

## Short Communication

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# Preparation of benzo-18-crown-6 ether side-chain polysiloxane used as open tubular column gas chromatographic stationary phase

Ruonong Fu\* and Chun Huang

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

Zaifu Huang and Wei Xu

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

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### ABSTRACT

A new kind of poly(crown ether), 3-propylbenzo-18-crown-6-substituted polysiloxane, was synthesized and used as a stationary phase for gas capillary column chromatography. The efficiency, polarity and selectivity of this phase were characterized. The data showed that fused-silica capillary columns coated with this stationary phase possess a weak polarity and higher selectivity for some positional isomers such as cresol and dimethylphenol isomers.

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### INTRODUCTION

Side-chain crown ether polymers were first used as open tubular column gas chromatographic stationary phases in 1985 by Fine *et al.* [1]. Since then several types of side-chain crown ether polysiloxanes have been studied as capillary gas chromatographic stationary phases [2–10]. 18-Crown-6-substituted polysiloxane was synthesized and used as a stationary phase coated on fused-silica capillary columns by Rouse *et al.* in 1988 [2]. They then prepared a series of oligoethylene oxide-containing polysiloxanes for use in capillary gas supercritical fluid chromatog-

raphy in 1989 [3]. Wu *et al.* in 1990 [4] synthesized *n*-undecyloxymethyl-18-crown-6 polysiloxane and used it to coat fused-silica capillary columns, which were similar to Carbowax-20M in terms of polarity and selectivity. Wu synthesized a stationary phase by substituting 2,3-benzo-11-[(propyloxy)methyl]-18-crown-6 onto a polysiloxane backbone [5]. Azocrown ether,  $\omega$ -undecylene azo-18-crown polysiloxane and  $\omega$ -undecylene azo-15-crown-5 polysiloxane were used by Wu *et al.* [6] as stationary phases on fused-silica capillary columns in 1992. These columns have the unique characteristic of separating aniline and other basic compounds without derivatization. We developed 3-propylbenzo-15-crown-5-substituted and 4-propylbenzo-15-crown-5-substituted polysiloxane and

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\* Corresponding author.

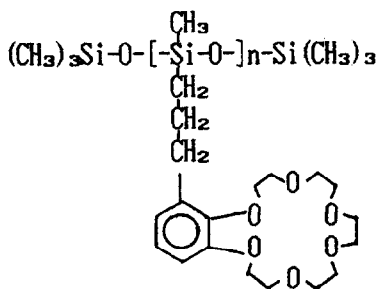


Fig. 1. The structure of PSO-B-18C6.

dibenzo-14-crown-4 polysiloxane used as open tubular column gas chromatographic stationary phases [7–10]. The results showed that these stationary phases have unique selectivity for the separation of some geometric isomers such as cresol, dimethylphenol, dinitrotoluene, etc.

In this work a new kind of poly(crown ether), 3-propylbenzo-18-crown-6-substituted polysiloxane, was synthesized and used as the capillary column stationary phase and compared with the other (crown ether) polysiloxane stationary phases. The structure of poly(crown ether) siloxanes studied is shown in Fig. 1. The aim of this work was to determine the effect of the structure of poly(crown ether) siloxane on the retention behaviour of different solutes.

## EXPERIMENTAL

### *Synthesis of poly(methylsiloxane) containing a 3-propylbenzo-18-crown-6 side-chain (PSO-B-18C6)*

PSO-B-18C6 was prepared by a hydrosilylation reaction between poly(methylhydrosiloxane) and 3-propylbenzo-18-crown-6 (B-18C6). A 0.3524-g (*ca.* 0.001 mol) amount of B-18C6 (obtained from Department of Environmental Science, Wuhan University) and 0.06463 g (*ca.* 0.001 mol) of poly(methylhydrosiloxane) [Merck-Schuchardt (Hohenbrunn, Germany); degree of polymerization 35] were placed in 25 ml of dry, freshly distilled toluene in a dry three-neck round-bottom flask. The mixture was stirred and heated to 110°C under reflux in a nitrogen atmosphere until the solid reactant was

dissolved in the toluene. A 30- $\mu\text{l}$  volume of fresh catalyst solution (0.87 mg of chloroplatinic acid dissolved in 1 ml of isopropyl alcohol) was then added to the reactant solution and the solution was continuously heated and stirred for 6–15 h until the Si–H bond was no longer detectable by IR spectroscopy ( $2140\text{ cm}^{-1}$ ). Generally, after 11 h the Si–H bond had almost disappeared and ethylene was then bubbled through the mixture for 1.0 h to react with all of the residual Si–H units. After the mixture was cooled it was left alone for 2 days. The brown precipitate that had formed was then taken out and dissolved in a small amount of methylene dichloride. After adding a small amount of methanol to the polymer solution a brown product was obtained. The product was centrifuged at *ca.* 700 g for 30 min dried in air for 24 h, removing the solvent. It was then dried in a vacuum oven at 40°C for 24 h to obtain the final product.

