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Terminally carboxyl oligo(ethylene oxide) monomethyl ethers-substituted side chain liquid crystalline polysiloxane polymer as stationary phase in capillary gas chromatography for the separation of polynuclear aromatic hydrocarbons

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Abstract

Through esterification, acyl halide addition and monomer-grafting reactions, three new side chain liquid crystalline polysiloxane polymers containing an oligo(ethylene oxide) monomethyl group as their respective terminal group, poly (4-[(2-methylethoxy)carbonyl]phenyl 4-[4-(allyloxy)-phenyl]benzoate) (PBPBE1), poly (4-[(2-(2-methylethoxy)-ethoxy)carbonyl]phenyl 4-[4-(allyloxy)-phenyl]benzoate) (PBPBE2) and poly (4-[(2-(2-(2-methylethoxy) ethoxy) ethoxy) carbonyl]phenyl 4-[4-(allyloxy)-phenyl]benzoate) (PBPBE3) were synthesized. These liquid crystalline polysiloxane polymers were coated onto the inner surface of a capillary column (I.D.=0.32 mm, film thickness $d_f \approx 0.2 \mu\text{m}$) to test the chromatographic behavior of the critical pairs 5–6, 9–10 and 11–12 from the Supelco 610M standard mixture polynuclear aromatic hydrocarbon compounds. Results show that the experimental columns give better separation resolution and can be employed over a wider temperature range than the commercial HP-5 capillary column (Hewlett–Packard). © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, GC; Polysiloxane stationary phases; Polynuclear aromatic hydrocarbons (PAH)

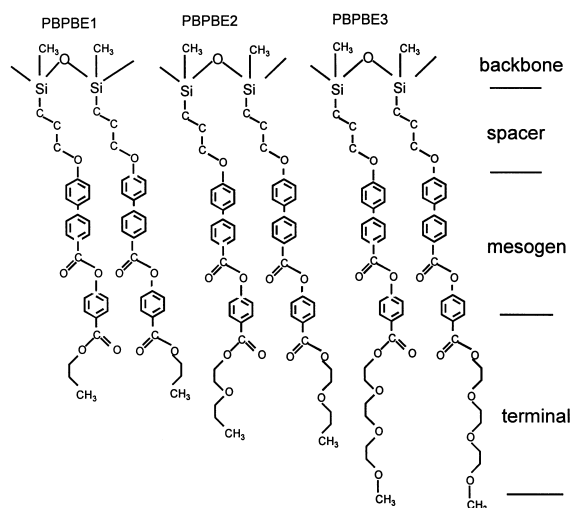
1. Introduction

The potential uses of side-chain liquid crystalline polymers (SCLCP) have received much attention recently [1–5]. Applications such as use in stationary phases for high resolution gas chromatography have been reported [6–12]. A significant advancement in this respect was achieved by coupling mesomorphic monomers to a stable polysiloxane polymer. It has generally been thought that nematic phases give improved resolution over smectic phases in gas chromatography due to greater diffusion in the former, and thus, possess higher efficiency. How-

ever, improved selectivity was achieved by using smectic phases [6].

This study provides three new side chain liquid crystalline polysiloxane polymers containing an oligo(ethylene oxide) monomethyl group as their respective terminal group. The side chain molecules of the liquid crystalline polysiloxane polymers in the mesophase temperature region form an ordered arrangement as shown in Scheme 1.

