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Short Communication

Gas chromatographic separation of polycyclic aromatic hydrocarbons on a mesomorphic copolysiloxane stationary phase

Hongju Wang, Tongmou Gen, Rounong Fu, Jiya Zhu, Xiuzhen Wei, Hueisheng Li and Jihua Liu

Department of Chemical Engineering, Bejing Institute of Technology, P.O. Box 327, Beijing 100081 (China)

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ABSTRACT

A mesomorphic copolysiloxane was prepared and used as a selective stationary phase for capillary column gas chromatography. It was found to have an operating temperature range of 70–280°C and unique selectivity for some isomeric compound separations such as those of three-, four- and five-ring polycyclic aromatic hydrocarbons.

INTRODUCTION

The gas chromatographic (GC) analysis of samples consisting of isomeric solutes with nearly identical vapour pressures remains a challenge. Moreover, the problem is often compounded by the complexity of mixtures containing classes of materials such as polycyclic aromatic hydrocarbons (PAHs) [1]. Thus, even with columns of the highest available efficiency, it is fair to say even today that the resolution of isomers such as five-ring PAHs (including, *e.g.*, the carcinogenic benzo[*a*]pyrene) is not entirely satisfactory [2].

In contrast, it has been recognized for some time that liquid-crystalline (mesomorphic) stationary phases provide enhanced GC separations of many isomeric compounds, including PAHs, on the basis of solute geometry [2]. As a result, a number of liquid-crystalline phase have been introduced [3–5], the best known being the commercially available materials developed by Janini and co-workers [6–9]. An example of the remarkable shape selectivity of nematic mesophases is that they yield baseline separations of most parent PAHs, which was achieved for the first time with packed columns containing BMBT [N,N′-bis(*p*-methoxybenzylidene)-α,α′-bi-*p*-toluidine] stationary phase [6].

However, the utility of such low-molecular-weight liquid-crystalline phases is limited by the excessive column bleeding at elevated temperatures, the moderate column efficiency and the restricted useful mesomorphic temperature ranges. As a result, the coupling of liquid crystal functional groups on to a polysiloxane backbone via a flexible alkyl spacer has been successfully accomplished [10,11]. The methylene spacers between the liquid-crystal-

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Correspondence to: Prof. R. Fu, Department of Chemical Engineering, Beijing Institute of Technology, P.O. Box 327, Beijing 100081, China.

line substituents and the polysiloxane help to preserve the original characteristics of the liquid crystals [12]. Significant improvements in efficiency and thermal stability over the monomeric stationary phases were obtained with the development of these polysiloxane phases. In addition, Markides *et al.* [13] have shown that they provide good resolution, *e.g.*, of PAHs, with open-tubular columns.

Copolymers composed of two different liquid-crystalline moieties have been repored. Biphenylcarboxylic esters of polysiloxanes constitute a large group of liquid-crystalline copolymers [11,13,14] and several procedures for their synthesis of chromatographic applications have been described [13–16]. Not only nematic but also smectic–nematic and smectic copolymers are suitable as stationary phases [11,14,17]. Polymers with the cholesteric mesophase are also known [11] although to a much smaller extent. The mesomorphic copolysiloxanes usually shown a wider range of the mesophase than their corresponding homopolymers. These copolymers have high thermal resistance and show good behaviour of the column; further improvement in their properties is possible by cross-linking in the column [15].

In this paper, the synthesis of a mesomorphic copolysiloxane stationary phase that can be used over a wide temperature range is described and its chromatographic properties as a capillary GC stationary phase are discussed. The selectivity for isomeric PAHs is also demonstrated.

EXPERIMENTAL

A Model SP-3700 gas chromatograph (Beijing Analytical Instrument Factory, Beijing, China) equipped with a capillary split injection system and a flame ionization detector was used for evaluation of retention behaviour. All chemicals used for synthesis were of analytical-reagent grade.

