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Journal of Chromatography A, 840 (1999) 225–233

JOURNAL OF
CHROMATOGRAPHY A

Preparation and study of two polysiloxanes with pendant hand-basket type calixarene stationary phases for capillary gas chromatography

Li-feng Zhang^{a,*}, Lei Chen^b, Xue-ran Lu^b, Cai-ying Wu^b, Yuan-yin Chen^b

^aDepartment of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

^bDepartment of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

Received 24 September 1998; received in revised form 21 January 1999; accepted 25 January 1999

Abstract

In this study two novel pendant hand-basket type calixarene gas chromatography stationary phases were prepared by hydrosilylation of ω -undecenyloxymethyl dimethyl calix[4]-15C5 and ω -undecenyloxymethyl dimethyl calix[4]-18C6 with dichloromethane followed by condensation reaction with silanol-terminated polydimethylsiloxane. Important stationary phase properties of these two novel stationary phases such as column efficiency, polarity, and selectivity were examined and compared with those of ω -undecyloxymethyl-18-crown-6, 2,3-benzo-9-propyloxymethyl-15-crown-5 and 2,3-benzo-11-propyloxymethyl-18-crown-6. Excellent thermostability from 60 to 330°C with onset bleeding temperatures at 308°C have been found. The mechanism of specific selectivity for position isomers based on the calix[4]crown ether ring, the molecular size of the solute and its shape are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Calixarene stationary phases; Polysiloxane stationary phases; Stationary phases, GC

1. Introduction

Crown ethers and cyclodextrins have been widely applied in chemistry, especially in analytical chemistry, using the cavity structure and strong electronegative effect of heteroatoms on the cavity ring [1,2]. The use of crown ethers and cyclodextrins as gas chromatography (GC) stationary phases began in the mid-1980s [3–5] and has been successful [6–9]. Calixarenes are the third generation host molecules after crown ethers and cyclodextrins, which possess good complexation ability both with ions and neutral

molecules [10–12]. However, up till now, there has been no report on the application of calixarenes in GC and the reasons are due to the high melting point of calixarene derivatives which leads to difficulties in coating them onto the internal wall of the capillary column, thus resulting in poor column efficiency. A facile method to resolve this problem is to attach the calixarene molecule directly onto a polymer substrate, such as polysiloxane. Recently, we have developed two materials as GC stationary phases, involving a calixarene unit which was directly dissolved into OV-1701 or attached onto the main chain of polysiloxane [13,14]. Most importantly, GC results showed a high column efficiency and unique selectivity for aromatic isomers. In this paper, we

*Corresponding author. Tel.: +65-874-7880; fax: +65-779-1691.
E-mail address: chmzlf@nus.edu.sg (L.-f. Zhang)

2.1.1. Synthesis of PSOC[4]-11-15C5

5,11,17,23-Tetra-*tert.*-butyl-25,27-dimethoxy-26,28-[2'-(ω' -undecenyloxymethyl)-3',6',9'-trioxa-dodecyl ether] dioxo-calix[4]arene (0.4 g, 0.39 mmol) was stirred with methylchlorosilane (2.0 g, 21.2 mmol), anhydrous benzene (10 ml) and H_2PtCl_6 -iso-PrOH solution (0.1 M, 50 μl) at 40°C under argon atmosphere for 20 h. TLC showed that all the calixacrown ether had been consumed. After removal of the volatile, the obtained yellow viscous gum was stirred with silanol-terminated polydimethylsiloxane (average number-average molecular mass $M_n=500$) (0.4 g, 0.8 mmol) in anhydrous benzene (10 ml) at 50°C under argon atmosphere for 10 h. Trimethylchlorosilane (0.7 g, 6.4 mmol) was added to the reaction mixture and the reaction continued for another 10 h. After removal of the solvent, the residue was dissolved in dichloromethane (20 ml) and washed with methanol–water (1:1, v/v) until the rinsed water remained neutral. The resulting pale-yellow viscous gum (0.75 g) was obtained after removal of the solvent ($M_n=7830$ (gel permeation chromatography). IR (KBr) (ν , cm^{-1}) 2962, 2924, 2855 (C–H), 1097–1031 (C–O–C and Si–O–Si), 869 (Ar–H), 720 [-(CH_2) $_n$ -, $n>4$]. $^1\text{H-NMR}$ (ppm, CCl_4 , tetramethylsilane), 7.02 (s, 4H, ArH), 4.50–3.50 (m, 29H, ArOCH_3 , OCH_2 , OCH and ArCH_2Ar), 3.07 (d, $J=11$ Hz, 4H, ArCH_2Ar), 1.40–1.20 [m, 36H, $\text{C}(\text{CH}_3)_3+(\text{CH}_2)_9$], 0.76 [s, 18H, $\text{C}(\text{CH}_3)_3$], 0.50 (t, 2H, CH_2Si), 0.03 (s, 160H, SiCH_3). According to the $^1\text{H-NMR}$ data, the calix-crown content was $3.39 \cdot 10^{-4}$ mol of polysiloxane g^{-1} .