Polynuclear aromatic hydrocarbons (PAHs) are a group of chemicals with two or more fused benzene rings (see Fig. 1). The United States Environmental Protection Agency lists PAHs as priority pollutants,



Scheme 1.

since some are carcinogens or mutagens. Some of them, pairs of 5–6, 8–9–10, 11–12 and 13–15, are isomeric compounds, and can not be thoroughly resolved, with the exception of compounds 13–15, by commercial GC–MS capillary columns (e.g. HP-5 and Ultra 2 capillary columns from Hewlett–Packard

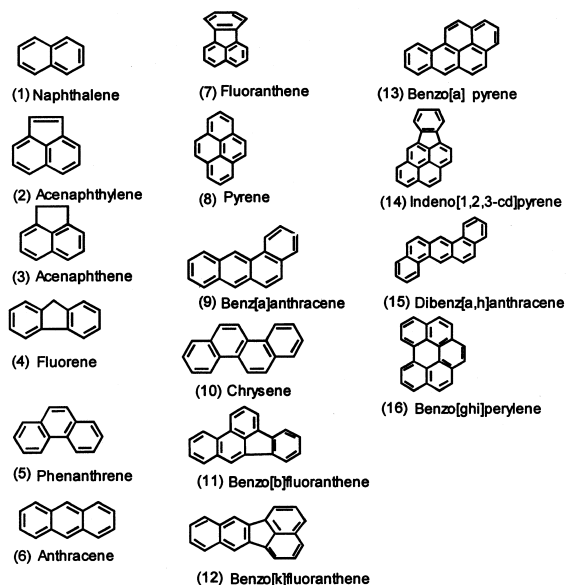


Fig. 1. Molecular structure of Supelco 610M PAHs standard mixtures.

and CP-sil PAH-CB from Chrompack). In this study, we will use these polymer materials as stationary phases for GC–MS chromatography to test their chromatographic behavior and compare the selectivity of the SCLCP stationary phase columns with commercial capillary columns.

As far as we know, this is the first example of side chain liquid crystalline polysiloxane polymers containing an oligo(ethylene oxide) monomethyl group which are attached to the mesogenic groups.

2. Experimental

2.1. Materials

The stationary phase materials used in this study are polysiloxane polymers PBPBE1, PBPBE2 and PBPBE3. Their synthesis procedures have been reported in our previous papers [13,14]. The mesophase type and transition temperatures are listed in Table 1. The polysiloxane polymers have an average molecular mass of 18 900, with a polydispersity of 2.8 as measured by gel permeation chromatography (polystyrene standards).

3. Technique

The properties of the liquid crystalline polysiloxane polymers were determined by using a differential scanning calorimeter (Perkin–Elmer DSC-7), a polarized optical microscope (Olympus BH-2 with a

Table 1

Thermal transition temperature (°C), mesophase types and enthalpies changes for the liquid crystalline polysiloxane polymers PBPBE1, PBPBE2 and PBPBE3

Polymers	Heating rate (10°C min ⁻¹) cooling rate (10°C min ⁻¹)
PBPBE1	<i>S</i> _c 286°C (4.3 J g ⁻¹) <i>I</i> <i>I</i> 274°C (1.2 J g ⁻¹) <i>S</i> _c
PBPBE2	<i>S</i> _c 214.0°C (1.1 J g ⁻¹) <i>I</i> <i>I</i> 206°C (0.8 J g ⁻¹) <i>S</i> _c
PBPBE3	<i>T</i> _g 40°C <i>S</i> _c 148°C (3.8 J g ⁻¹) <i>I</i> <i>I</i> 142°C (3.5 J g ⁻¹) <i>S</i> _c 38°C <i>T</i> _g

*T*_g: glassy state; *S*_c: smectic C mesophase; *I*: isotropic phase.

LINKAM THMS 600 hot stage) and an X-ray diffractometer (Siemens D5000 apparatus).

