# Smectic Biphenylcarboxylate Ester Liquid Crystalline Polysiloxane Stationary Phase for Capillary Gas Chromatography

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**Smectic liquid crystalline polysiloxanes offer unique selectivities when used as stationary phases in capillary gas chromatography. Retention can be correlated to solute molecular size and shape. In this study, biphenylcarboxylate esters, as mesomorphic moieties, were coupled via flexible spacers of different length to a polysiloxane backbone. The resultant phase showed smectic characteristics from 100 °C to 300 °C, with unsurpassed selectivity for the separation of various isomeric polycyclic aromatic compounds. Important stationary phase properties including efficiency, temperature stability, and selectivity before and after cross-linking have been examined for this new liquid crystalline phase.**

Since the first application of liquid crystalline compounds as stationary phases in gas chromatography (*1*), the use of several mesomorphic phases have been reported (*2*). Liquid crystalline phases provide unique selectivity for the separation of many groups of chemical compounds. This includes the possibility to separate geometrical and optical isomers because of an ordered arrangement of the liquid crystalline molecules in the stationary phase. The separation mechanism is based on molecular geometry with solute retention related to characteristics such as length-to-breadth ratio (*3*) and planarity of the solute. Dispersion, polarity, and induced polarity interactions between the solute and the stationary phase and vapor pressure of the solute can at the same time contribute to retention.

Until recently, mainly monomeric rodlike molecules have been utilized as mesomorphic stationary phases in gas chromatography (*2, 4*). Attempts to improve the thermal stability and efficiency of stationary phases containing liquid crystals have been reported (*5–7*). A significant advancement in this respect was achieved by the coupling of mesomorphic monomers to a stable polysiloxane backbone (*8–12*). Properties of the monomeric mesomorphic molecules can be preserved in both linear and cross-linked polymers if flexibility is built into the phase structure (*11*). Finkelmann et al. (*12*) first reported the use of mesomorphic polysiloxanes as stationary phases in gas chromatography.

The mesomorphic side chains of the polysiloxane can show either nematic or smectic properties. Nematic liquid crystals are only structurally restricted in that the long axes of the mesomorphic moieties maintain a parallel or nearly parallel arrangemant over macroscopic distances. The smectic structure is more organized with mesomorphic molecular packings arranged in layers, and a more or less structured packing within the layers. There are a number of different structures within the smectic temperature region, and according to the chronological order in which the various smectic phases were first observed, the letters A to I were designated (*13*).

It has generally been thought that nematic phases gave improved resolution over smectic phases in gas chromatography, due to greater diffusion in the former, and thus possess higher efficiency (*14*). Improved selectivity is, however, achieved by using smectic phases (*15, 16*). Low-order smectic phases (e.g., A and C) can provide a combination of efficiency and selectivity for optimal resolution (*16*). Ordered smectic phases (e.g., B and E), on the other hand, have inferior properties because the laminar structure and compact arrangement of molecules show resistance to penetration and dissolution of solutes (*14, 17*). In a previous paper, the syntheses of several mesomorphic liquid crystalline polysiloxanes were reported, and a poly(mesomorphic/pentenyl)siloxane showed superior selectivity for isomeric polycyclic aromatic compounds in the smectic range (*18*). However, this polymer possessed a limited smectic region and could not be used over a wide temperature range.

In this work, the synthesis of a new smectic liquid crystalline polysiloxane stationary phase which can be used over a wide temperature range is presented, and its chromatographic properties before and after cross-linking are discussed. The selectivity for isomeric polycyclic aromatic compounds is also demonstrated.