Synthesis

For the synthesis of the mesomorphic copolysiloxane, 4-[(4′-(allyloxy)phenylmethylacetyl]-4′-methoxybiphenyl (0.891 g, 2.475 mmol), 0.073 g (0.275 mmol) of N-(4-allyloxy benzylidene)-4′-methoxyphenylamine, 0.16 g (containing 2.5 mmol of Si–H) of poly(methylsiloxane) and 40 ml of dry toluene were mixed. The mixture was heated to 110°C under a nitrogen atmosphere and stirred for 24–72 h until no absorbtion band of Si–H was detectable by IR spectrometry (2140 cm^{-1}). The resulting copolymer was purified by filtration or precipitation with methanol. The copolymer was collected by centrifugation at 9000 rpm (13 000 *g*) for 25 min and dried in a vacuum oven to give a white solid. The copolymer side-chain proportions were governed by the starting molar proportions of the reactants. Table I shows the structures and the phase transition temperatures of the mesomorphic copolysiloxane and its corresponding homopolym-(Allyloxy)phenylmethylacetyl]-4′-methoxybiphenyl and N-(allyloxy benzylidene)-4′-methoxyphenylamine were both prepared in the laboratory. Poly(methysiloxane) was obtained from the Merck–Schuchardt (Munich, Germany).

Column preparation

Fused-silica capillary columns (0.28 mm I.D.) (Yongnian Optical Fibre Factory, Hebei, China) were purged with dry nitrogen at 220°C for 5 h before coating. The mesomorphic copolysiloxane was dissolved in methylene chloride (35°C) at a concentration of about 4.0 mg/ml, which gave a film thickness of 0.33 μm using the static coating procedure. Before filling the capillary, the coating solution was carefully filtered through a glass filter.

RESULTS AND DISCUSSION

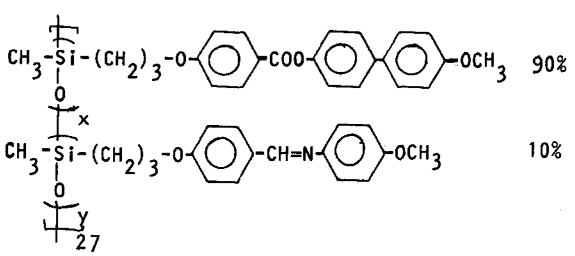
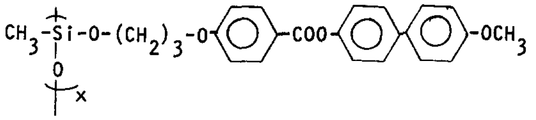
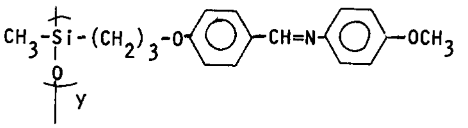
Table II gives the characteristics of four fused-silica capillary columns coated with this copolymer. The stationary phase provides satisfactory column efficiencies (3650 plates/m, anthracene solute; 250°C) owing to the flexibility of the polosiloxane backbone and the concomitant low surface tension, which facilitate the homogeneous coating of the mesomorphic copolysiloxane phase on the untreated fused-silica columns. Column 5 coated with 90:10 I–II (see Table I) mixed stationary phase was used for comparison.

The selectivity and polarity of mesomorphic copolysiloxane are represented by McReynolds constants. These parameters and average polarities are given in Table III. These parameters are also listed for PEG-20M for comparison. The average polarity of the copolymer is lower than that of PEG-20M. It is a medium-polar stationary phase. Rohrschneider

TABLE I

STRUCTURES AND PHASE TRANSITION TEMPERATURES OF THE COPOLYMER STUDIED AND ITS CORRESPONDING HOMOPOLYMER

Transition temperatures were measured by hot-stage light-polarized microscopy.

Polymer[a]		Phase transitions (°C)[b]
		c78n276i
	I	n138n287i
	II	n102n140i

[a] 27 is the degree of polymerization of poly(methysiloxane).

[b] c = crystalline; n = nematic; i = isotropic.