3.1. Capillary column preparation

Preparation procedures for the three capillary columns coated with polymers PBPBE1, PBPBE2 and PBPBE3 are similar. Taking PBPBE1 as an example: a fused-silica capillary tube with 0.32 mm I.D. (Hewlett–Packard, Avondale, PA, USA) was used. The capillary column was washed with 20 cm³ methylene chloride before coating. The stationary phase, 20 mg of polysiloxane polymer PBPBE1, was dissolved in 10 cm³ methylene chloride, which was degassed before use. The coating solution was filtered before use by a syringe filter (PTFE, pore size 0.2 μm). The filtered solution was placed in a screw cap septum bottle and was forced through the capillary by nitrogen gas. After filling, the column was sealed at one end with a microflame gas torch. The column was then vacuumed and the solvent evaporated, completing static coating. The sealed end of the column was next cut off and cross-linking was performed by injection of vapor phase *azo-tert.*-butane (Lancaster, UK) with a nitrogen carrier at room temperature for 30 min and a flow-rate of 10 cm³ min⁻¹. Both ends of the column were sealed and then the column was heated from 50°C to 220°C at 20°C min⁻¹ and remained at 220°C for 1 h. Both ends of the column were reopened and the column was cleaned with 10 cm³ methylene chloride with a nitrogen carrier, then dried with pure nitrogen. Finally, the column was installed on a gas chromatography apparatus and conditioned at 260°C for 12 h by a continuous nitrogen stream at 1.2 cm³ min⁻¹. The column prepared for the chromatogram tests was 30 m long with an internal diameter of 0.32 mm. The gum film of the coated SCLCP was 0.2 μm thick.

3.2. Column evaluation

The solute standards were obtained commercially from Supelco (610M PAHs standard mixture). A Hewlett–Packard Model 5890 series II gas chromatograph equipped with a 5972 series mass-selective detector and 6890 series injector with an autosampling controller was used for column evalua-

tion. Helium was used as the carrier gas at a constant volume flow-rate of 1.2 cm³ min⁻¹.

4. Results and discussion

Polymers PBPBE1, PBPBE2 and PBPBE3 have similar molecular structure except for the terminal group having one, two and three oligo(ethylene oxide) units respectively. Polymers PBPBE1 and PBPBE2 are brittle at room temperature, whereas polymer PBPBE3 is soft. Polymers PBPBE1 and PBPBE2 show only a mesophase/isotropic transition temperature in the heating and cooling scans. However, polymer PBPBE3 displays a glass transition temperature and a mesophase transition temperature. From X-ray diffraction analysis, we find a reflection peak at the small angle region, which is indicative of smectic mesophase. The values of the calculated layer spacing (calculated by the Bragg equation) are much smaller than two times the length of the side chain molecule, when the side chain is fully extended. Therefore the side chain molecule tilts toward the polysiloxane polymer backbone (is not perpendicular to the backbone) and we consider it a smectic C mesophase. The transition temperatures, thermodynamics data and the mesophase type of the polysiloxane polymers are listed in Table 1. The resulting polymers show a higher smectic/isotropic transition temperature than those of our previous report in which an oxycarbonylphenyl-4-yl 4-phenylbenzoate was used as a mesogenic group [14]. The mesophase/isotropic transition temperature drops and the mesophase temperature range narrows as well, with increasing length of the terminal group for both the polymers of the previous report and of this report. Rather small variations in terminal group length lead to rather large changes of terminal behavior of the polysiloxane polymers in mesophase transition temperatures and mesophase temperature regions.

Figs. 2–5 respectively illustrate the chromatograms of the PAH mixtures resulting from use of PBPBE1, PBPBE2 and PBPBE3 as the stationary phase and a commercial column (HP-5, Hewlett–Packard, crossed-linked 5% phenyl methyl silicone). Peaks were identified by comparison with the retention time of peaks generated by pure single-PAH samples. As seen from Figs. 2 and 3 and Fig. 4, all