## EXPERIMENTAL SECTION

**Synthesis of the Liquid Crystalline Polysiloxane.** The liquid crystalline phase, see Figure 1, was prepared by the following procedure. The precursor alkenes were prepared by the method of Jones et al. (*18*) and used without further modification. Equimolar amounts, $4 \times 10^{-3}$ mol, of each of the two liquid crystalline alkenes were added to a Teflon vial containing 0.5 g of polymethylhydrosiloxane (av $M_w$ 2270, Petrarch Systems, Inc., Bristol, PA) and 25 mL of toluene. The liquid crystals were allowed to dissolve before the newly prepared catalyst ($H_2PtCl_6 \cdot 6H_2O$, 50 ppm in 2-propanol) was added. This vial was then capped and placed in an oven at 80 °C overnight. The reaction was complete after 18 h as indicated by the absence of the Si–H band at 2180 $cm^{-1}$ in the infrared spectrum. Toluene was then removed under vacuum. The resulting polymer was dissolved in 5 mL of methylene chloride and the solution was filtered through a Millipore filter. To the resulting solution, 15 mL of methanol was added to precipitate the polymer. The polymer was fractionated five additional times as above and dried overnight under vacuum at 40 °C. Transition temperatures for the liquid crystalline phase were investigated using three independent methods; a Thomas-Kofler hot-stage light microscope using cross-polarized light, differential scanning calorimetry (Perkin-Elmer DSC-2 heated from 30 to 300 °C, at 10 °C $min^{-1}$ in an $N_2$ atm), and capillary gas chromatography.

**Capillary Column Preparation.** Fused silica capillary tubing with either 0.20 mm or 0.32 mm i.d. (Hewlett-Packard, Avondale, PA) was used. Capillaries were purged with nitrogen gas at 250 °C for 2 h before coating. The stationary phases, SE-54 (Alltech Associates) and the liquid crystalline polymer, were dissolved in methylene chloride. The coating solutions were filtered before use by placing a metal filter (2-$\mu$m pore diameter) in a Swagelok fitting between a short length of stainless steel tubing (50 mm × 6 mm o.d.) and a 5-mL gastight glass syringe with a Luer Lock coupling and forcing the coating solution through the filter.

After static coating, cross-linking was performed for several of the columns using azo-*t*-butane (*19*). The columns to be cross-linked were purged with azo-*t*-butane vapors in nitrogen gas at room temperature for 1 h and at a flow rate of 3 $cm^3$ $min^{-1}$.

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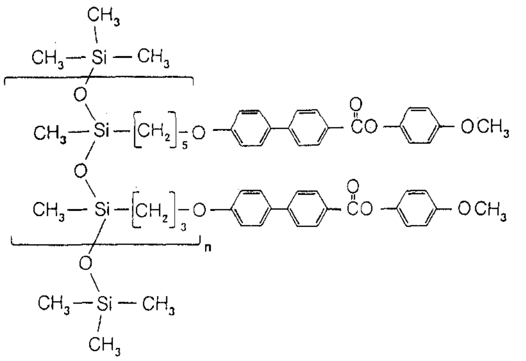

**Figure 1.** Chemical structure of the liquid crystalline polysiloxane with $n \approx 17$.

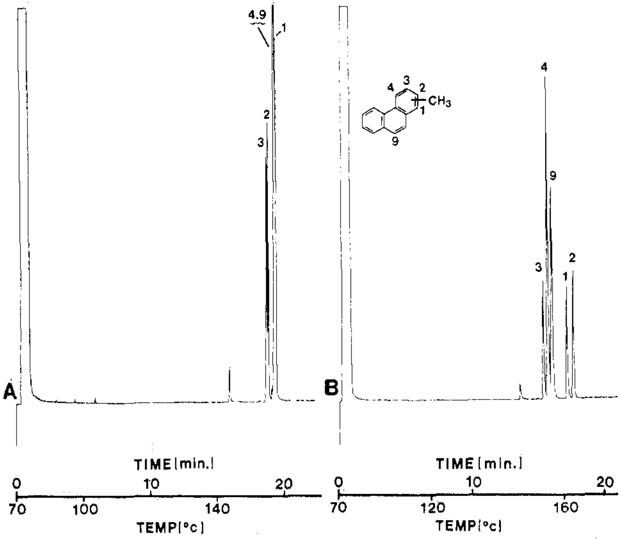

**Figure 2.** Chromatograms of isomeric methylphenanthrenes with (A) SE-54 and (B) liquid crystalline phase: temperature programmed from 70 °C to 100 °C in (A) and to 120 °C in (B) at 10 °C min$^{-1}$ after an initial 2-min isothermal period, then at 4 °C min$^{-1}$; splitless injection. For other conditions, see text.

