

Short Communication

Comparison of crown ether side-chain polysiloxanes with and without liquid crystalline character as stationary phases for capillary gas chromatography

Wei Zhou, Ruonong Fu* and Rongji Dai

Department of Chemical Engineering, Beijing Institute of Technology, Beijing, 100081 (China)

Zaifu Huang and Yanfei Chen

Department of Environmental Science, Wuhan University, Wuhan (China)

(First received August 4th, 1993; revised manuscript received October 19th, 1993)

ABSTRACT

Two new GC stationary phases were prepared, one a side-chain liquid crystalline polysiloxane containing crown ether (PSC-11), and the other a new kind of side-chain crown ether (PSCP-11-15C-5) which has a similar structure to PSC-11. The main chromatographic characteristics, including efficiency, polarity and selectivity, were examined and compared. The mechanism of specific selectivity for positional isomer compounds based on the crown ether ring and liquid crystal is discussed.

INTRODUCTION

Crown ethers are used as chromatographic stationary phases because of the good selectivity resulting from the cavity structure and strong electronegative effect of heteroatoms on crown ether ring. A few papers have appeared concerning the use of side-chain crown ether polysiloxanes as stationary phases for capillary GC since 1988 [1–4]. On the other hand, side-chain liquid crystal polysiloxanes were first used as stationary phases in GC in 1982 by Finkelmann *et al.* [5]. Both types have high efficiency and are suitable for the separation of geometrical isomeric compounds.

In 1989, Percec and Rodenhouse [6] synthesized several side-chain liquid crystalline polysiloxanes containing a crown ether. If crown ether compounds have mesomorphic properties, they may possess some special effects. So far, there is only one example of the use of this material as a stationary phase for GC, by our laboratory [7]. The aim of the work was to compare the chromatographic behaviours of a new kind of side-chain liquid crystalline polysiloxane containing crown ether (PSC-11) (Fig. 1) with those of a new kind of side-chain crown ether (PSCP-11-15C-5) (Fig. 1) which has a similar structure to PSC-11. As there is an isopropylidene group between two phenyls of the side-chain, this crown ether has no mesomorphic properties. The properties of specific selectivity

* Corresponding author.

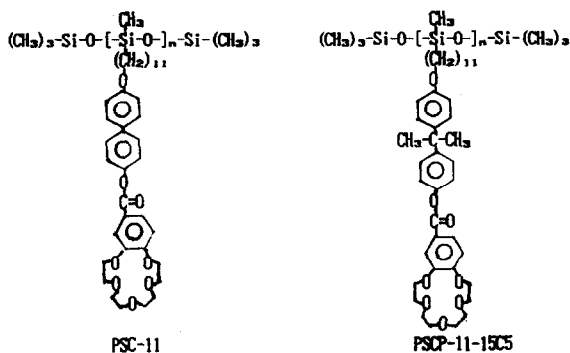


Fig. 1. Structures of the two stationary phases studied.

for positional isomeric compounds based on the crown ether ring and liquid crystal are also discussed. Once the features of mesomorphic crown ethers have been elucidated, it seems certain that their chromatographic characteristics will be improved.

EXPERIMENTAL

Synthesis of poly(methylsiloxane) containing 4-(10-undecen-1-yloxy)-4'-(4'-carboxybenzo-15-crown-5)biphenylside-chain (PSC-11)

PSC-11 was synthesized by the hydrosilylation of 4-(10-undecen-1-yloxy)-4'-(4'-carboxybenzo-15-crown-5)-biphenyl (OC-9) with poly(methylhydrosiloxane), which was prepared as described previously [7]. A 0.3210-g ($ca. 5 \times 10^{-4}$ mol) amount of OC-9 (obtained from the Department of Environmental Science, Wuhan University, China) and 0.0324 g (0.0000143 mol) of poly(methylhydrosiloxane) (Merck-Schuchardt, Hohenbrunn bei München, Germany; degree of polymerization = 35) were dissolved in 17 ml of dry, freshly distilled toluene in a dry, three-necked, round-bottomed flask. The reaction mixture was heated to 110°C under nitrogen and 44 μl of fresh catalyst solution (0.0576 g of chloroplatinic acid dissolved in 10 ml of isopropyl alcohol) were injected. The temperature of the reaction mixture was held at 110°C until IR analyses showed that the hydrosilylation reaction was complete. generally, after 26 h the Si-H bond had almost disappeared. Ethylene was then bubbled through the mixture for 1 h to react with all of the residual Si-H units. Purification was performed by several precipitations from metha-

nol. The product was centrifuged at $ca. 10\,000$ g and 6°C for 30 min and dried in air to remove the solvent.

