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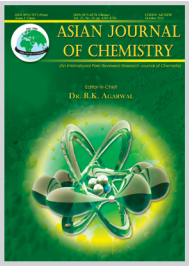

Chiral Nematic Liquid Crystalline Copolymers as Stationary Phase Materials in Capillary Gas Chromatography

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A new series of liquid crystalline polysiloxanes with a very wide range of mesomorphic temperatures has been prepared. They contain 4-cholesteryl-(10-undecen-1-yloxy) biphenyl-4'-carboxylate mesogenic and 4-biphenyl-4'-allyloxybenzoate mesogenic side groups displaying enantiotropic nematic and chiral nematic phases. The mesomorphic polysiloxane specimen with the widest temperature range was used as the stationary phase in a gas chromatography capillary column and it showed unique separation properties for polycyclic aromatic compounds.

Key Words: Polysiloxanes, Chiral nematic, Polycyclic aromatic hydrocarbon.

INTRODUCTION

Liquid crystals have been used as stationary phases[1-3] in gas chromatography (GC) to separate a variety of compounds including isomeric mixtures, which can not be separated on conventional stationary phases. Conventional stationary phase separation of analytes is based on differences in vapour 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 behaviour of liquid crystalline materials permitting the separation of isomers based on their individual molecular geometries (length-to-breadth)[4].

Finkelmann and Rehage[5] were the first to synthesize thermotropic side-chain liquid crystalline polymers. Since then, nematic, smectic and chiral nematic liquid crystalline polymers and elastomeric liquid crystalline networks containing a polysiloxane backbone[6,7] have been synthesized. 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 leading group 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 liquid crystal polymers of nematic or smectic phase have been reported as stationary phases[8,9]. Chiral nematic liquid crystals have also attracted particular interest on due to their unusual helical supermolecular structure, which can be used as a stationary phase in gas chromatography. Therefore, to take advantage of all these properties and to prepare a gas chromatography stationary phase with optimum separation properties, we selected polysiloxane as the polymer backbone and used an 11-methyl unit as the spacer and modified this backbone with a new series of chiral nematic liquid crystalline polymers.

Chiral nematic polymers can be obtained by copolymerization of a nematogenic monomer (4-biphenyl 4'-allyloxybenzoate) with a chiral comonomer (4-cholesteryl-(10-undecen-1-yloxy)biphenyl-4'-carboxylate)[10,11]. A chiral nematic mesophase can be realized by changing the composition of mesogens attached onto a polysiloxane backbone. These materials tend to form chiral nematic mesophases over a broad temperature range. For the preparation of novel stationary phases in gas chromatography, we selected the chiral nematic mesophase polymers with the widest range of temperatures.

Polycyclic aromatic hydrocarbons (PAHs) are well suited for analysis by gas chromatography using liquid crystalline stationary phases because their molecular geometries have some distinct differences. Interestingly, PAHs have been separated based on their large variations in carcinogenic activity. The chiral nematic polysiloxane described herein has merit and has been used to successfully separate PAH.

EXPERIMENTAL

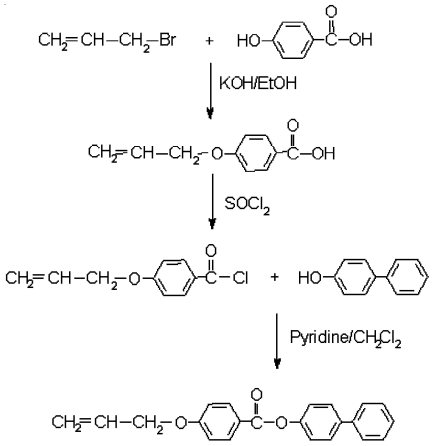
^{1}H NMR spectra were recorded on a Varian VXR-300 or Bruker 300 MHz spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were 10 ºC/min. 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.

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.