### *Column preparation*

Fused-silica capillaries (0.25 mm I.D., Yongnian Optical Fibre Factory, Hebei, China) were used. Capillaries were purged with nitrogen at 240°C for 6 h before coating. The PSO-B-18C6 was dissolved in methylene dichloride at a concentration of about 4 mg/ml using the static coating procedure. The columns coated with PSO-B-18C6 were conditioned under nitrogen at 140, 160, 180, 200, 220 and 240°C for 2 h at each temperature.

### *Column evaluation*

Column evaluation was carried out with a Model SP-3700 gas chromatograph (Beijing Analytical Instrumental Factory, Beijing, China) and an HP-5890-II gas chromatograph (Hewlett-Packard, China) equipped with a flame ionization detector using nitrogen as carrier gas. Solutes were injected using the split mode (the split ratio was 80:1). Time measurements were obtained using an HP-3390 A integrator. The efficiency of columns was determined as the number of plates per metre for *n*-octanol at 140°C. For evaluation of the selectivity of this stationary phase some standard mixtures of phenols and some positional isomers were used.

TABLE I  
CHARACTERISTICS OF PSO-B-18C6 CAPILLARY COLUMNS

Column size: 10 m × 0.25 μm I.D.; O = 1-octanol.

Column No.	Stationary phase	Film thickness (μm)	Capacity factor	Column temperature (°C)	Flow-rate (cm/s)	Column efficiency (plates/m)	Compound tested
1	PSO-B-18C6	0.28	1.03	140	12.8	2890	O
2	PSO-B-18C6	0.19	1.97	140	13.3	6090	O
3	PSO-B-18C6	0.26	1.05	140	14.7	6160	O
4	PSO-B-18C6	0.26	1.04	140	18.0	5700	O
5	PSO-B-15C5 <sup>a</sup>	0.28	1.58	140	13.6	4240	O

<sup>a</sup> Poly(crown ether) siloxane, from ref. 7.

## RESULTS AND DISCUSSION

Table I shows the characteristics of the four columns coated with PSO-B-18C6. For comparison the efficiency of 3-propylbenzo-15-crown-5-substituted polysiloxane (PSO-B-15C5) is also given [7]. The data indicate that this stationary phase can be easily coated on fused-silica capillary columns and that generally very high efficiency is achieved. The efficiency of column 1 is lower than the efficiency of the other columns because the temperature was not well controlled during the coating. To test the effect of temperature on the column efficiency coated with PSO-B-18C6, the height equivalent to a theoretical plate (HEPT) was determined at different temperatures and at a constant flow-rate of carrier gas. Fig. 2 illustrates a plot of HEPT ( $h$ ) vs. column temperature ( $T$ ) for *n*-octanol on the

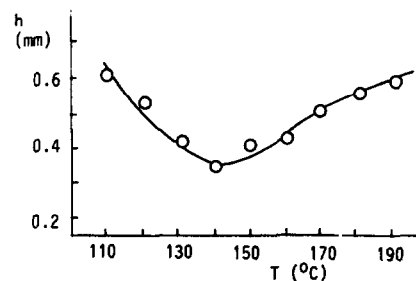


Fig. 2. Plot of HETP against column temperature at a constant flow-rate of carrier gas. Test compound: *n*-octanol. Column 2.

columns. It indicates that the column efficiency has a maximum value at about 140°C, which is equal to the transition temperature. In Fig. 3 a plot of the relative retention ( $\alpha$ ) of nonanol and octanol against the column temperature shows a change in the slope at *ca.* 140°C. This phenomenon occurs in all poly(crown ether) siloxanes, and was called the liquid–liquid transition point by Fine *et al.* [1]. The polarity of PSO-B-18C6 represented by McReynolds constants is listed in Table II, and for comparison the McReynolds constants of SE-30, PEG-20M and PSO-B-3-18C5 (studied by Wu *et al.* [6]) are also given. The average polarity of the liquid phase investigated is lower than that of PEG-20M and the other poly(crown ether) siloxanes. On the other hand, the polarity of this phase is higher than that of SE-30. Thus it is a low-polarity liquid phase. PSO-B-3-18C6 prepared by Wu *et al.* [6]

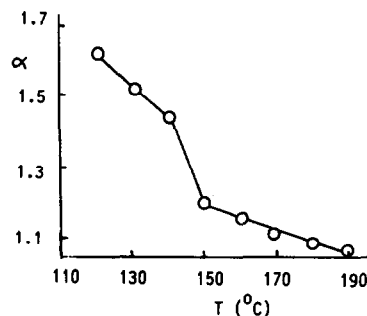


Fig. 3. Plot of  $\alpha$  (nonanol/octanol) vs. column temperature on column 2.

TABLE II  
McREYNOLDS CONSTANTS OF PSO-B-18C6 COLUMNS<sup>a</sup>

X' = Benzene; Y' = 1-butanol; Z' = 2-pentanone; U' = nitropropane; S' = pyridine.