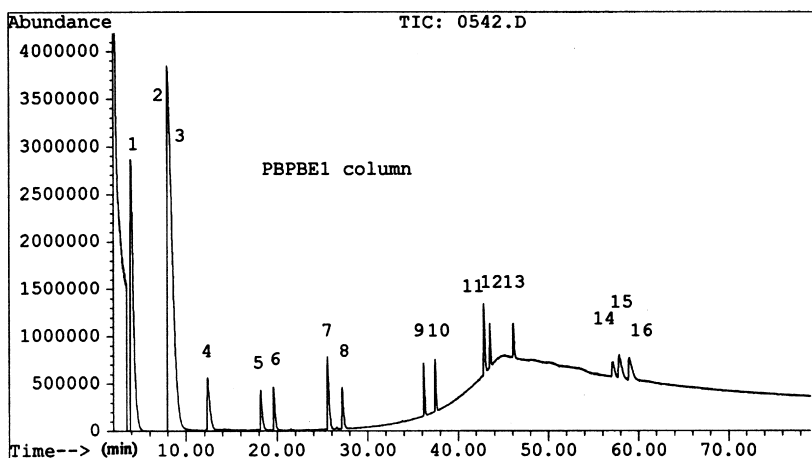


Fig. 2. Chromatograms of Supelco 610M PAHs standard mixtures with PBPBE1 liquid crystalline polysiloxane polymer as the stationary phase. Temperature programmed from 50°C to 100°C at 20°C min⁻¹ and to 260°C at 3°C min⁻¹; splitless injection.

sixteen standard PAH species except acenaphthylene (compound 2, Fig. 2) and acenaphthene (compound 3, Fig. 2) can be thoroughly resolved. By inspection of the PAHs with failed resolution, we find the shape factor (length/width ratio of solutes molecule) to be the dominant separation mechanism in SCLCP. It is worth noting that the chromatographic peaks of the critical pairs (compounds 5–6, 9–10 and 11–12) are very close. Using the chromatographic behavior of the above four columns, we compared the values of

the calculated peak resolution (R_s), separation factor (α), retention factor (k') and theoretical plates (N) for PBPBE1, PBPBE2, PBPBE3, and the commercial capillary column, which are listed in Table 2 based on the three critical PAH pairs 5–6, 9–10 and 11–12. In Table 2, we find the PBPBE3 capillary column shows the highest theoretical plates among the three SCLCP columns. The theoretical plates increase with the length of the terminal group of the polysiloxane polymers. This is attributed to the better

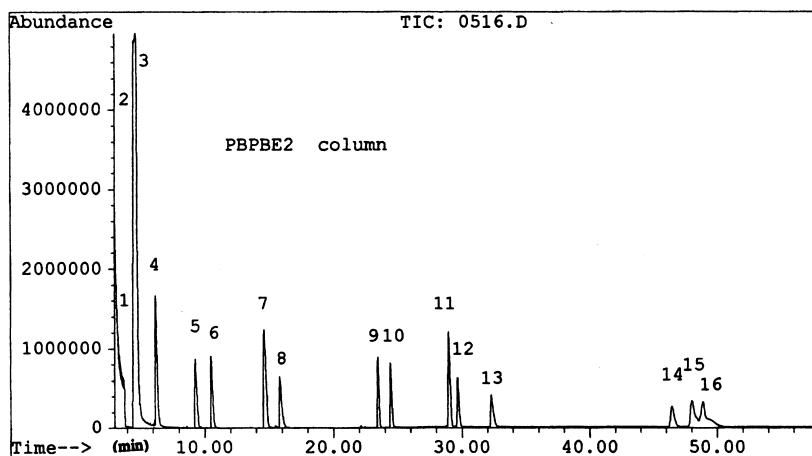


Fig. 3. Chromatograms of Supelco 610M PAHs standard mixtures with PBPBE2 liquid crystalline polysiloxane polymer as the stationary phase. Temperature programmed from 50°C to 120°C at 20°C min⁻¹ and to 240°C at 3°C min⁻¹; splitless injection.