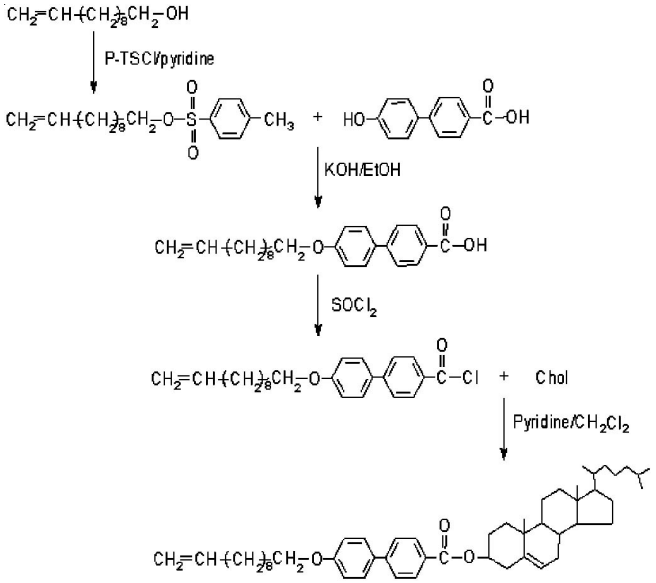
Synthesis of monomers: The synthesis of monomers 4-biphenyl 4'-allyloxybenzoate (M1) and 4-cholesteryl-(10-undecen-1-yloxy) biphenyl-4'-carboxylate (M2) were outlined in **Schemes I and II**. The detailed synthetic procedures for the intermediary compounds and monomers were similar to those reported previously[12]. ^{1}H NMR chemical shifts of M1 were 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). ^{1}H NMR chemical shifts of M2 were 0.67-2.15 (m, 55H, -CH_2- and -CH_3); 2.01 (m, 2H, =C-CH_2-); 2.43 (d, 2H, -O-C-CH_2-C=); 3.98 (t, 2H, -O-CH_2-); 4.78-5.04 (m, 3H, =CH_2 and -O-CH-); 5.38 (d, 1H =CH-); 5.75 (m, 1H =CH-); 6.95-8.07 (m, 8 aromatic protons).

Synthesis of copolysiloxanes P1-P6: All copolysiloxanes P1-P6 were synthesized by the hydrosilylation of poly(methyl hydrogen siloxane) with different ratios of both monomers in the presence of a platinum divinyl tetramethyl disiloxane catalyst. Experiment details concerning their synthesis and purification were identical to those reported previously[13]. The reaction mixture was refluxed (75 ºC) under nitrogen 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.

Preparation of the column: A deactivated fused silica capillary column with an I.D. 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) 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 ºC water bath. The column was then placed under vacuum and the solvent evapourated, 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 ºC to 200 ºC at 4 ºC/min and maintained at 200 ºC 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 gas chromatography apparatus and conditioned at 200 ºC for overnight.



Scheme-I: Synthesis of monomers M1



Scheme-II: Synthesis of monomers M2

RESULTS AND DISCUSSION

The six polymers (**P1-P6**). Table-1 summarizes the thermal transitions and thermodynamic parameters of obtained polymers **P1-P6** and also includes the molecular structures and ratios of copolymers used in their preparation[12,14]. Polymer **P1** presented a nematic phase while polymers **P2-P6** presented only the chiral nematic phase. Polymer **P6** exhibited the widest range of temperatures for the chiral nematic mesophase, a glass transition at 30.6 ºC and a chiral nematic to isotropic phase transition at 253.0 ºC upon differential scanning calorimeter heating scan. In the cooling scan, the isotropic to chiral nematic phase transition presented at 225.6 ºC. The thermal decomposition temperature of polymer **P6** exceeded 316.9 ºC by TGA determination. The mesophase identifications were achieved by optical polarizing microscopic observation. Polymer **P6** showed the characteristic chiral nematic texture at 132.8 ºC and the texture exhibited a typical chiral nematic phase planar texture with moire fringe (Fig. 1). Polymer **P6** showed a very wide temperature range of the chiral nematic phase and high thermal stability. All of these factors indicated that polymer **P6** was well suited to be a gas chromatographic stationary phase and thus we selected this new material for all further studies.