Synthesis of poly(methylsiloxane) containing 2-[4-(10-undecen-1-yloxy)-phenyl]-2-[4'-(4'-carboxybenzo-15-crown-5)phenyl]propane (PSCP-11-15C-5)

The synthesis method is the same as that for PSC-11 above except that 0.2765 g of 2-[4-(10-undecen-1-yloxy)phenyl]-2-[4'-(4'-carboxybenzo-15-crown-5)phenyl]propane (CP-9) and 0.0195 g of poly(methylhydrosiloxane) were used.

Technique

Thermal transitions were determined using a Perkin-Elmer DSC-7 differential scanning calorimeter. A hot-stage light-polarized microscope was used to observe the thermal transition temperature and to analyse the anisotropic textures.

Column preparation

Fused-silica capillaries (0.25 mm I.D.) (Yongnian Optical Fibre Factory, Hebei, China) were used. The capillaries were purged with nitrogen at 240°C for 6 h before coating. The capillaries were statically coated with a solution of 0.4–0.5% (w/v) PSC-11 or PSCP-11-15C-5 in dichloromethane and flushed with nitrogen for 2 h and then conditioned at 120, 140, 160, 180 and 200°C for 2 h each and finally at 220°C for 4 h.

Column evaluation

The GC separations were carried out on an SP-3700 gas chromatograph (Beijing Analytical Instrument Factory, Beijing, China) equipped with a flame ionization detector using nitrogen as carrier gas. The output of the detector was connected to an HP-3390A integrator. Solutes were injected using the split mode (80:1). The polarity of the columns was tested by measuring the McReynold's constants.

RESULTS AND DISCUSSION

The transition temperatures of the monomers (OC-9 and CP-9) and polymers (PSC-11 and PSCP-11-15C-5) were measured by using a hot-

TABLE I
LIQUID CRYSTALLINE TRANSITION TEMPERATURES OF OC-9, PSC-11, CP-9 AND PSCP-11-15C-5 OBTAINED USING A HOT-STAGE POLARIZED MICROSCOPE

Material	Transition temperature (°C) ^a	
	Heating	Cooling
OC-9	k 120 n 137 i	k 101 n 137 i
PSC-11	k 143 n 190 i	k 90 n 189 i
CP-9	s 93 l	
PSCP-11-15C-5	s 98 l	

^a Abbreviations: k = crystalline; n = nematic; s = smectic; i = isotropic; l = liquid.

stage light-polarized microscope. The results are given in Table I. The phase transition temperatures determined with a Model DSC-7 apparatus are given in Table II. The data suggest that the polymer PSC-11 has a wider mesomorphic temperature range than that of the monomer (OC-

TABLE II
PHASE TRANSITION TEMPERATURE OF OC-9, PSC-11, CP-9 AND PSCP-11-15C-5 OBTAINED USING THE DSC-7

Stationary phase	Transition temperature (°C) ^a	
	Heating	Cooling
OC-9	k 117 n 136 i	k 96 n 133 i
PSC-11	s 141 s 169 n 199 i	s 90 s 108 s 157 n 194 i
CP-9	s 94 l	
PSCP-11-15C-5	s 101 l	

^a See Table I.

TABLE III
CHARACTERISTICS OF PSC-11 AND PSCP-11-15C-5 CAPILLARY COLUMNS

Compound tested: anthracene.

Stationary phase	Film thickness (μm)	k	Column temperature (°C)	Flow-rate (cm/s)	Column efficiency (plates/m)
PSC-11	0.30	14.9	190	14.7	4410
PSCP-11-15C-5	0.27	11.6	190	13.3	3390

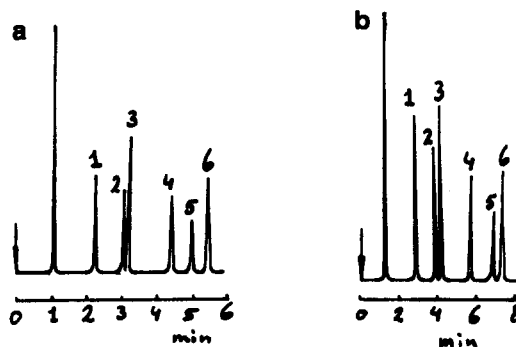


Fig. 2. Chromatograms of substituted naphthalenes on (a) PSC-11 and (b) PSCP-11-15C-5 columns at 160°C. Peaks: 1 = naphthalene; 2 = 2-methylnaphthalene; 3 = 1-methylnaphthalene; 4 = 2,6-dimethylnaphthalene; 5 = 1,5-dimethylnaphthalene; 6 = 1,2-dimethylnaphthalene.

9), whereas PSCP-11-15C-5 has no mesomorphic property. Because the mesomorphic temperature range of PSC-11 is suitable for the cGC separation of a variety of isomeric compounds, it meets the demands for a stationary phase.

