_2Cl_2); ^{1}H-NMR chemical shifts: 1.24∼1.77 (m, 17H, –CH_2– and –CH_3), 1.98 (m, 2H, =CH–CH_2–), 3.95 (t, 2H, –O–CH_2–C), 4.78∼4.95 (m, 2H, =CH_2),5.74 (d, 1H, =CH–) 6.32 (q, 1H, –C*H–), 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%.



Scheme 1: Synthesis of monomer M1.

6. Synthesis of Copolysiloxanes P1–P3

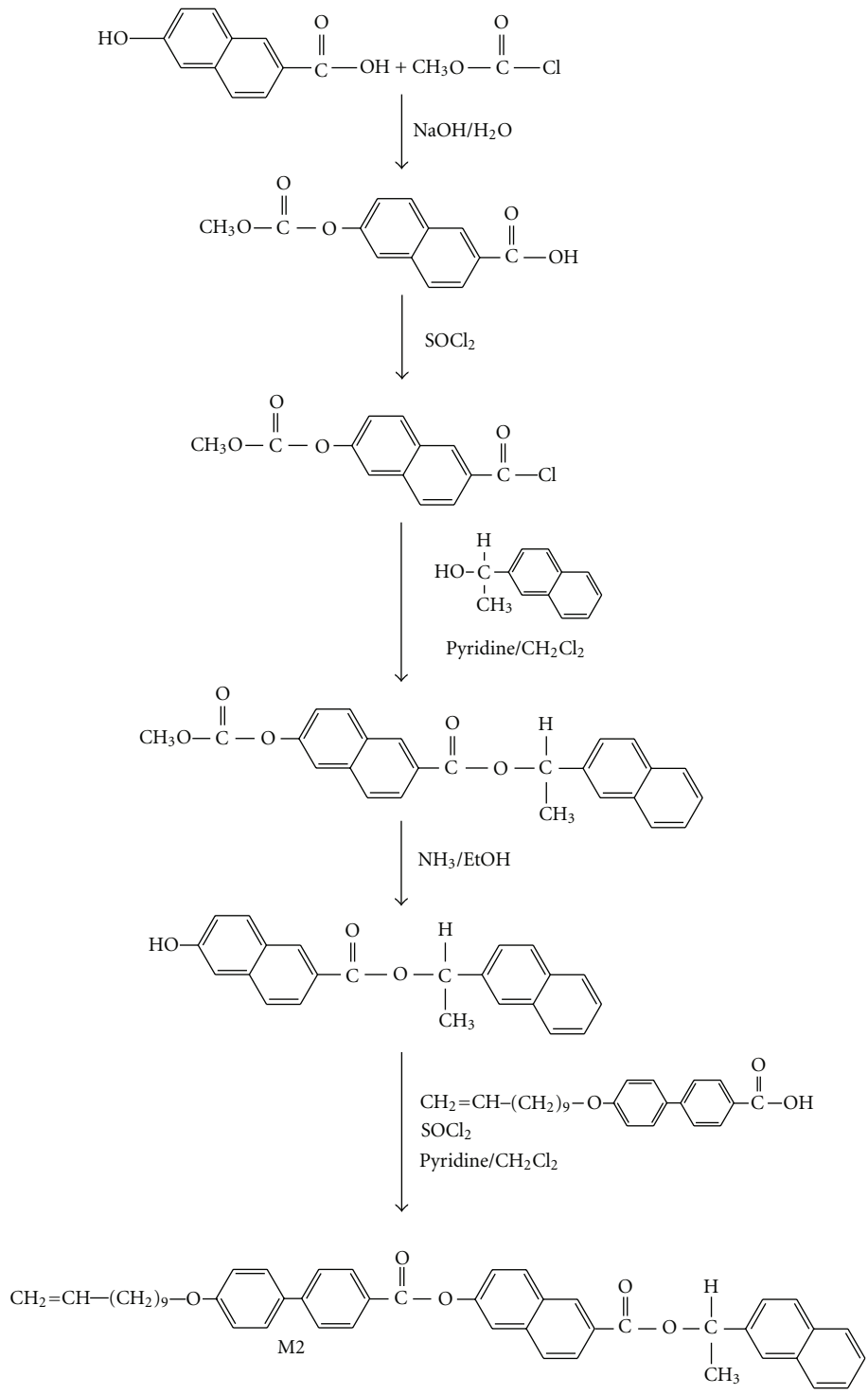
All liquid crystalline copolysiloxanes **P1–P3** were synthesized by the hydrosilylation of poly(methylhydrogensiloxane) with different ratios of both monomers in the presence of a platinum divinyl tetramethyl disiloxane catalyst. A general synthetic procedure is described below. An olefinic monomer 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 were then injected with a syringe. The reaction mixture was stirred at 75°C for 2 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 methylene chloride solution into methanol and then dried under vacuum.

