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Unusual behaviour of a new kind of side chain crown ether polysiloxanes used in capillary gas chromatography

Peng Jing^a, Ruonong Fu^{b,*}, Wei Zhou^b, Rongji Dai^b, Zaifu Huang^c, Yanfei Chen^c

^a*Department of Applied Chemistry and Fine Chemical Engineering, College of Chemical Engineering, Xi'an Jiaotong University, Shaanxi Prov., 710049, China*

^b*Department of Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China*

^c*Department of Environmental Science, Wuhan University, Wuhan 430072, China*

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Abstract

A new side chain crown ether polysiloxane (PSCP-3-15C5) has been prepared and characterized in chromatography. Its chromatographic behaviour was compared with that of the other side chain crown ether polysiloxane (PSCP-11-15-C5), which has a longer spacer. The unusual effects caused by the length of the spacer on the polysiloxane backbone are described. An interesting phenomenon, liquid–liquid transition occurring in the measurement of phase transition on PSCP-3-15-C5, is discussed.

Keywords: Stationary phases, GC; Polysiloxanes; Crown ether polysiloxanes

1. Introduction

Crown ethers have found wide application in analytical chemistry. Due to their special structure and the strong electronegative effect of heteroatoms on the crown ether ring, they are capable of strong interaction with polar compounds and are used as solvent extraction reagents, membranes for ion selective electrodes, etc. The use of crown ethers in gas chromatography began in 1985 [1] and showed that the stationary phase exhibits a unique separation power for polar compounds. Since then, a few crown ethers with small molecular masses have been developed as stationary phases [2–4]. However, the difficulty of coating them on the capillary columns and their low thermal stability hindered their useful-

ness as new stationary phases. The shortcomings were overcome by employment of a polysiloxane backbone with a substituted crown ether as the stationary phase, as reported first by Rouse et al. [5]. Thereafter, many new polysiloxane stationary phases have been prepared and used for GC separation [6–11]. Since almost all new crown ether stationary phases developed in capillary gas chromatography are based on the polysiloxane backbone, substitution on the backbone is diverse, depending on different chromatographic needs.

Our previous paper [12] has discussed the performance of poly(methylsiloxane) containing 2-[4-(10-undecan-1-yloxy)-phenyl]-2-[4'-(4'-carboxybenzo-15-crown-5)phenyl]propane (PSCP-11-C5) for GC separation. Its main chromatographic characteristics were examined. Of particular interest has been the influence on column performance of the spacer

*Corresponding author.

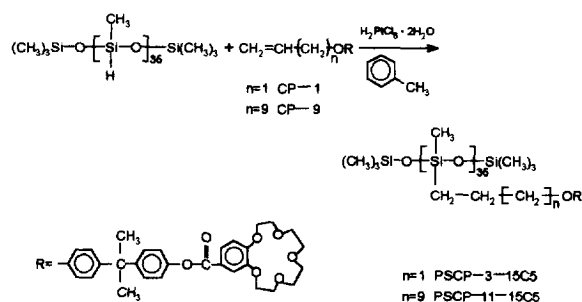


Fig. 1. Scheme of the preparation of PSCP-3-15-C5 and PSCP-11-15-C5.

between the polysiloxane backbone and the crown ether group. In this work, a new short-spacer side chain crown ether polysiloxane, 2-[4-(3-propane-1-yloxy)-phenyl]-2-[4'-(4'-carboxybenzo-15-crown-5)-phenyl]propane (PSCP-3-15-C5) has been synthesized (see Fig. 1). Its chromatographic properties have been examined and compared with those of PSCP-11-15-C5. The results obtained show that the spacer on the polysiloxane backbone plays a role in its film-forming ability and selectivity. This paper also describes a puzzling phenomenon, liquid-liquid transition, caused by alternation of column temperature.