Both ends of the columns were sealed with a microtorch and the columns were heated from 40 °C to 220 °C at 4 °C min$^{-1}$ and held at 220 °C for 60 min. Finally, the columns were conditioned at 280 °C for 10 h under nitrogen purge. The columns used for the standard chromatograms in this study were 10 m long with an internal diameter of 320 μm and a liquid crystalline gum film thickness of 0.25 μm.

**Column Evaluation.** The solute standards were either obtained commercially or synthesized in our laboratories. Hewlett-Packard Model 5790 and 5890 gas chromatographs equipped with flame ionization detectors were used for column evaluation. Hydrogen was used as carrier gas at a linear velocity of 50–100 cm s$^{-1}$. The amount of injected standard compounds varied from 1 to 20 ng per component.

## RESULTS AND DISCUSSION

The structure of the liquid crystalline linear polysiloxane is shown in Figure 1. The mesomorphic moiety is attached to the polysiloxane backbone via alkyl chain spacers containing three and five carbon atoms. An ordered mesophase that is more or less independent of the main polymeric backbone is thus created (*8*). Structural elements used in the mesomorphic side chain, and their positions, will have an influence on the achieved order obtained in the thermotropic range. Smectic phases are often a result of weak terminal and strong lateral attraction forces (*20*). Transversal dipoles, like the carboxylic groups in the liquid crystalline chain, and the methyl termination should structurally force the phase to exhibit smectic order. Flexible spacers that decouple motions between liquid crystalline moieties and the polysiloxane backbone will increase the possibility of arrangement of the mesomorphic chains into well-defined layers.

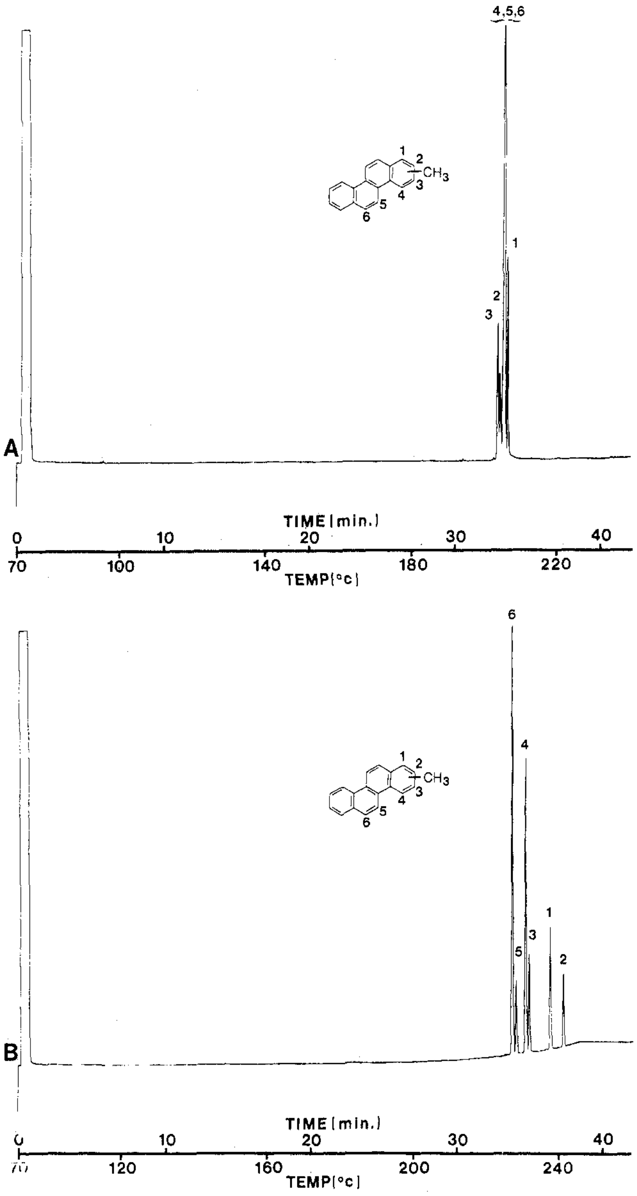

**Figure 3.** Chromatograms of isomeric methylchrysenes with (A) SE-54 and (B) liquid crystalline polysiloxane. Conditions are given in Figure 2. Length-to-breadth ratios (*3*) for methylchrysene isomers are (6) = 1.48, (5) = 1.48, (4) = 1.51, (3) = 1.63, (1) = 1.71, and (2) = 1.85.