7. Preparation of the Column

A deactivated fused silica capillary column with an ID 0.32 mm × 30 m (Restek) was used. The capillary was washed with methylene chloride (20 mL) before coating. The stationary phase (31.3 mg of copolymer and 1 mg of dicumyl peroxide as crosslinking agent) was dissolved in methylene chloride (10 mL). The solution was placed in a rinsing reservoir and forced through the capillary column by N_2 gas. After filling, the column was sealed at one end and was placed in a 40°C water bath. The column was then placed under vacuum and the solvent evaporated, completing the static coating procedure. The sealed end of the column was opened. The column was cross-linked in a gas chromatography oven, with an oven temperature program of 40°C to 200°C at 4°C/min, and maintained at 200°C for 6 h. The column was cleaned with 10 mL of methylene dichloride using N_2 carrier gas. Finally, the column was installed on a GC apparatus and conditioned at 200°C for overnight.

8. Results and Discussion

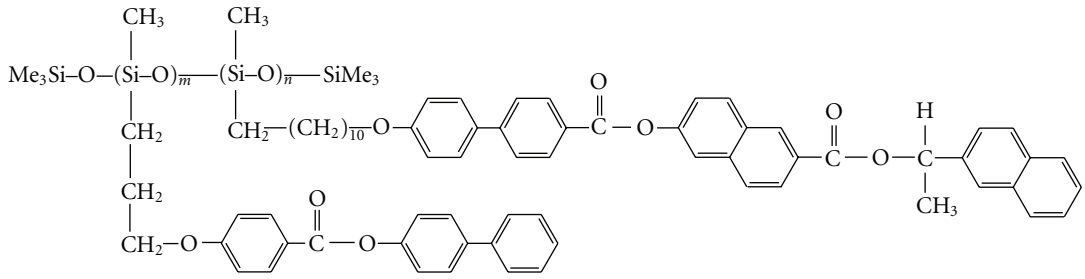
Three polymers (**P1–P3**) were successfully synthesized. Table 1 summarizes the thermal transitions, monomer feeding ratios, and the structure of the obtained polymers **P1–P3**. These polymers all presented the cholesteric phase. Polymer **P3** exhibited the widest range of temperatures for the cholesteric mesophase, a glass transition at 53.2°C, and a phase transition form cholesteric to isotropic at 234.8°C based on DSC heating scan. During the cooling scan, the phase transition forms isotropic to cholesteric presented at 225.4°C. Furthermore, the thermal decomposed temperature of polymer **P3** exceeded 237.7°C by TGA determination. The mesophase identifications were achieved by optical polarizing microscopic observation. Polymer **P3** showed a characteristic cholesteric texture at 136.5°C, and the texture exhibited a typical cholesteric phase planar texture with moire fringe (Figure 1). In short, polymer **P3** showed a very



Scheme 2: Synthesis of monomer M2.

wide temperature range of the cholesteric phase and high thermal stability. All these factors indicated that polymer **P3** is well suited to be a GC stationary phase, and thus we selected this new material for further investigation.

The capillary column coated with **P3** polymer was termed the liquid crystal polymer (LCP) column. Using this LCP column, good separation for the most of 14 PAHs species was achieved (Figure 2), with an exception for the compounds 2 and 3. Since these two compounds were difficult to separate using single temperature program, we adopted another strategy. We reanalyzed these 14 species of PAHs by classifying them into several groups based on



Scheme 3

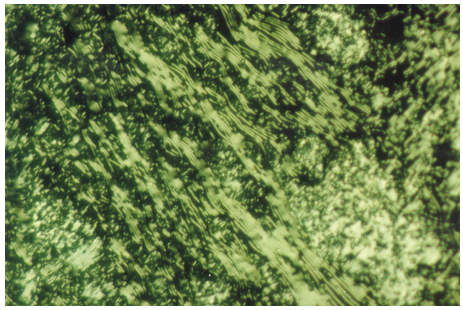


Figure 1: Typical optical micrograph of polymer P3 (cholesteric texture, 136.5°C, magnification ×200).

Table 1: Summary of the thermal transitions, monomer feeding ratios, and the structure of the copolymers. For more details see Scheme 3.