2. Experimental

2.1. Synthesis of poly(methylsiloxane) containing 2-[4-(3-propane-1-yloxy)-phenyl]-2-[4'-(4'-carboxybenzo-15-crown-5)phenyl]propane (PSCP-3-15-C5)

Poly(methylsiloxane) containing 2-[4-(3-propane-1-yloxy)-phenyl]-2-[4'-(4'-carboxybenzo-15-crown-5)phenyl]propane (PSCP-3-15-C5) was prepared by a hydrosilylation reaction between poly(methylhydro)siloxane and 2-[4-(3-propen-1-yloxy)phenyl]-2-[4'-(4'-carboxy-benzo-15-crown-5)phenyl]propane (CP-1) as described previously [11] (See Fig. 1). A mixture of 0.28 g of CP-1 (obtained from the Department of Environmental Science, Wuhan University), 0.03 g of poly(methylhydro)siloxane [Merck-Schuchardt (Schuchardt, Hohenbrunn, Germany)]; the polymerization degree of the polymer

used for synthesis of PSCP-3-15-C5 and PSCP-11-15-C5 is 35] and 25 ml of pure toluene in a dry, three-necked flask was stirred under a nitrogen atmosphere. A 25- μl volume of fresh catalyst solution (11.4 mg of chloroplatinic acid/1 ml of isopropanol) was injected. The reflux temperature was held at 110°C until IR analysis showed that the Si-H bond had almost disappeared (after 24 h). Ethylene was then bubbled through the mixture to react all of residual Si-H units. Purification was performed by several precipitations from methanol. The product was dried overnight in a vacuum oven.

2.2. Instrumentation

A Varian SP-3700 gas chromatograph, equipped with a flame ionization detector, and a Hewlett-Packard Model 3390A integrator were used for chromatographic evaluation. Fused-silica capillaries were obtained from Yongnian Optical Fibre Factory (Hebei Prov., China). Determination of the transition temperature for the crown ether was performed with a Perkin-Elmer Model DSC-7 differential scanning calorimeter (Perkin-Elmer). The retention times were obtained by two injections of a solution of test probes. All test probes used are of analytical reagent grade.

2.3. Column preparation

For comparison, column PSCP-3-15-C5 was prepared using the same method as that used for column PSCP-11-15-C5, as described previously [12].

3. Results and discussion

To compare PSCP-3-15-C5 and PSCP-11-15-C5, anthracene and 1-octanol were employed as test compounds to measure the column efficiency. The results are given in Table 1. The data show that PSCP-3-15-C5 possesses lower column efficiency (less than 1500 plates/m) than PSCP-11-15-C5 does (3000 plates/m), which indicates that the crown ether polysiloxane with a long and flexible spacer is coated on the capillary wall more easily than that with a short and rigid spacer. The higher column efficiency of PSCP-11-15-C5 could be explained by

Table 1
Column efficiency of PSCP-3-15-C5 and PSCP-11-15-C5

Column size (m×mm)	Stationary phase	Film thickness (μm)	Column temperature (°C)	Linear velocity (cm/s)	Column efficiency (plates/m)	Compound tested ^a
10×0.25	PSCP-3-15-C5	0.29	160	11.5	1053	O
10×0.25	PSCP-3-15-C5	0.29	220	11.0	1538	A
10×0.25	PSCP-11-15-C5	0.27	180	16.0	3070	A

^a O, 1-octanol; A, anthracene

the fact that the long non-polar spacer may lower its viscosity and therefore lead to better diffusivity of the solutes.

Measurements of selectivity and polarity of the two crown ether stationary phases are given by the McReynolds' constant (ΔI), retention index (I) and the average polarity (see Table 2). Comparison of the

values of the average polarity shows that shortening of the chain length can increase the average polarity. The retention indices of five McReynolds' probes indicate that these probes elute in different sequences on the two columns, namely, the elution sequence on column PSCP-3-15-C5 is benzene; 1-butanol; pyridine; nitropropane; 2-pentanone, and on the

Table 2
McReynolds' constants of PSCP-3-15-C5 and PSCP-11-15-C5^a

Stationary phase		McReynolds constants					Average polarity
		X'	Y'	Z'	U'	S	
PSCP-3-15-C5	I	872	930	1202	1082	1077	388
	ΔI	219	340	575	430	378	
PSCP-11-15-C5 ^b	I	870	898	887	1007	1013	291
	ΔI	217	308	260	355	314	

^a X', benzene; Y', 1-butanol; Z', 2-pentanone; U', nitropropane; S', pyridine.