[20] and McReynolds [21] proposed that liquid-crystalline stationary phases have low or medium polarities as determined by the sum of the retention indices of test substances that react in different ways with the stationary phase. It is known, however, that the interaction of the liquid-crystalline stationary phase with the chromatographed substances depends not only on the polarity of the phase but also on the interaction of the substance with the ordered structure of the liquid crystal. Therefore, for a more complete characterization of the liquid-crystalline stationary phase, additional substances such as xylenes [22], diethylbenzene and ethylbenzene isomers, toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene [23] should be tested.

To determine the effect of temperature on column efficiency, the height equivalent to a theoretical plate (HETP) was measured at different temperatures and a constant flow-rate of the carrier gas. Fig. 1 shows a plot of HETP *vs.* column temperature (t) for anthracene on the two mesomorphic copolysiloxane capillary columns. It is clear that the column efficiency increases with increasing temperature.

TABLE II

CHARACTERISTICS OF THE MESOMORPHIC COPOLYSILOXANE CAPILLARY COLUMNS USED

Test compound: anthracene.

Column No.[a]	Column dimensions (length × I.D.)	Column efficiency (plates/m)	Column temperature (°C)
1	10 m × 0.28 mm	2060	205
2	10 m × 0.28 mm	2070	218
3	19 m × 0.28 mm	3650	250
4[b]	13 m × 0.28 mm	1720	220
5	10 m × 0.25 mm	810	225

[a] The capillary film thicknesses are about 0.28–0.33 μm.

[b] DCUP (dicumyl peroxide) 10% and V4 [tetra(methylvinyl)cyclotetrasiloxane] 4.4% cross-linked column. The method of cross-linking was similar to that of Liu *et al.* [18].

TABLE III

SELECTIVITIES AND POLARITIES OF THE MESOMORPHIC COPOLYSILOXANE STUDIED

Stationary phase	McReynolds constant (ΔI)[a]					
	X′	Y′	Z′	U′	S′	Mean
Copolymer	251	264	330	429	420	339
PEG-20[b]	322	536	368	572	510	461

[a] X′ = Benzene; Y′ = butanol; Z′ = 2-pentanone; U′ = nitropropane; S′ = pyridine.

[b] From ref. 19.

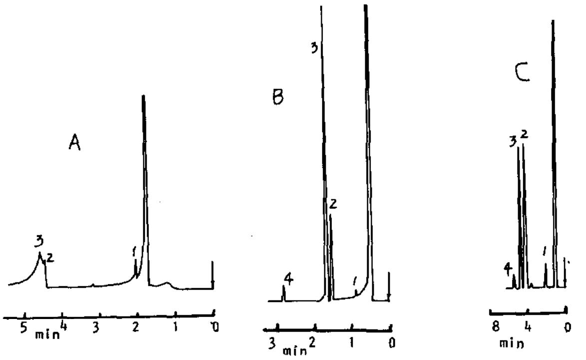


Fig. 2. Chromatograms of isomeric three-ring PAHs on (A) SE-30, (B) copolymer (column 1) and (C) mixed column (column 5). Column temperature, 225°C. Peaks: 1 = fluorene; 2 = anthracene;) 3 = phenanthrene; 4 = carbazole.

Fig. 2 shows chromatograms of three-ring PHA isomers on capillary columns coated with a nonpolar stationary phase (SE-30), with the mesomorphic copolymer and with a mixed stationary phase. The resolution is best when the liquid-crystalline copolymer is used. This is a result of both the high selectivity of the column and its high chromatographic efficiency. Columns can be easily coated with the copolymer to produce efficient columns that lead to the narrow peaks.

To illustrate the practical utility of the mesomorphic copolysiloxane solvents, we present as examples the separation of three-, four- and five-ring PAHs with this copolymer in Fig. 3. The resolution of isomers such as anthracene–phenanthrene, benzo[*a*]anthracene–triphenylene–chrysene and benzo[*a*]pyrene–benzo[*e*]pyrene–pyrene with "slightly polar" phases such as SE-52 and SE-54 is not entirely satisfactory [24,25], whereas isomers of four-ring PAHs were separated here on a 10-m column with a film thickness of 0.33 μm. Fig. 4 shows the temperature-programmed separation of a mixture