No transition from smectic to nematic was found in the liquid crystalline phase. In the cross-polarized light microscope, a distinct smectic order was discernible, and the transitions were as follows: glassy–118 °C–smectic–300 °C–isotropic. Only one transition could be observed in the DSC curve at 133 °C when the polymer was heated for the first time. This transition was absent after repeated heating or cross-linking. The 15 °C higher transition temperature found in the DSC curve is possibly due to the fast heating rate of 10 °C min$^{-1}$.

The separations of isomeric three- and four-ring methyl-substituted polycyclic aromatic hydrocarbons (PAH) on the liquid crystalline polysiloxane and SE-54 are illustrated in Figures 2 and 3. The resolution of these PAH is superior with the liquid crystalline phase compared to the nonpolar SE-54.

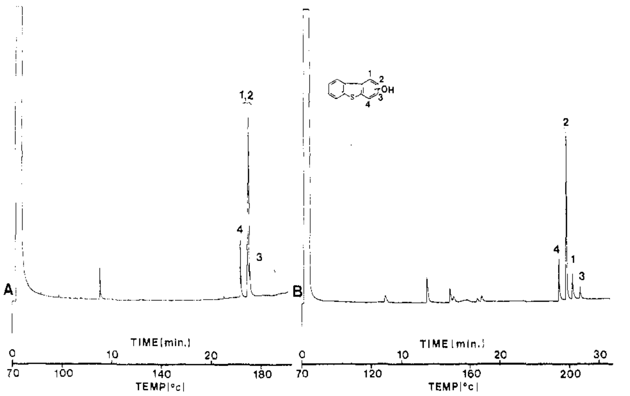

**Figure 4.** Chromatograms of isomeric hydroxydibenzothiophenes with (A) SE-54 and (B) liquid crystalline polysiloxane. Conidtions are given in Figure 2.

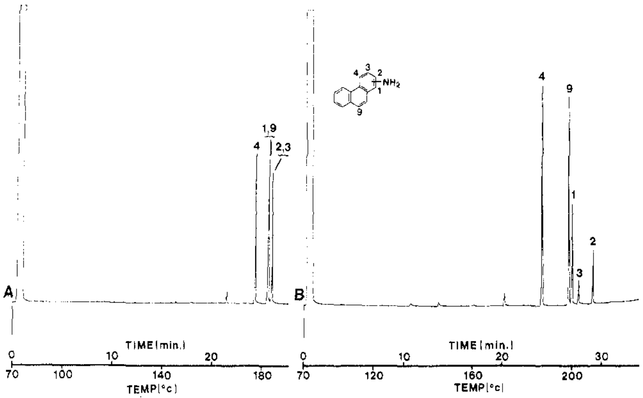

**Figure 5.** Chromatograms of isomeric aminophenanthrenes with (A) SE-54 and (B) liquid crystalline polysiloxane. Conditions as in Figure 2.

All isomers of the methylphenanthrenes and methylchrysenes are separated with the liquid crystalline phase. Base line separation of all of the methylchrysene isomers on a single phase is reported here for the first time (Figure 3). This separation is improved from the results earlier reported for the same compounds on a nematic polysiloxane phase (*10*) in which 3-methylchrysene and 4-methylchrysene were only partially resolved. It should also be noted that the order of elution of these isomers on the liquid crystalline phase in this study strickly adheres to the length-to-breadth ratio as is shown in Figure 3.

The selectivity for polar substituted PAH and heterocyclic isomers is illustrated in Figures 4–6. All of these isomer classes exhibit better selectivity with the liquid crystalline phase than with SE-54. Several of the aminophenanthrene isomers are reported to be strongly mutagenic (*21*), and their identification is therefore of great importance. The liquid crystalline phase shows good selectivity for nitrogen heterocyclic compounds that contain tertiary nitrogen heteroatoms, but lower efficiency was noticed for one of the isomers (see Figure 6). In the same figure, it can be seen that the selectivity and efficiency for aliphatic hydrocarbons are lower with the liquid crystalline phase than with the methyl silicone phase. Two factors can contribute to this impaired resolution with the liquid crystalline phase. First, the solubility of nonpolar solutes in this phase is low because it contains polar functional groups. Second, alkane molecules consist of random chains with freely rotating bonds that do not fit well into the laminar structure of the smectic phase. The alkane molecules must straighten out to get maximum interaction with the mesophase (*20*). While greater energy is required for dissolution of a solute in an ordered mesophase than in an isotropic liquid (*2*), the loss of energy in rotational and vibrational movement in the alkanes can lower the net energy and, thus, lower the solubility for these solutes in the liquid crystalline phase.