^b From Ref. [12].

Table 3
Relative retention for positional isomers on PSCP-3-15-C5 and PSCP-11-15-C5

Compound tested	PSCP-3-15-C5			PSCP-11-15-C5		
	Relative retention (α)	Column temperature	Elution sequence ^a	Relative retention (α)	Column temperature	Elution sequence ^a
Xylene						
<i>o</i> -	1.29	80°C	<i>m,p,o</i>	1.27	90°C	<i>p,m,o</i>
<i>m</i> -	1.00			1.01		
<i>p</i> -	1.02			1.00		
Chlorotoluene						
<i>o</i> -	1.00	100°C	<i>o,m,p</i>	1.00	90°C	<i>o,m,p</i>
<i>m</i> -	1.07			1.07		
<i>p</i> -	1.14			1.11		
Bromotoluene						
<i>o</i> -	1.00	100°C	<i>o,p,m</i>	1.00	90°	<i>o,m,p</i>
<i>m</i> -	1.07			1.07		
<i>p</i> -	1.01			1.11		

^a The isomer listed on the left elutes earlier than those on the right.

PSCP-11-15-C5 column the elution order is benzene; 2-pentanone; 1-butanol; nitropropane and pyridine. Therefore, it can be concluded that the spacer on the polysiloxane backbone of this kind of crown ether stationary phase may influence its selectivity for some compounds. The data shown in Table 3 also confirm this conclusion. At the tested temperature, chlorotoluene isomers elute in the same sequence on column PSCP-3-15-C5 as on column PSCP-11-15-C5, however, the elution order of xylene and bromotoluene isomers on the PSCP-3-15-C5 column is different from that on the PSCP-11-15-C5 column. In addition, α values given in the table also demonstrate that PSCP-3-15-C5 exhibits higher selectivity for some isomers, e.g. *p*-chlorotoluene, and in some cases exhibits lower selectivity for others, e.g. *p*-bromotoluene, than does the PSCP-11-15-C5 column. It is suggested that the selectivity of two stationary phases is not determined only by the length of the spacer on the polysiloxane backbone.

Why do the two stationary phases having a given crown ether moiety exhibit different selectivity? A possible explanation may be that, if the spacer length is short enough, the restricted mobility of the less flexible chain could cause the analyte molecules to be sandwiched between two adjacent crown ether moieties. The interaction should then be by a selective charge transfer mechanism.

To determine the phase transition temperature for PSCP-3-15-C5, the partition ratio, k , of *n*-dodecane, the relative retention time (α) for 1-octanol–1-nonanol and anthracene–phenanthrene were calculated at 10°C intervals in the range of 60–200°C. Fig. 2A shows the $\log k$ vs. $1/T$ plot for *n*-dodecane. Fig. 2B, C show the $\log \alpha$ vs. $1/T$ plots for 1-octanol–1-nonanol and anthracene–phenanthrene, respectively. The significant changes in the slopes for PSCP-3-15-C5 can be found in the temperature ranges 70–80, 140–160 and 190–220°C. In order to investigate what occurs in these temperature ranges, differential scanning calorimetry (DSC) for PSCP-3-15-C5 was performed. Comparison of the phase-transition temperature of the two crown ethers determined by DSC and GC is summarized in Table 4. The results imply that the phase transition for PSCP-3-15-C5 in the temperature ranges of 140–160 and 190–220°C, and that for PSCP-11-15-C5 in the range of 170–190°C may be liquid–liquid transition rather than solid–