TABLE-1
THERMAL TRANSITIONS AND MOLECULAR STRUCTURES AND RATIOS OF COPOLYMERS

Polymer	Monomer feed ratio M1/M2 (mol %)	Phase transitions (ºC) heating/cooling
P1	100/0	g 65.9 N 174.5 I I 169.0 N
P2	90/10	g 45.7 N* 176.5 I I 173.2 N*
P3	80/20	g 57.4 N* 212.1 I I 207.6 N*
P4	70/30	g 31.6 N* 213.7 I I 213.0 N*
P5	60/40	g 42.5 N* 227.4 I I 224.2 N*
P6	50/50	g 30.6 N* 253.0 I I 225.6 N*

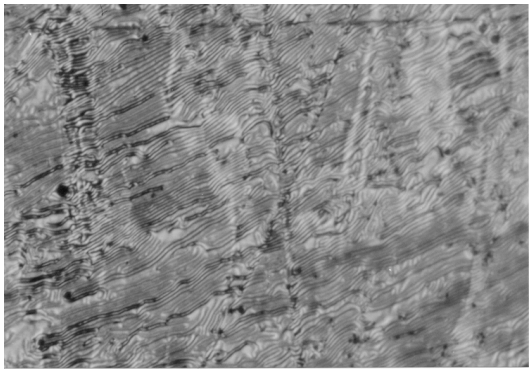


Fig. 1. Typical optical micrograph of polymer P6, chiral nematical texture, 132.8 ºC, magnification 200x

The capillary column coated with **P6** polymer was termed the LCP column. The LCP column yielded 3871 plates/m (as tested with triphenylene, 220 ºC and flow rate 1.1 mL/min). This column demonstrated good column efficiency for the separation of 15 polycyclic aromatic hydrocarbons.

Good separation of most of the 15 species of PAHs on the LCP column was achieved (Fig. 2) with the exception of compounds 11, 12 and 13. PAHs 11, 12 and 13 were isomers, which were difficult to separate using the original temperature program. Therefore, we reanalyzed these 15 species of PAHs by classifying them on the basis of the number of rings in their structures, *i.e.*, as 2, 3, 4 and 5 ring PAHs and by altering the temperature programs to optimize the resolution. The separations of the 2, 3, 4 and 5 ring PAH compounds on LCP column are illustrated in Fig. 3a-3d. Table-2 contains accompanying information that summarizes the relative retention time data derived from optimized temperature programs, boiling points and length-to-breath ratios (L/B) for the isomers on the LCP column. Almost all the polycyclic aromatic hydrocarbons were well separated by the LCP column under the optimized conditions.

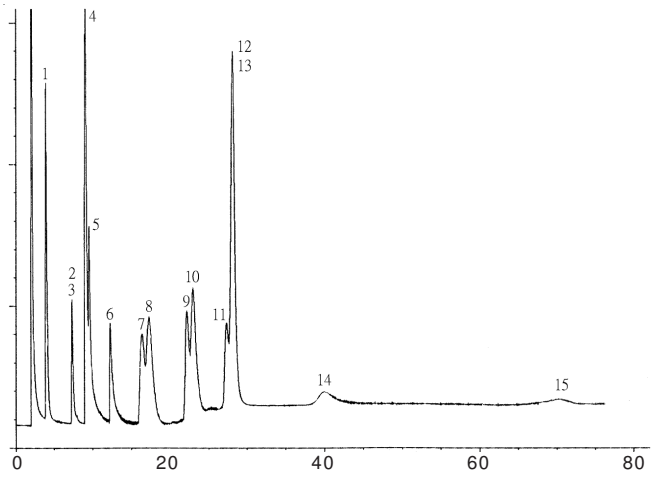


Fig. 2. Chromatogram of the 15 PAHs; chromatographic separation was performed as described in the experimental section using the temperature program 60 ºC over 1 min, then 5 ºC/min to 100 ºC, then 10 ºC/min to 140 ºC over 5 min, then 20 ºC/min to a final temperature of 230 ºC