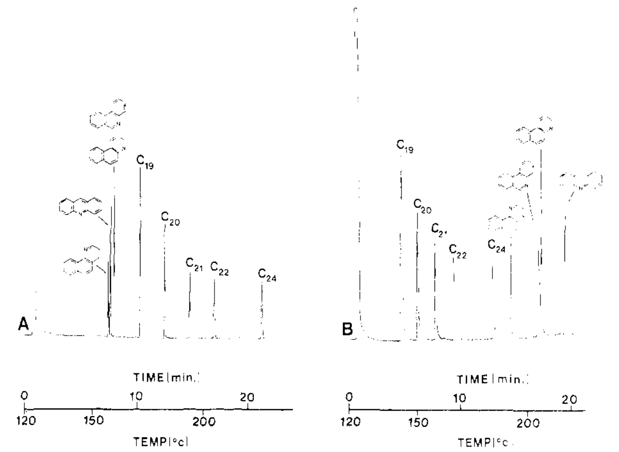

**Figure 6.** Chromatograms of nitrogen heterocycles and normal alkanes with (A) SE-54 and (B) cross-linked liquid crystalline polysiloxane: temperature programmed from 120 °C at 5 °C min$^{-1}$; split injection.

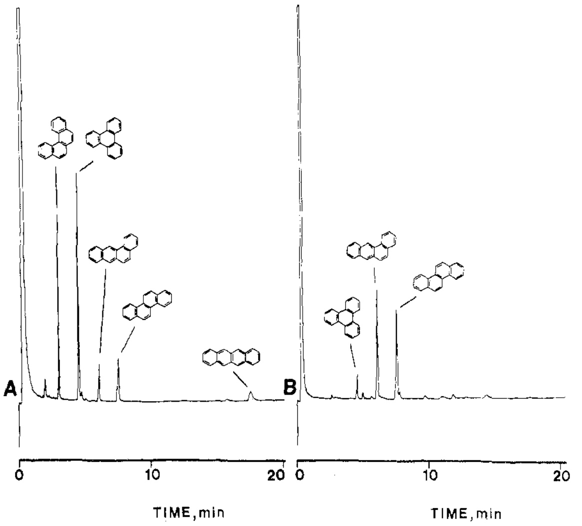

**Figure 7.** Chromatograms of isomeric four-ring PAH separated with the liquid crystalline polysiloxane: (A) standard reference compounds and (B) HPLC fraction of a coal tar extract. Isothermal separation was at 220 °C. Split injection was used.

The unsurpassed selectivity for unsubstituted four-ring PAH with the liquid crystalline phase is demonstrated in Figure 7. Isomers of four-ring PAH from an HPLC fraction of a coal tar extract and corresponding standard solutes are here separated on a 10-m column with a film thickness of 0.25 μm. Triphenylene and chrysene are particularly difficult to separate on other available GC phases.

The mesomorphic molecular organization can be locked to some extent in the polymer structure by cross-linking of the polysiloxane chains. Cross-linking hinders the mobility of the polymer backbone. The mesomorphic side groups should not be effected by the cross-linking, and the liquid crystalline properties of the cross-linked system should be similar to those of the linear polymer (*8*). Most chromatographic properties did not change significantly after cross-linking of the phase. The retention, however, increased with cross-linking. Typical columns containing film thikcnesses of 0.1–0.25 μm produced approximately 4000 plates m$^{-1}$ ($k' \geq 15$) after immobilization with azo-*t*-butane and rinsing with dichloromethane.