Polymer	Monomer feeding ratio M1/M2 (mol %)	Phase transitions, °C, heating scan (cooling scan)
P1	10/90	g 66.0 N* 196.6 I (I 185 N*)
P2	20/80	g 54.1 N* 213.2 I (I 209.4 N*)
P3	30/70	g 53.2 N* 234.8 I (I 225.4 N*)

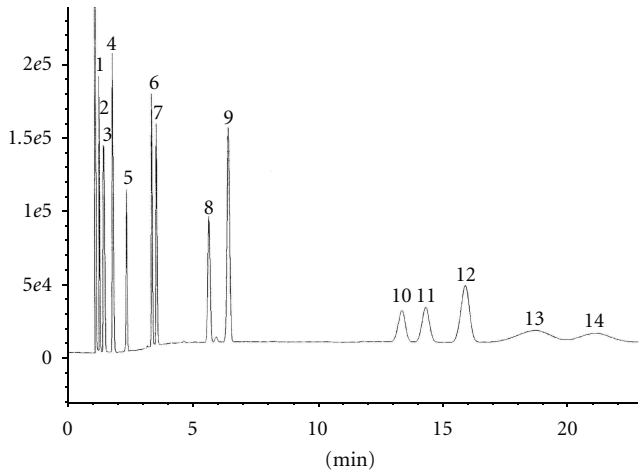


Figure 2: The chromatogram of 14 PAHs. The chromatographic separation was performed as described in the Experimental using the nitrogen flow of 50 KPa, the injector temperature of 230°C, and the detector temperature of 250°C. The temperature program: 170°C held for 2 min. then went to a final temperature of 230°C by 70°C/min.

the number of rings within their structures, that is, two, three, four, and five-ring PAHs, and altering the temperature program to optimize the separation resolution. We used the LCP column with different structure characteristics and different chosen temperatures to carry on the separation. Table 2 summarizes the accompanying information containing the relative retention time data derived from optimized temperature programs, boiling points, and the length-to-breath ratios (L/B) for the isomers in the LCP column. By this strategy, all the PAH compounds can be well separated by the LCP column.

The compound families that contain different isomers (e.g., compounds 6-7, molecular weight 178; compounds 8-9, molecular weight 202; compounds 10, 11, and 12, molecular weight 228) were difficult to separate by commercial capillary column chromatography. However, the cholesteric liquid crystal polymer has an unusual helical supermolecular structure; it shows high similarity to the nematic LC except a twisted angle in each layer. This special molecular structure may confer beneficial effects on the stationary phase for the separation of compounds with different L/B dimensions. For example, phenanthrene (compound 6, L/B = 1.459) elutes earlier than anthracene (compound 7, L/B = 1.559); triphenylene (compound 10, L/B = 1.12) elutes earlier than benz [a]anthracene (compound 11, L/B = 1.58); triphenylene (compound 10, L/B = 1.12) elutes earlier than chrysene (compound 12, L/B = 1.72). In summary, we found that the LCP column showed a good resolution for separation of PAH isomers.

9. Conclusion

Side-chain liquid crystalline polysiloxanes with wide temperature ranges of cholesteric phase have been proven to be useful in separating PAH compounds. The obtained polymers showed very high thermal stability and had wide temperature ranges associated with the cholesteric liquid crystal phase. These results may be due to the twisted packing structure of the cholesteric mesophase exhibited by the new stationary

Table 2: Relative retention times of PAHs with different numbers of rings on the LCP column, their boiling points, and their L/B ratios.

Compounds	Temperature	Relative retention time	Boiling point (°C)	L/B
Two rings	170°C isocratic			
Naphthalene (1)		1	217.9	1.242
Biphenyl (2)		1.111	255.0	—
Diphenylmethane (3)		1.141	264.5	—
Three rings	170°C isocratic			
Acenaphthene (4)		1	279	—
Fluorene (5)		1.354	295	1.399
Phenanthrene (6)		2.741	340	1.459
Anthracene (7)		3.240	342	1.559
Four rings	220°C isocratic			
Fluoranthene (8)		1	384	1.142
Pyrene (9)		1.203	404	1.119
Triphenylene (10)		3.303	425	1.12
Benz[a]anthracene (11)		3.692	437.6	1.58
Chrysene (12)		4.287	448	1.72
Five rings	230°C isocratic			
Benzo[a]pyrene (13)		1	495	1.149
Dibenz[a,h]anthracene (14)		1.467	524	1.782

phases. Because the separation is based on molecular shape, isomers that have very similar intrinsic properties could be separated by these kinds of mesomorphic polymer stationary phases. The prepared column described here displayed high column efficiency and holds great promise for the separation of a wide range of PAH compounds.

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