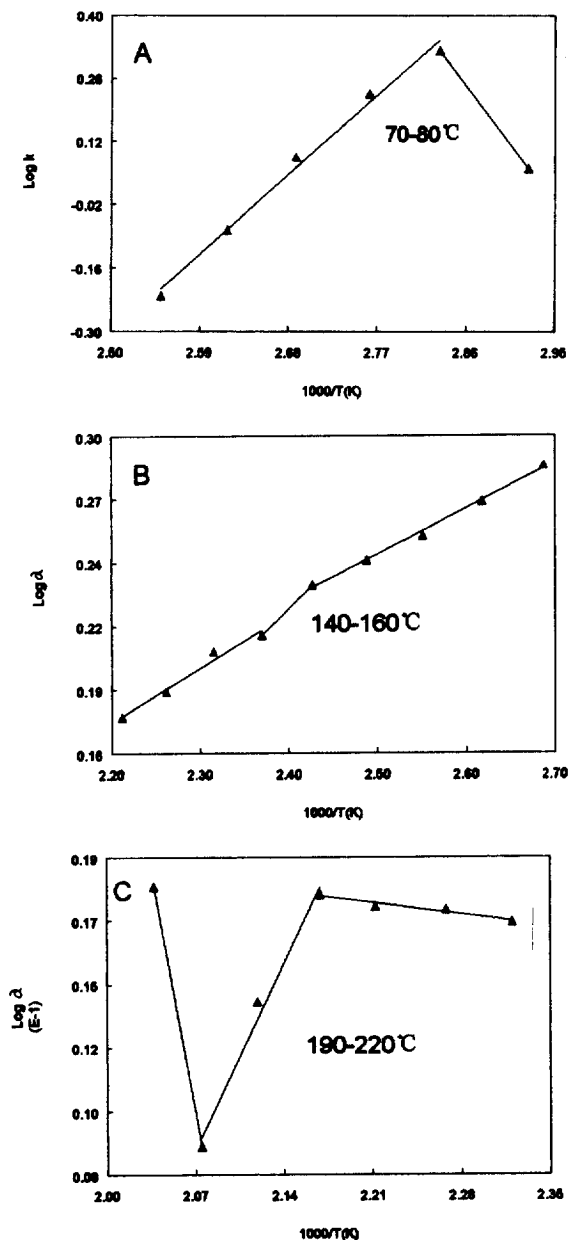


Fig. 2. (A) Plot of $\log k$ against the reciprocal of the absolute temperature for *n*-dodecane on the PSCP-3-15-C5 column. (B) Plot of $\log \alpha$ against the reciprocal of the absolute temperature for 1-octanol–1-nonanol on the PSCP-3-15-C5 column. (C) Plot of $\log \alpha$ against the reciprocal of the absolute temperature for anthracene–phenanthrene on the PSCP-3-15-C5 column.

Table 4
Phase transition temperature of PSCP-3-15-C5 and PSCP-11-15-C5

Column	Transition temperature	
	(DSC method)	(GC method)
PSCP-3-15-C5	70°C (s-l) ^a	70–80°C (s-l) 140–160°C (l-l); 190–220°C (l-l)
PSCP-11-15-C5 [16]	101°C (s-l)	90–110°C (s-l); 170–190°C (l-l)

^a l, liquid; s-solid.

liquid transition temperatures. The rationale for this is seen in Figs. 3–7, where reasonably good chromatographic peaks were obtained below or at the liquid–liquid transition temperature. If solid–liquid transition was occurring, adsorption of solutes, as evidenced by peak tailing and broadening, would dominate at temperatures below the transition temperatures. To the best of our knowledge, the liquid–liquid transition has been reported in several papers [1,6–10,13–16] in the research of other crown ether stationary phases. However, no one has mentioned the cause of the liquid–liquid transition. What leads to liquid–liquid transition on the crown ether stationary phases? It may be assumed to be a consequence of conformational changes in the crown ether ring, such as its stretching, twisting and folding, under the induction of a specific guest molecule (solute) when the column temperature is elevated. Such conformational changes of the crown ether ring, which produce heat changes that are too small to be