2.1.2. Synthesis of PSOC[4]-11-18C6

The methodology for synthesis of PSOC[4]-11-18C6 is similar to the preparation of PSOC[4]-11-15C5 by replacing the starting materials with 5,11,17,23-tetra-*tert.*-butyl-25,27-dimethoxy-26,28-[2'-(ω'' -undecenyloxymethyl)-3',6',9',12'-tetraoxa-tetradecyl] dioxo-calix[4]arene (0.4 g). $M_n=8700$, the calixcrown content was $1.02 \cdot 10^{-4}$ mol of polysiloxane g^{-1} .

2.2. Column preparation

Fused-silica capillaries were obtained from Yong

Ning Fused Capillary Plant (Hebei Province, China). The capillaries were rinsed with methanol and purged with nitrogen gas at 250°C for 2 h to remove acidic impurities. The column was then statically coated with a solution of 0.5% (w/v) PSOC[4]-11-15C5 or PSOC[4]-11-18C6 in dichloromethane. All columns were conditioned at 290°C for 10 h under a slow nitrogen flow before use

2.3. Column evaluation, instruments and methods

All chromatographic results were obtained on a SC-7 gas chromatograph (Sichuan Analytical Apparatus Plant, China) equipped with a capillary column split injection system (split ratio 50:1) and flame ionization detector. Nitrogen was used as the carrier gas at a linear velocity of 12–15 cm s^{-1} and flow rate of 0.35–0.44 ml min^{-1} . The polarity and efficiency of the column were tested by measuring the McReynold's constants and number of plates per meter for naphthalene at 120°C. The glass transition temperature was determined by the slope change of the $\log k'$ versus $1/T$ plot using naphthalene. The selectivity of the two stationary phases was demonstrated using standard mixtures of alcohol and aromatic hydrocarbons as well as some polar position isomers. The thermostability of the stationary phases was tested by measuring column bleeding.

3. Results and discussion

Table 1 summarizes the chromatographic properties of these two calix[4]-crown ether polysiloxane columns. The theoretical plate number is >3500 plates m^{-1} for all columns with good reproducibility. The peak asymmetry factor for octanol on fused-silica columns explains the chemical inertness of the columns. It also indicates that calix[4]-crown ether polysiloxane possesses good film-forming ability, although this ability of calixarene is very poor, which demonstrate that the combination of polysiloxane with calixarene could greatly improve the film-forming ability of the latter.

Fig. 3 presents the chromatogram of the Grob test mixture obtained from PSOC[4]-11-15C5. It can be seen that the mixture was well separated and each peak shape is symmetric. An appreciable difference

Table 1
Chromatographic properties of POSC[4]-11-15C5 and POSC[4]-11-18C6 columns

Stationary phase	Column	Column size [length (m) ×I.D. (mm)]	Film thickness (μm)	Column efficiency ^a (plates m^{-1})	Capacity factor (k')	Peak asymmetry
POSC[4]-11-15C5	1	10×0.25	0.22	3580	4.35	1.00
	2	20×0.25	0.20	3820	4.02	1.01
	3	25×0.25	0.21	3625	4.23	1.02
POSC[4]-11-18C6	1	10×0.25	0.21	3760	4.46	1.01
	2	10×0.25	0.20	3850	4.30	1.01
	3	20×0.25	0.22	3552	4.60	1.00

^a Test compound, naphthalene; column temperature, 120°C.

is that both 1,3-butanediol and 1-octanol exhibited a longer retention time than *n*-decane and *n*-undecane, but shorter than *n*-dodecane. This is in contrast to the case with the nonpolar columns. Thus, it is obvious that the phase has a strong hydrogen-bonding force to alcohol, but compared with PSOB-3-15C5 where both 1,3-butanediol and 1-octanol eluted even behind *n*-dodecane [7], such hydrogen interaction between PSOC[4]-11-15C5 and alcohol is much weaker. It is easy to understand that, in PSOC[4]-11-15C5, the huge nonpolar calix[4]arene units weakened the hydrogen interaction between the crown ether and the solute. Another noticeable difference is that 2,6-dimethylphenol (2,6-DMP) eluted before 2,4-dimethylaniline (2,4-DMA), which is in contrast to the result on the crown ether polysiloxane column of PSO-11-18C6. This difference is caused by the steric hindrance of 2,6-DMP, even the hydrogen-bonding force of 2,6-DMIP is larger than that of 2,4-DMA.