Table III summarizes the chromatographic properties of the two types of stationary phase. The data indicate that PSC-11 possesses a higher column efficiency than PSCP-11-15C-5 and the reproducibility is good. As PSCP-11-15C-5 has an isopropylidene group between two phenyls of the side-chain, it has no mesomorphic property and the movement of the crown ether ring is less flexible than that of the previously studied PSO-B-15C-5 [2]. As a result, its film-forming ability is lower than that of PSC-11 and PSO-B-15C-5 [2].

The polarities of these two stationary phases are expressed by the McReynolds constants at 120°C (Table IV). It is found that these two novel stationary phases have moderate polarity

TABLE IV

McREYNOLDS CONSTANTS OF THE PSC-11 AND PSCP-11-15C-5 COLUMNS

Stationary phase	McReynolds constants ^a						
	X'	Y'	Z'	U'	S'	Av. polarity	b
PSC-11	201	336	238	397	345	303	0.2391
PSCP-11-15C-5	217	308	260	355	314	291	0.2536
Carbowax-20M ^b	322	536	368	572	510	462	0.2235
PSO-B-15C5 ^c	121	254	192	293	284	229	—
Liquid crystalline copolymer ^d	251	264	330	429	420	339	—

^a X' = benzene; Y' = 1-butanol; Z' = 2-pentanone; U' = nitropropane; S' = pyridine; b = slope of the curve obtained when the logarithm of the adjusted retention times of *n*-alkanes are plotted as a function of the number of carbon atoms.

^b From ref. 8.

^c From ref. 2.

^d From ref. 9.

between those of Carbowax-20M and PSO-B-15C-5, and therefore are suitable for the separation of polar and easily polarizable compounds.

Fig. 2 shows the excellent separations of substituted naphthalenes on both PSC-11 and PSCP-11-15C-5. The results demonstrate that these two stationary phases have unique selectivity for the separation of substituted naphthalenes.

Fig. 3a illustrates the separation of substituted benzenes on PSC-11 and Fig. 3b shows the same separation on PSCP-11-15C-5. 2,3-DNT and 2,4-DNT coeluted on the latter stationary phase.

The chromatograms suggest that because PSC-11 has mesomorphic properties, its chromatographic characteristics are superior for the separation of substituted benzenes.

ACKNOWLEDGEMENT

This work was kindly supported by the National Science Foundation of China.

REFERENCES

- 1 C.Y. Wu, C.-M. Wang, Z.-R. Zeng and X.-R. Lu, *Anal. Chem.*, 62 (1990) 968.
- 2 J. Ge, R. Fu, A. Zhang, Z. Huang and B. Zhang, *J. Microcolumn Sep.*, 3 (1991) 121.
- 3 A. Zhang, J. Ge, Z. Guan, J. Deng, H. Liu, J. Zhu, R. Fu, Z. Huang and B. Zhang, *J. Chromatogr.*, 521 (1990) 128.
- 4 C.A. Rouse, A.C. Finlinson, B.J. Tarbet, J.C. Pixton, N.M. Djordjevic, K.E. Markides, J.S. Brandshaw and M.L. Lee, *Anal. Chem.*, 60 (1988) 901.
- 5 H. Finkelmann, R.J. Laub, W.L. Robert and C.A. Smith, in M. Cooke, A.J. Dennis and G.L. Fischer (Editors), *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry*, Columbus, OH, 1982, p. 275.
- 6 V. Percec and R. Rodenhouse, *Macromolecules*, 22 (1989) 4408.
- 7 R. Fu, P. Jing, J. Gu, Z. Huang and Y. Chen, *Anal. Chem.*, 65 (1993) 2141.
- 8 W.O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 9 H. Wang, T. Gen, R. Fu, J. Zhu, X. Wei, H. Li and J. Liu, *J. Chromatogr.*, 609 (1992) 414.

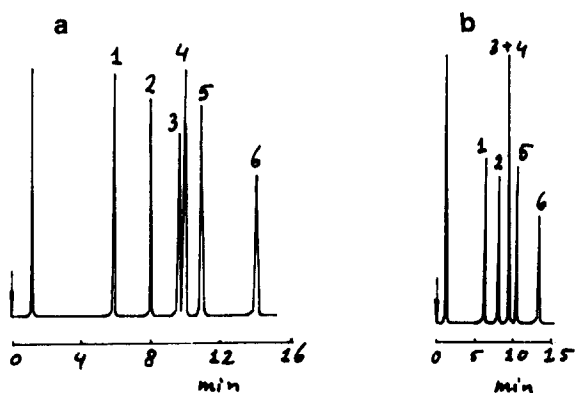


Fig. 3. Chromatograms of dinitrotoluene (DNT) isomers on (a) PSC-11 and (b) PSCP-11-15C-5 columns at 180°C. Peaks: 1 = 2,6-DNT; 2 = 2,5-DNT; 3 = 2,3-DNT; 4 = 2,4-DNT; 5 = 3,5-DNT; 6 = 3,4-DNT.