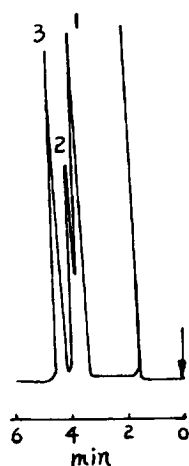


Fig. 3. Chromatogram of dichlorobenzene isomers on the PSCP-3-15C5 column (10 m×0.25 mm) at 110°C; peaks: 1, *m*-dichlorobenzene; 2, *p*-dichlorobenzene; 3, *o*-dichlorobenzene.

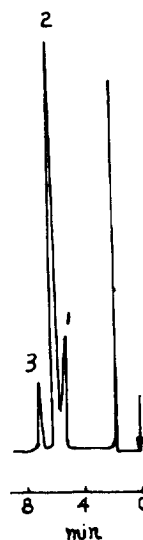


Fig. 4. Chromatogram of dimethyloxybenzene isomers on the PSCP-3-15-C5 column (10 m×0.25 mm) at 130°C; peaks: 1, *o*-dimethyloxybenzene; 2, *p*-dimethyloxybenzene; 3, *m*-dimethyloxybenzene.



Fig. 5. Chromatogram of nitrochlorobenzene isomers on the PSCP-3-15-C5 column (10 m×0.25 mm) at 150°C; peaks: 1, *m*-nitrochlorobenzene; 2, *p*-nitrochlorobenzene; 3, *o*-nitrochlorobenzene.

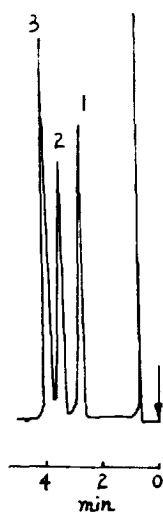


Fig. 6. Chromatogram of nitromethylbenzene isomers on the PSCP-3-15-C5 column (10 m×0.25 mm) at 160°C; peaks: 1, *o*-nitromethylbenzene; 2, *m*-nitromethylbenzene; 3, *p*-nitromethylbenzene.

detectable by DSC, influence its interaction with solutes. As a result, the transition temperature range above its melting temperature can be determined by GC. However, whether or not such conformational

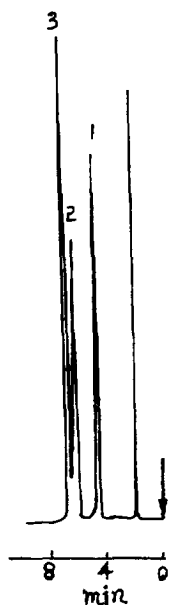


Fig. 7. Chromatogram of naphthalene derivatives on the PSCP-3-15-C5 column (10 m×0.25 mm) at 180°C; peaks: 1, naphthalene; 2, 2-methylnaphthalene; 3, 1-methylnaphthalene.

changes could influence the selectivity of the two crown ether stationary phases in the transition range (which is still being investigated in our laboratory) has not been determined so far.

4. Conclusion

For PSCP-3-15-C5 and PSCP-11-15-C5, the spacer on polysiloxane backbones influences their ability to form a film the capillary wall. PSCP-11-15-C5, with a flexible and long spacer, is easier to coat onto capillary tubings and possesses high column efficiency. The selectivity for some compounds on the columns is also affected.

Liquid–liquid transition observed in the measurement of phase transition for PSCP-3-15-C5 and PSCP-11-15-C5 by GC may be due to conformational changes of the crown ether ring caused by temperature. The results may suggest promising prospects for the use of capillary GC to investigate conformational changes of host molecules (stationary phase) that are not detectable by DSC.

Acknowledgments

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