The selectivity and average polarity of these two novel stationary phases are represented by the McReynold's constants in Table 2. This shows that the calixcrown ether polysiloxanes yield a lower polarity compared to PSO-11-18C6 [15], PSOB-3-15C5 or PSOB-3-18C6 [7]. This result indicates that aromatic calixarenes play an influential role in the contribution to the polarity of the stationary phase.

The operating temperature range is dependent on the glass transition temperature and column bleeding. The glass transition temperature was determined by the slope change of the $\log k'$ vs. $1/T$ plot for naphthalene. Both curves A and B were extrapolated along the linear section of the graph to arrive at an intersection point which corresponds to the T_g value of the stationary phase. PSOC[4]-11-15C5 and

PSOC[4]-11-18C6 columns demonstrated the changes of the grades at 100°C for PSOC[4]-11-15C5 and 107°C for PSOC[4]-11-18C6, respectively, which corresponded to phase changes in the columns and was 62 or 57°C below that of POS-11-18C6 [15]. This indicates that PSOC[4]-11-15C5 and PSOC[4]-11-18C6 stationary phases have lower minimum operating temperatures than PSOC[4]-11-15C5 (Fig. 4).

The column bleeding was measured by heating the column from 120 to 330°C at a rate of 6°C min^{-1} . The column began to bleed at 308 or 306°C, and the shift of baseline was $5.06 \cdot 10^{-15}$ A for PSOC[4]-11-15C5 and $8.60 \cdot 10^{-15}$ A for PSOC[4]-11-18C6 at 330°C. From the above, we can see that the calixcrown ether polysiloxanes are capable at a higher operating temperature range than crown ether polysiloxane and benzocrown ether polysiloxane stationary phase which started bleeding at 200 or 246°C (Table 3). This clearly indicated that much improvement of the thermostability had been achieved compared with other kinds of chiral stationary phases by incorporation of calixcrown ether as the side chain of polysiloxane.

The synthesized new stationary phase showed excellent separation abilities for aromatic structural isomers. It is interesting to note that the orders of eluents were not only dependent on the dipole-dipole interaction, the steric hindrance between the analytes and the stationary phase might also play an important role in separation. This is expected since in the calixcrown ether, the cavity of the crown ether is highly shielded by the rigid calixarene ring, and it is not easy for large analyte molecules to interact with calixcrown or to enter its cavity. As an