The effect of temperature on selectivity was studied by observing the relative retentions of anthracene–phenanthrene and benz[*a*]anthracene–chrysene. The curves before and after cross-linking are similar and no phase transitions are visible chromatographically over the range 100–300 °C. The resolution of anthracene and phenanthrene was found to be slightly less (0.5–2%) with the cross-linked phase than with the gum. Finally, the temperature stability was higher for the cross-linked phase than for the gum phase. The cross-linked columns could be used up to 280 °C without significant bleeding or deterioration of the phase film.

**Registry No.** 1-Methylphenanthrene, 832-69-9; 2-methylphenanthrene, 2531-84-2; 3-methylphenanthrene, 832-71-3; 4-methylphenanthrene, 832-64-4; 9-methylphenanthrene, 883-20-5; 1-methylchrysene, 3351-28-8; 2-methylchrysene, 3351-32-4; 3-methylchrysene, 3351-31-3; 4-methylchrysene, 3351-30-2; 5-methylchrysene, 3697-24-3; 6-methylchrysene, 1705-85-7; 1-hydroxydibenzothiophene, 69747-83-7; 2-hydroxydibenzothiophene, 22439-65-2; 3-hydroxydibenzothiophene, 69747-77-9; 4-hydroxydibenzothiophene, 24444-75-5; 1-aminophenanthrene, 4176-53-8; 2-aminophenanthrene, 3366-65-2; 3-aminophenanthrene, 1892-54-2; 4-aminophenanthrene, 17423-48-2; 9-aminophenanthrene, 947-73-9; phenanthridine, 229-87-8; benzo[*f*]quinoline, 85-02-9; acridine, 260-94-6; benzo[*h*]quinoline, 230-27-3; benzo[*c*]phenanthrene, 195-19-7; triphenylene, 217-59-4; benz[*a*]anthracene, 56-55-3; chrysene, 218-01-9; naphthacene, 92-24-0; nonadecane, 629-92-5; eicosane, 112-95-8; heneicosane, 629-94-7; docosane, 629-97-0; tetracosane, 646-31-1.

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# Performance of an Automated Gas Chromatograph–Silica Furnace–Atomic Absorption Spectrometer for the Determination of Alkyllead Compounds

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**An automated gas chromatograph–atomic absorption spectrometer was used to study the decomposition–atomization process for alkyllead compounds in a heated quartz tube. Longer term stability of the system was achieved with a purging cycle in which the quartz furnace was flushed with large air flows during solvent elution prior to returning to normal reducing atmospheres in hydrogen. The system response was optimized by using univariate procedures; it was insensitive to changes in atomizer surface temperatures above 800 °C. No changes in atomization efficiency for quantities of lead between 30 pg and 30 ng were observed, suggesting that excess lead scavenger was present. Although less efficient than hydrogen, other gases also supported the decomposition–atomization of the analytes. A major portion of the lead not atomized in air or nitrogen was deposited on the surface of the quartz walls and was revolatilized and atomized extremely rapidly if hydrogen was admitted to the furnace. Hydrogen radicals are postulated to mediate both the revolatilization and atomization steps.**

The use of a silica tube furnace as a convenient atomization device for the determination of covalent hydrides by atomic absorption spectrometry (AAS) was initially suggested by Chu et al. (*1*). This detector has rapidly gained wide acceptance (*2–4*) and has been successfully used by several groups for the gas chromatographic determination of covalent hydrides (*5*, *6*) and a variety of organometallics (*7*, *8*) including organoselenium (*9*, *10*), organoarsenicals and -mercurials (*11*), organotins (*12*, *13*), and organoleads (*14*, *15*). These custom-designed chromatographic detectors offer a virtually element specific detection as well as an impressive sensitivity, and they are inexpensive. However the mechanism of atomic vapor generation is not well understood, and only a limited consideration has been given to the automation of gas chromatograph–silica furnace systems required for large numbers of environmental samples.

Although the term thermal or electrothermal has often been used to describe the atomization process within silica tubes, researchers are becoming increasingly aware that the surface material and composition of the gaseous atmosphere profoundly influence the sensitivity of these devices. Whereas silica furnaces are normally operated at 800–900 °C for the detection of arsine or selenium hydride, temperatures of 1700–1800 °C are optimal for their atomization from graphite

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