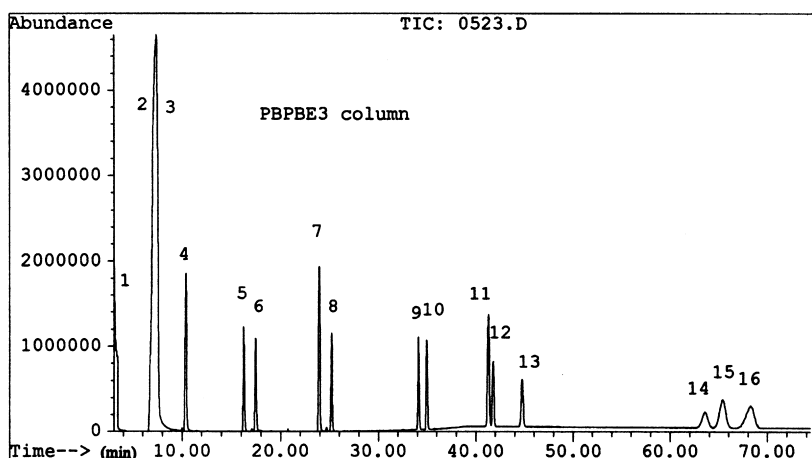


Fig. 4. Chromatograms of Supelco 610M PAHs standard mixtures with PBPBE3 liquid crystalline polysiloxane polymer as the stationary phase. Temperature programmed from 50°C to 70°C at 10°C min⁻¹ and to 220°C at 4°C min⁻¹; splitless injection.

film-forming ability of the polysiloxane polymer. The peak resolutions (R_s) of the three SCLCP columns are higher than those of the commercial capillary column. In terms of the calculated theoretical plates (N), the commercial capillary column is higher than the SCLCP column.

Fig. 6 shows the relationship of the separation factors for anthracene (6) vs. phenanthrene (5) and chrysene (10) vs. benz[*a*]anthracene (9) with the reciprocal column temperature when using PBPBE1,

PBPBE2 and PBPBE3 column and commercial capillary column (HP-5). The PBPBE1, PBPBE2 and PBPBE3 columns show better resolution than the commercial capillary column. What's more, polymer PBPBE1 shows the largest separation factor. As observed in Fig. 6, the temperature ranges of chromatographic separation ability, 115°C [anthracene (6) vs. phenanthrene (5)] and 120°C {chrysene (10)/benz[*a*]anthracene (9)} for the PBPBE1 column, 80°C [anthracene (6) vs. phenan-

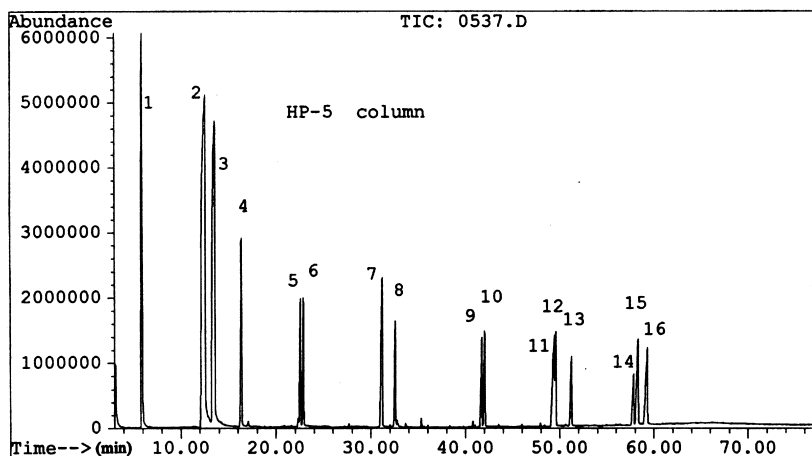


Fig. 5. Chromatograms of Supelco 610M PAHs standard mixtures with HP-5 commercial capillary column. Temperature programmed from 50°C to 100°C at 20°C min⁻¹ and to 290°C at 3°C min⁻¹; splitless injection.