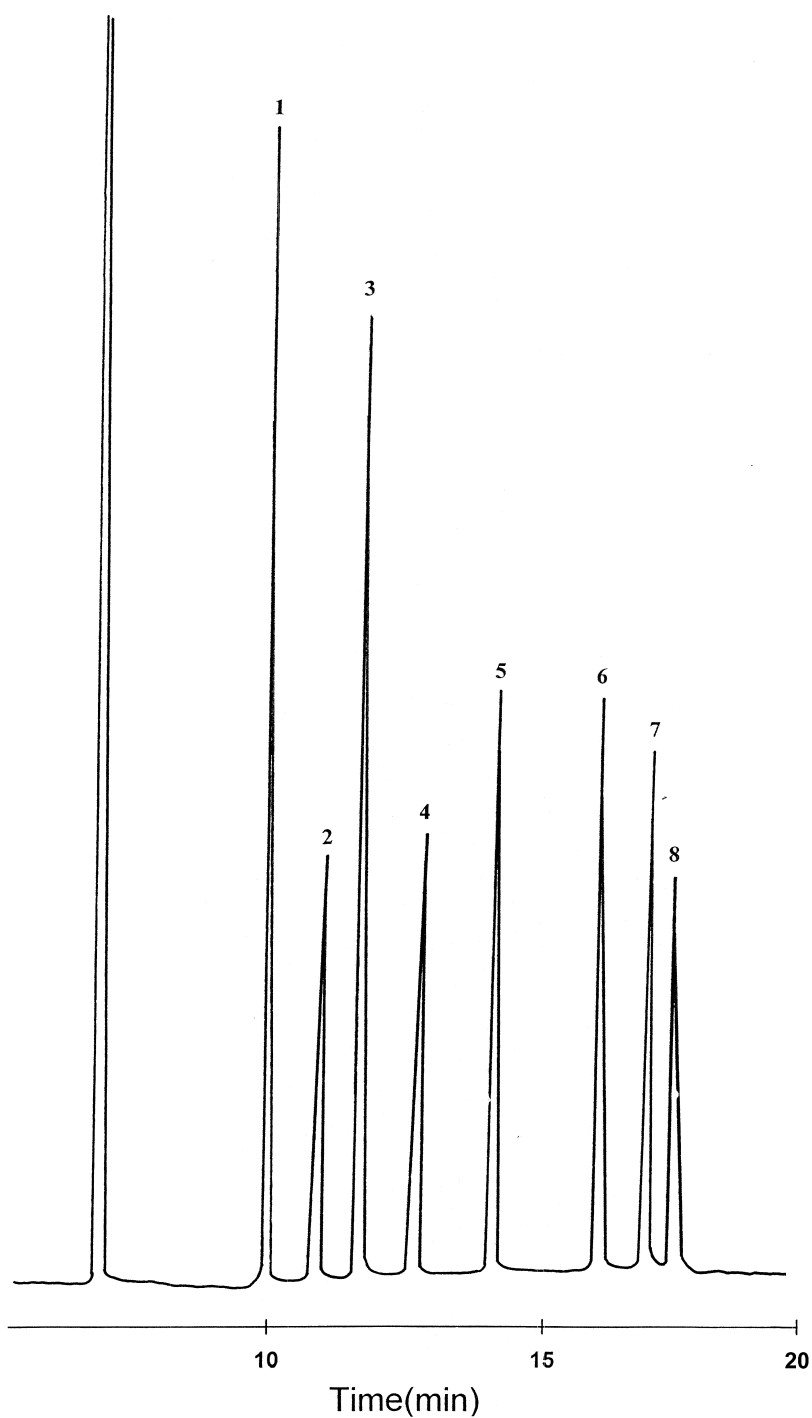


Fig. 3. Chromatogram of Grob test mixture on PSOC[4]-11-15C5. The temperature was 110°C. Peaks: 1=*n*-decane, 2=*n*-undecane, 3=1,3-butanediol, 4=1-octanol, 5=*n*-dodecane, 6=2,6-dimethylphenol, 7=(2,4-dimethylphenyl)amine, 8=naphthalene.

Table 2
McReynold's constants for POSC[4]-11-15C5 and POSC[4]-11-18C6^a

Stationary phase	X'	Y'	Z'	U'	S'	Mean
POSC[4]-11-15C5	165	248	70	187	132	160
POSC[4]-11-18C6	195	250	100	198	133	175
ω -Undecyloxymethyl-18-crown-6 (PSO-11-18C6) ^b	304	229	141	252	218	229
2,3-Benzo-9-propyloxymethyl- 15-crown-5 (PSOB-3-15C5) ^c	149	380	383	456	456	365
2,3-Benzo-11-propyloxymethyl- 18-crown-6 (PSOB-3-18C6) ^c	210	381	452	461	465	394

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

^b Ref. [14].

^c Ref. [7].

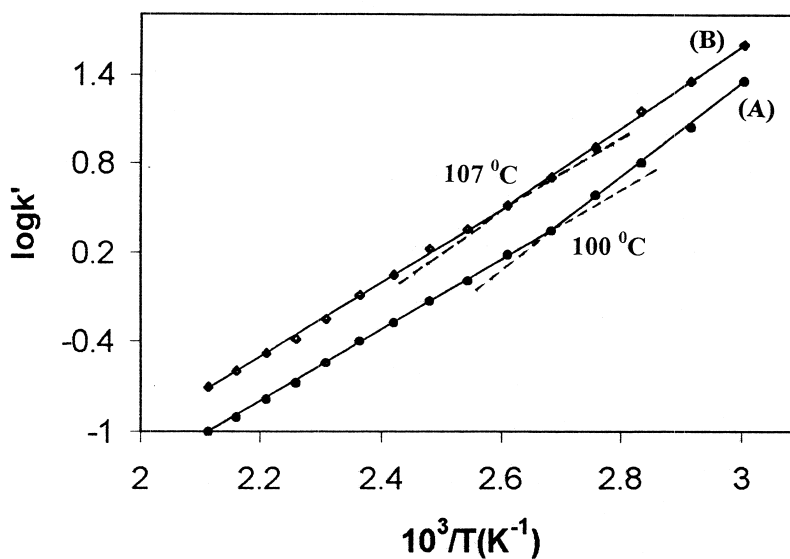


Fig. 4. Plot of $\log k'$ vs. reciprocal absolute temperature: (A) on PSOC[4]-11-15C5, (B) on PSOC[4]-11-18C6.