Stationary phase	McReynolds constants					Average polarity
	X'	Y'	Z'	U'	S'	
PSO-B-18C6						
Column 1	167	254	201	399	358	276
Column 2	174	257	194	369	331	265
Column 3	181	260	191	377	341	270
Column 4	177	242	190	372	336	264
PSO average	175	253	194	379	342	269
Carbowax-20 M <sup>b</sup>	322	536	368	572	510	462
PSO-B-15C5	198	390	196	371	434	318
PSO-B-3-18C6 <sup>c</sup>	216	381	452	461	465	394
SE-30 <sup>b</sup>	15	44	53	64	41	43

<sup>a</sup> From ref. 8.

<sup>b</sup> From ref. 11.

<sup>c</sup> From ref. 5.

has higher polarity than PSO-B-18C6: perhaps the benzene on PSO-B-18C6 is not linked to the spacer, being distant from the main chain.

The selectivity of PSO-B-18C6 is shown by the separation power of disubstituted benzene isomers. Table III lists the relative retention values of isomers of dichlorobenzene, dibromobenzene and cresol. It is well known that generally the separation of isomers of cresol is very difficult, although poly(crown ether) columns possess a unique ability to separate isomeric phenol com-

pounds. The data in Table III show that the  $\alpha(p/m)$  value of *p*- and *m*-cresol isomers reached 1.02, which is similar to that of PSO-B-15C5. In Table IV the  $\alpha$  value of dimethylphenol isomers is given, and the data for PSO-B-15C5 are also listed for comparison. The data indicate that 2,4/2,5-dimethylphenol isomers are better separated on PSO-B-18C6 than on PSO-B-15C5. These columns have an excellent capacity to separate di- and trinitrotoluene isomers, as shown in Figs. 4 and 5.

TABLE III  
RELATIVE RETENTION ( $\alpha$ ) OF DISUBSTITUTED BENZENES ON THE PSO-B-18C6 COLUMN

Compound	Column temperature (°C)	Isomer	k' value on PSO-B-18C6	$\alpha(p/m)$
Dichlorobenzene	120	<i>m</i> -	0.85	1.18
		<i>p</i> -	1.00	
		<i>o</i> -	1.23	
Dibromobenzene	120	<i>m</i> -	3.46	1.05
		<i>p</i> -	3.62	
		<i>o</i> -	4.40	
Cresol	140	<i>o</i> -	1.48	1.02
		<i>p</i> -	2.00	
		<i>m</i> -	2.03	

TABLE IV

RELATIVE RETENTION ( $\alpha$ ) OF DIMETHYLPHENOL ISOMERS ON PSO-B-18C6 AND PSO-B-15C5

Column temperature (°C)	Isomer	$\alpha$ value			
		PSO-B-18C6		PSO-B-15C5	
150	2,6-	1.00		1.00	
	2,5-	1.58	$\alpha(2,5/2,6) = 1.58$	1.65	$\alpha(2,5/2,6) = 1.65$
	2,4-	1.62	$\alpha(2,4/2,5) = 1.02$	1.65	$\alpha(2,4/2,5) = 1.00$
	2,3-	1.96	$\alpha(2,3/2,4) = 1.21$	2.11	$\alpha(2,3/2,4) = 1.28$
	3,5-	2.14	$\alpha(3,5/2,3) = 1.09$	2.31	$\alpha(2,5/2,3) = 1.09$
	3,4-	2.54	$\alpha(3,4/3,5) = 1.19$	2.73	$\alpha(3,4/3,5) = 1.18$
140	2,6-	1.00			
	2,5-	1.81	$\alpha(2,5/2,6) = 1.81$		
	2,4-	1.84	$\alpha(2,4/2,5) = 1.02$		
	2,3-	2.31	$\alpha(2,3/2,4) = 1.26$		
	3,5-	2.54	$\alpha(3,5/2,3) = 1.10$		
	3,4-	2.79	$\alpha(3,4/3,5) = 1.10$		

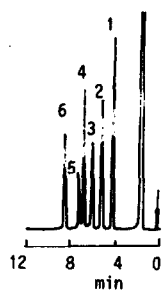


Fig. 4. Chromatogram of the separation of dinitrotoluene (DNT) isomers at 200°C. Peaks: 1 = 2,6-DNT; 2 = 3,5-DNT; 3 = 2,5-DNT; 4 = 2,4-DNT; 5 = 2,3-DNT; 6 = 3,4-DNT.

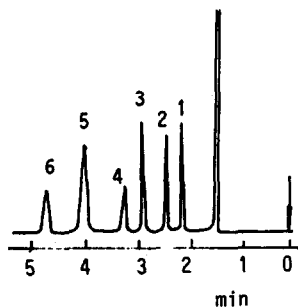


Fig. 5. Chromatogram of the separation of trinitrotoluene (TNT) isomers at 180°C. Peaks: 1 = 2,4,6-TNT; 2 = 2,3,6-TNT; 3 = 2,3,5-TNT; 4 = 2,4,5-TNT; 5 = 2,3,4-TNT; 6 = 3,4,5-TNT.

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