Table 2

The values of the peak resolution (R_s), separation factor (α), retention factor (k') and theoretical plates (N) for the critical pair compounds, 5–6, 9–10 and 11–12

Parameter	PBPBE1			PBPBE2			PBPBE3			Commercial capillary column		
	5–6	9–10	11–12	5–6	9–10	11–12	5–6	9–10	11–12	5–6	9–10	11–12
R_s	4.6	3.98	3.1	4.2	5.0	2.3	4.8	3.9	3.04	1.6	1.24	0.5
α	1.14	1.10	1.08	1.13	1.04	1.03	1.09	1.03	1.03	1.01	1.01	1.003
k'	14.0	37.1	45.7	9.74	23.4	28.7	16.5	34.98	40.79	21.9	41.05	48.60
	(based on 5)	(based on 9)	(based on 11)	(based on 5)	(based on 9)	(based on 11)	(based on 5)	(based on 9)	(based on 11)	(based on 5)	(based on 9)	(based on 11)
N	22 530	92 854	92 618	30 508	238 436	179 497	78 122	404 496	272 836	209 764	418 509	983 984
	(based on 5)	(based on 9)	(based on 11)	(based on 5)	(based on 9)	(based on 11)	(based on 5)	(based on 9)	(based on 11)	(based on 5)	(based on 9)	(based on 11)

threne (5)] and 85°C [chrysene (10)/benz[*a*]anthracene (9)] for the PBPBE2 column, and 70°C [anthracene (6) vs. phenanthrene (5)] and 75°C [chrysene (10)/benz[*a*]anthracene (9)] for the PBPBE3 column, are all wider than those for the commercial capillary column, which are 60°C [anth-

racene (6) vs. phenanthrene (5)] and 65°C [chrysene (10)/benz[*a*]anthracene (9)]. In order to test the chromatographic behavior, authentic coal tar (a gift from the China Steel Chemical Corporation) was used. Fig. 7a and b and Fig. 8a–c respectively show the chromatograms of the coal tar by the use of

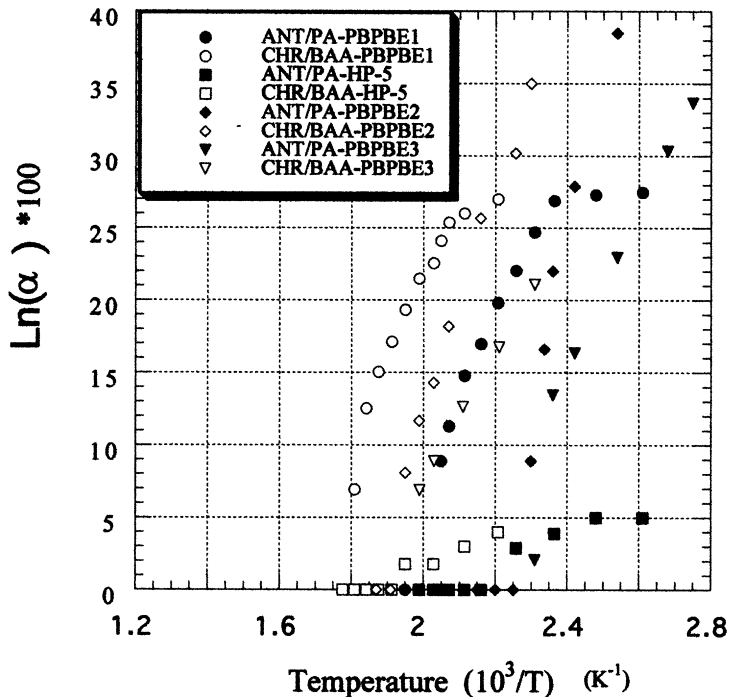


Fig. 6. Relationship between the natural logarithm of separation factor and reciprocal column temperature for anthracene (6)/phenanthrene (5) and chrysene (10)/benz[*a*]anthracene (9) on PBPBE1, PBPBE2, and PBPBE3 capillary column and commercial capillary column.