Table 3
The thermostability of different kinds of polysiloxane stationary phases

Stationary phase	T_g (°C)	Starting bleeding temperature (°C)	End temperature (°C)	Shift of baseline (A)
POSC[4]-11-15C5	100	308	330	$5.06 \cdot 10^{-15}$
POSC[4]-11-18C6	107	306	330	$8.60 \cdot 10^{-15}$
POS-11-15C5 ^a	162	200	300	$4.5 \cdot 10^{-15}$
PSOB-3-15C5	137	230	305	$4.5 \cdot 10^{-13}$
PSOB-3-18C6	140	230	305	$6.0 \cdot 10^{-13}$

^a POS-11-15C5= ω -undecyloxymethyl-15-crown-5.

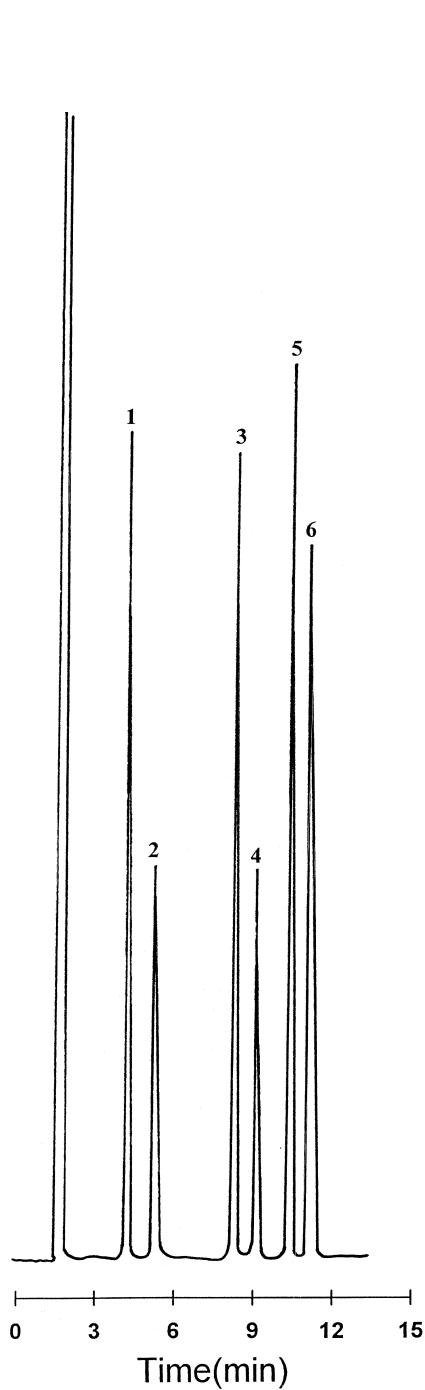


Fig. 5. Separation of dinitrotoluene (DNT) isomers. The temperature was programmed from 160 to 190°C at 3°C min⁻¹. Peaks: 1=3,4-DNT, 2=2,3-DNT, 3=2,6-DNT, 4=2,5-DNT, 5=2,4-DNT, 6=3,5-DNT.