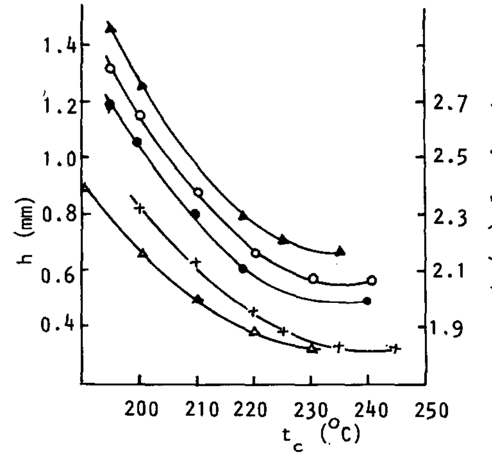


Fig. 1. Plot of HETP against temperature for anthracene on (○) column 1, (●) column 2, (×) column 3, (▲) column 4 and (△) column 5 (see Table II).

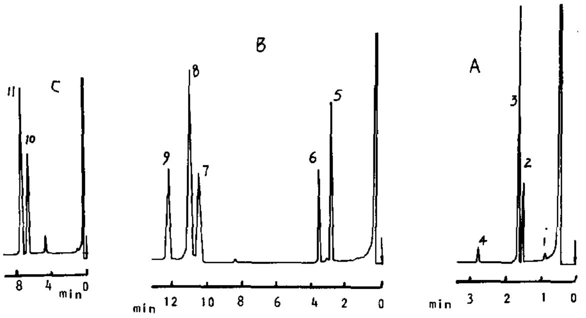


Fig. 3. Separations of (A) three-, (B) four- and (C) five-ring PAHs with the mesomorphic copolysiloxane stationary phase. Peaks: 1 = fluorene; 2 = phenanthrene; 3 = anthracene; 4 = carbazole; 5 = fluoranthene; 6 = pyrene; 7 = triphenylene; 8 = benzo[*a*]anthracene; 9 = chrysene; 10 = benzo[*e*]pyrene; 11 = benzo[*a*]perylene. Column temperatures: (A) 225°C (column 1); (B) 240°C (column 2); (C) 280°C (column 4).

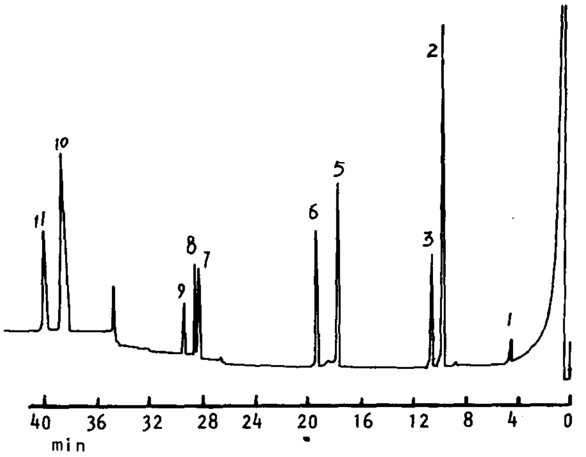


Fig. 4. Temperature-programmed separation of PAHs on column 3. Column temperature, 150°C for 3 min, then increased to 280°C at 4°C/min. Solutes as in Fig. 3.

of ten of the three- to five-ring PAHs encountered most frequently in environmental samples.

We note in passing that the elution order of the five-ring PAHs with conventional polymeric liquid phases is benzo[*e*]pyrene followed by benzo[*a*]pyrene [10]. In contrast, the elution pattern of these solutes with mesomorphic polysiloxanes is consistent with the degree of their rod-like geometry, the more rod-like being retained longer. Thus, benzo[*e*]pyrene elutes first with this copolymer, followed by benzo[*a*]pyrene.

CONCLUSIONS

A mesomorphic copolysiloxane was successfully synthesized and can be easily coated on capillary columns to give high thermal stability, high column efficiencies and high selectivity for the separation of PAHs. This copolymer reveals a wider range of the mesophase than its corresponding monomeric liquid crystals.

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