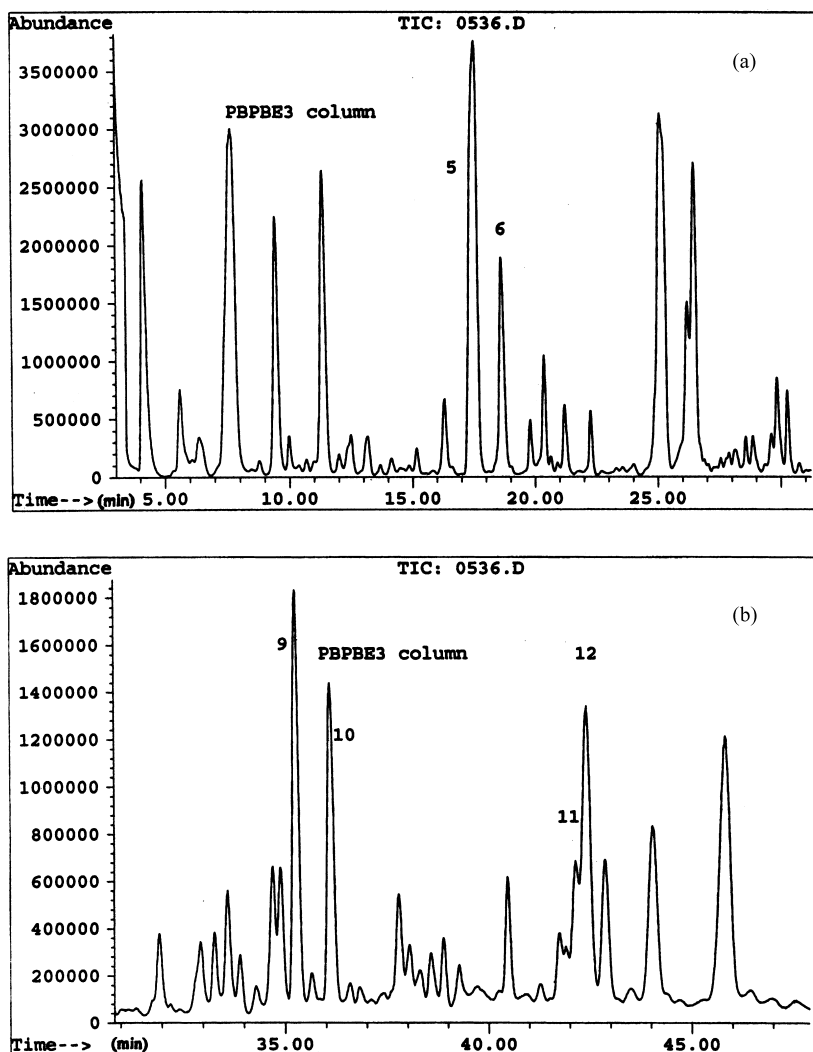


Fig. 7. (a,b) Chromatograms of coal tar on polysiloxane polymer PBPBE3. Temperature programmed from 50°C to 70°C at 10°C min⁻¹ and to 220°C at 4°C min⁻¹, splitless injection.

liquid crystalline polysiloxane polymer PBPBE3 and HP-5. Comparing Fig. 7 with Fig. 8, we found the PBPBE3 column obtained better chromatograms than the commercial capillary column for the authentic coal tar sample. Several peaks in Fig. 7 look like an overlapped peak, cf. peaks 11 and 12 for example. In addition, the resolution is much better on the PBPBE3 column, although the new phases give an interesting and maybe useful orthogonal selectivity and high enough efficiency that they can be rec-

ommended as complementary stationary phases for isomeric PAHs.