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	b.p. (ºC)	L/B
Two ring	80 ºC during 1,min, then 4 ºC/min to 110 ºC			
Naphthalene (1)		1	217.9	1.242
Biphenyl (2)		1.955	255.0	-
Diphenylmethane (3)		1.955	264.5	-
Three ring	80 ºC during 1,min, then 5 ºC/min to 100 ºC, then 10 ºC/min to 120 ºC			
Acenaphthylene (4)		1	280	-
Acenaphthene (5)		1.022	279	-
Fluorene (6)		1.308	295	1.399
Phenanthrene (7)		2.167	340	1.459
Anthracene (8)		2.515	342	1.559
Four ring	180 ºC isocratic			
Fluoranthene (9)		1	384	1.142
Pyrene (10)		1.178	404	1.119
Triphenylene (11)		3.557	425	1.12
Benz[a]anthracene (12)		4.099	437.6	1.58
Chrysene (13)		4.763	448	1.72
Five ring	240 ºC during 1 min, then 10 ºC/min to 250 ºC			
Benzo[a]pyrene (14)		1	495	1.149
Dibenz[a,h]anthracene (15)		2.156	524	1.782

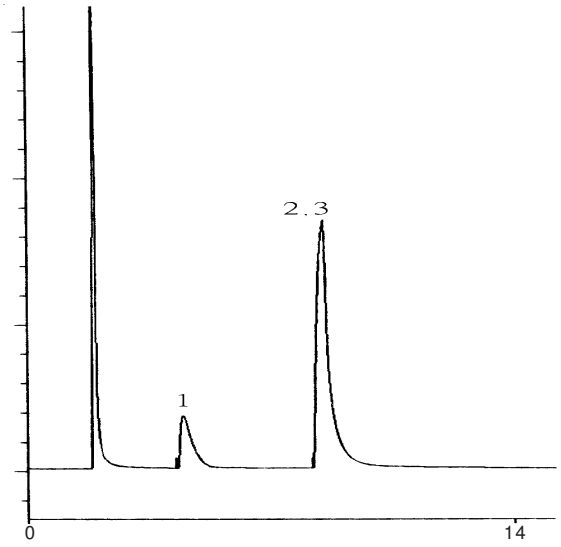


Fig. 3a. Polycyclic aromatic hydrocarbons with 2 rings

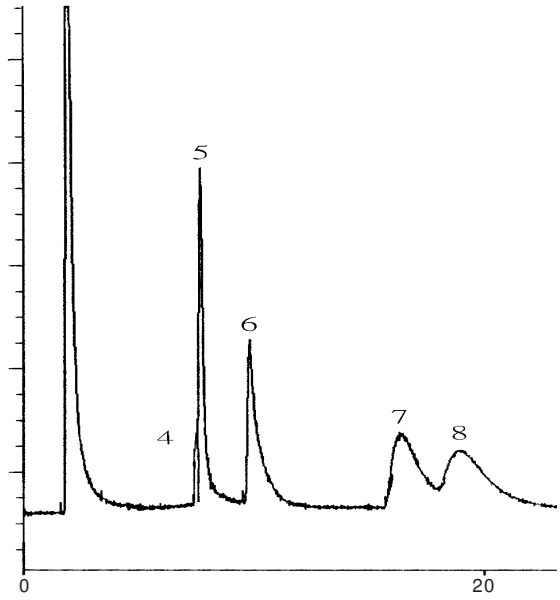


Fig. 3b. Polycyclic aromatic hydrocarbons with 3 rings

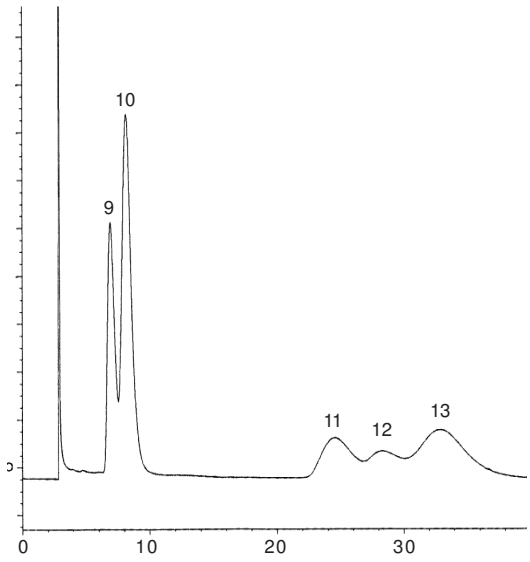


Fig. 3c. Polycyclic aromatic hydrocarbons with 4 rings

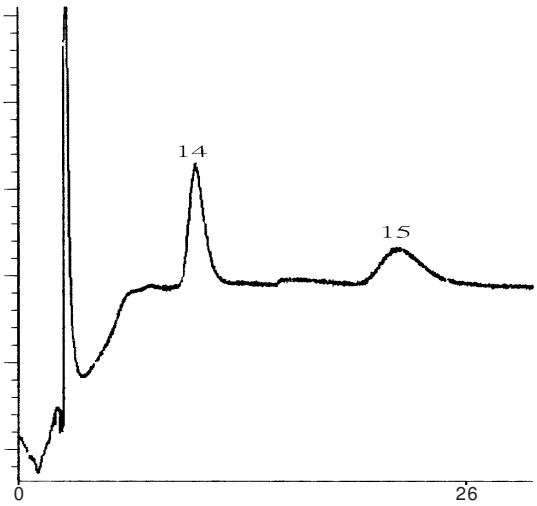


Fig. 3d. Polycyclic aromatic hydrocarbons with 5 rings

The liquid crystal polymer in the chiral nematic phase had an especially unusual helical supermolecular structure. This structure showed many similarities to the nematic phase, but every layer showed a twist in the angle. This molecular structure may confer to the stationary phase especially beneficial effects for separation of compounds with different L/B dimensions. The elution pattern of the polycyclic aromatic hydrocarbon solutes in this study by the mesomorphic polysiloxane was consistent with the degree of their rod-like geometry, with the more rod-like structures being retained longer. For example, phenanthrene (compound 