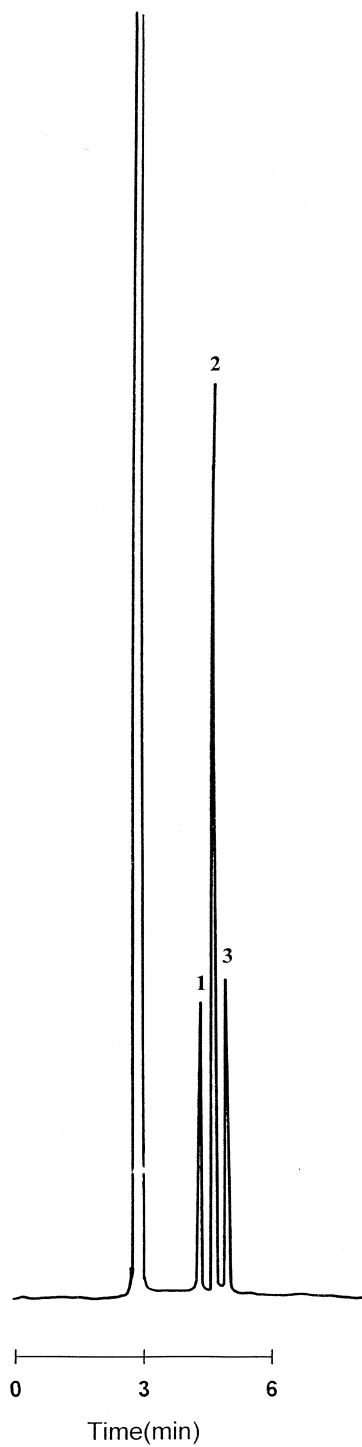


Fig. 6. Separation of xylene isomers. The temperature was 80°C. Peaks: 1=*p*-xylene, 2=*m*-xylene, 3=*o*-xylene.

example, the separation of dinitrotoluene isomers is illustrated as follows. The order of increasing dipole–dipole force of dinitrotoluene (DNT) isomers is $H_{2,5\text{-DNT}} < H_{2,4\text{-DNT}} < H_{2,6\text{-DNT}} < H_{3,5\text{-DNT}} < H_{3,4\text{-DNT}} < H_{2,3\text{-DNT}}$. However, the increasing retention time order is $H_{3,4\text{-DNT}} < H_{2,3\text{-DNT}} < H_{2,6\text{-DNT}} < H_{2,5\text{-DNT}} < H_{2,4\text{-DNT}} < H_{3,5\text{-DNT}}$ (Fig. 5) where the large nitro-substituted group plays an important role in their separation. A noticeable fact is that when the substituted group of the solute is small, the steric hindrance of the calixarene has no effect on the order of

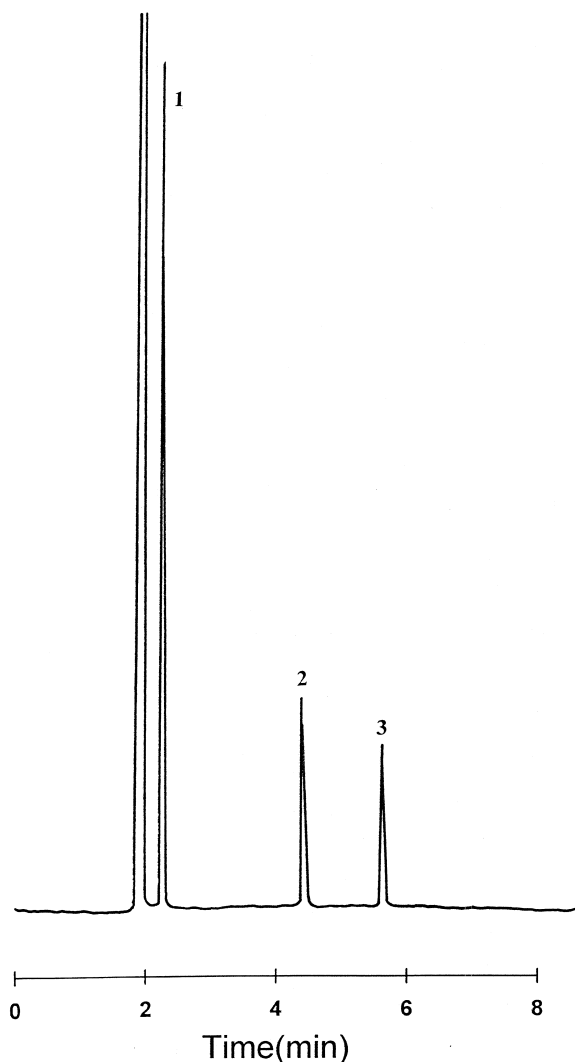


Fig. 7. Separation of nitrophenol (NP) isomers. The temperature was 250°C. Peaks: 1=*o*-NP, 2=*m*-NP, 3=*p*-NP.

eluent. This can be demonstrated in the elution of xylene isomers (Fig. 6), where the separation largely depends on the dipole–dipole interaction. Both stationary phases showed excellent separation ability for phenol isomers based on hydrogen interaction, dipole–dipole interaction and steric hindrance (Fig. 7).

4. Conclusions

PQSC[4]-11-15C5 and POSC[4]-11-18C6 are two novel stationary phases of low polarity with good film-forming ability and excellent thermostability which can be used up to 330°C with a starting bleeding temperature as high as 308°C. The phases present unique selectivity for aromatic position isomers.

Acknowledgements

The authors thank the National Science Foundation of China for financial support.

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