Acknowledgements

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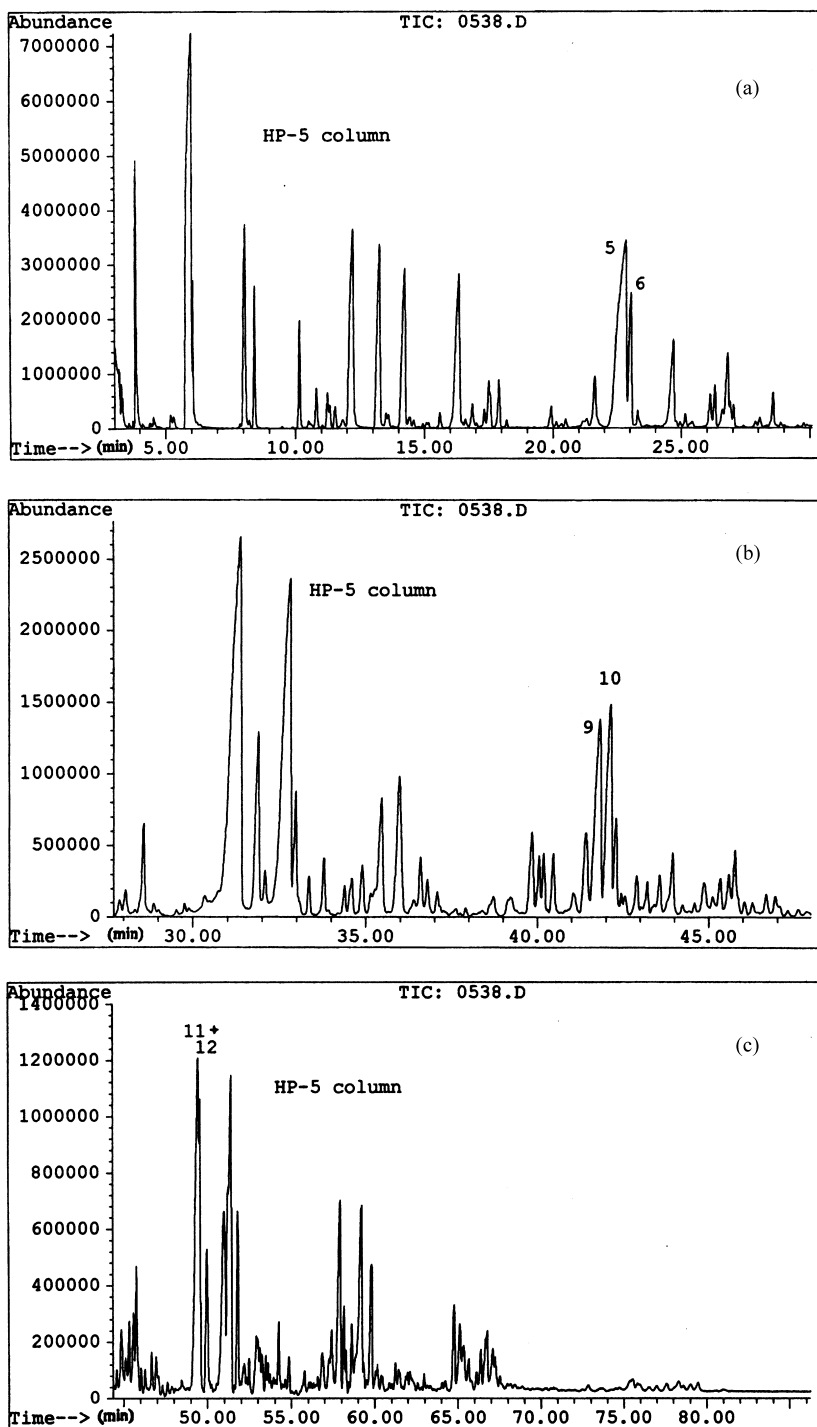


Fig. 8. (a,b,c) Chromatograms of coal tar on commercial capillary column. Temperature programmed from 50°C to 70°C at 10°C min⁻¹ and to 220°C at 4°C min⁻¹; splitless injection.

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