7, L/B = 1.459) elutes earlier than anthracene (compound 8, L/B = 1.559), triphenylene (compound 11, L/B = 1.12) elutes earlier than benz[a]anthracene (compound 12, L/B = 1.58) and triphenylene (compound 11, L/B = 1.12) elutes earlier than chrysene (compound 13, L/B = 1.72).

The compound families that were isomers (*e.g.*, compound 7-8, molecular weight 178; compound 9-10, molecular weight 202; compound 11,12 and 13, molecular weight 228) were difficult to separate by commercial capillary column chromatography. We found that the LCP column showed better resolution for the above isomeric compounds. Fig. 4 illustrates the relationship between the calculated peak resolution (Rs) and the temperature of four isomeric polycyclic aromatic hydrocarbon pairs (compounds 7-8, 9-10, 11-12, 11-13). Thus, the LCP column showed good resolution of isomers and the ability to effect chromatographic separation over wider temperature ranges.

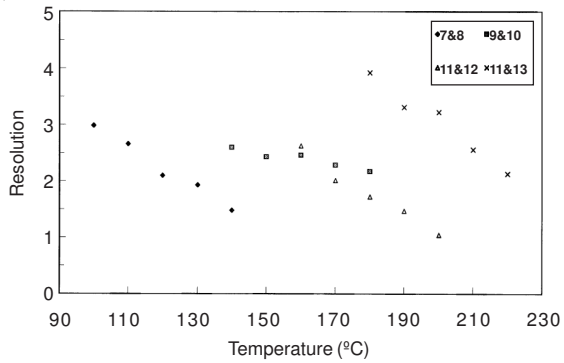


Fig. 4. Relationship between temperature and chromatographic resolution of isomeric polycyclic aromatic hydrocarbon compounds

Conclusion

In conclusion, the side-chain liquid crystalline polysiloxanes with wide temperature ranges of chiral nematic phase have been proven to be useful in separating many classes of compounds. The obtained polymers showed very high thermal stability and had wide temperature ranges associated with the chiral nematic liquid crystal phase. These results may be due to the twisted packing structure of the chiral nematic mesophase exhibited by the new stationary 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 very high column efficiency and holds great promise for the separation of a wide range of polycyclic aromatic hydrocarbon compounds.

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