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methoxy-substituted tetraphenyl-phenyl groups for gas chromotographic separations

Polysiloxanes-based stationary phases containing

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3,4-Di(4-methoxy phenyl)-2,5-diphenyl phenyl grafted polysiloxane (MTP) and 3,4-di(3,4,5-trimethoxy phenyl)-2,5-diphenyl phenyl grafted polysiloxane (TMP) were synthesized and statically coated on fused silica capillary columns. The MTP and TMP columns have efficiencies of almost 3400 (k = 3.74, 0.25 mm i.d.) and 3600 (k = 3.96, 0.25 mm i.d.) plates per m, respectively, which are determined by naphthalene at 120 °C. Both columns exhibited moderate polarity based on the McReynolds constants. The separation of the polyethylene pyrolysis products shows that the maximum operating temperature of the two columns can reach up to 360 °C and 370 °C, respectively. In addition, the solvation parameter indicated that the dipole–induced dipole, H-bond alkaline, and dispersive interactions were the main interactions between the solutes and the stationary phases. The separation performance of the new columns was evaluated by gas chromatography separation of the Grob test mixtures. Several mixtures with π -conjugated structure were also well separated on the new columns. This work demonstrated the promising future of the new type of stationary phases in GC analysis.

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1. Introduction

Polysiloxanes have received much attention in the last four decades for their exploitation as gas chromatography (GC) stationary phases because of their specific properties, such as good film-forming ability, wide operational temperature range, and high chemical activity for derivatization.¹⁻³ These characteristics make polysiloxanes ideal candidates for GC stationary phases.⁴

The polysiloxane properties have also been found to be substantially improved by modifying the main or side chain of polysiloxanes.^{5,6} Introducing a phenyl group to the polysiloxane can improve its thermal stability, polarity, selectivity, and oxidation resistance.7-9 Initially, Martin used DC-550 (polymethylphenylsiloxane containing 25% phenyl) to separate ammonia, aliphatic amine and pyridine homologues, opening up a new application area for polysiloxanes as stationary phases in chromatography. Then, M. L. Lee et al. introduced a bicyclic group with large polarizability, which was composed of naphthyl,10 diphenyl,11 and dicyanobiphenyl,12 on the polysiloxane side chain, these phases achieved excellent resolution for isomers. Mayer et al.13 have synthesized polysiloxanes, called SOP-75, with as much as 75% diphenyl group content. These polysiloxanes exhibited a specific selectivity and can endure a temperature of up to 400 °C when they were utilized as GC stationary phases. However, their coating performance and usability at low temperature weakened because of the high diphenyl content that caused the stiff solid polymer structure. In brief, the above researches, regardless of different chromatographic methods, demonstrate the potential for using phenyl containing polysiloxanes in chromatographic separation.

However, low phenyl group content offers only a limited contribution to the abovementioned properties of the stationary phase, while a high content of the phenyl group may weaken its coating performance and usability at low temperature. In order to settle this problem, using concentrated benzene rings to replace single phenyl as substituent groups is a good choice. Recently, our group has synthesized a series of polysiloxane stationary phases containing multiphenyl–phenyl units to enhance the polarizability of side chain, thereby their dipole-induced dipole interaction with polar solutes would significantly improved.^{14,15} Moreover, introducing polar substituent groups, such as methoxy group, to the polycyclic phenyl unit on the polysiloxane side chain made the phases exhibit a blend of polar and polarizable characteristics that resulted in unique selectivity for solutes having delocalized π -electrons.

Based on previous studies, two new polarizable stationary phases with 3,4-di(4-methoxy phenyl)-2,5-diphenyl phenyl grafted polysiloxane (MTP) and 3,4-di(3,4,5-trimethoxy phenyl)-2,5-diphenyl phenyl grafted polysiloxane (TMP) were synthesized as stationary phases for capillary GC. Chromatographic parameters, McReynolds constants, Abraham solvation parameter and thermal stability of the two phases were systematically

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evaluated and compared with each other. Separation performance of the columns was tested by various of mixtures, including *n*-alkanes, Grob test mixtures, substituted benzene isomers and aromatic mixtures.

2. Experimental

2.1 Reagents and apparatus

4-Methoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde were purchased from Wuhan Yuancheng Technology Development Co. Ltd. (Wuhan, China). Octamethylcyclotetrasiloxane, 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane were purchased from Dow Corning Corporation (Michigan, USA). All the reagents used in this work, except the abovementioned, were of analytical reagent grade and purchased from Sinopharm Chemical Regent Co. Ltd. (Beijing, China). A commercial column DB-17 coated with 50% diphenyl and 50% dimethylpolysiloxane (30 \times 0.25 mm, i. d.) was obtained from Agilent Technologies (Palo Alto, USA). Grob test mixtures were prepared according to the method described by Grob *et al.*¹⁶ The polyethylene pyrolysis samples were prepared according to ref. 17.

The fused silica capillary tubes coated with polyimide outside (0.25 mm, i.d.) were produced in our laboratory from fiber-level (SiO₂, 99.999% purity) raw tubes using a self-made drawing machine. All the test samples were separated on 30 m-long columns except the polyethylene pyrolysis samples separated on the 15 m-long columns.

A Shimadzu GC-2014C gas chromatograph (Shimadzu Scientific Instruments, Inc., Kyoto, Japan) equipped with a split/splitless injection system (injection split ratio: 30 : 1) and a flame ionization detector was used to perform all the GC measurements. Nitrogen (N₂, 99.999% purity) was employed as the carrier gas. A Shimadzu FTIR-8400S (Shimadzu Scientific Instruments, Inc., Kyoto, Japan) and a Bruker Avance-400 NMR spectrometer (Bruker BioSciences Corporation, Zurich, Switzerland) were used to confirm the structure of the synthesized stationary phases. Thermal gravity analysis test was conducted on an LCT-2 TGA analysis instrument (Beijing Optical Instrument Factory, Beijing, China).

2.2 MTP and TMP polymer synthesis and characterization

The MTP and TMP polymers were synthesized using a four-step procedure. Fig. 1 shows the corresponding reaction scheme.



Fig. 1 Reaction scheme for the preparation of MTP and TMP. MTP: R₄-OCH₃, R₃, R₅-H; TMP: R₃, R₄, R₅-OCH₃.

2.2.1 Synthesis of 1,2-di(4-methoxyphenyl)-2-hydroxy-(BHE1) ethanone and 1,2-di(3,4,5-trimethoxyphenyl)-2hydroxy-ethanone (BHE2). BHE1 was synthesized by condensing 4-methoxybenzaldehyde (11.0 g, 80.0 mmol) in the presence of thiamine hydrochloride (VB1) (1.2 g, 4.0 mmol) in 25.0 mL of KOH ethanol solution (1.0 mol L^{-1}). The reaction was run at 60 °C for 2 h. Following cooling with ice, the crude product was filtered and washed with distilled water. The product was then re-crystallized from ethanol to provide pure BHE1 (8.0 g, 74% yield) as light yellow crystals, mp 108.9-110.2 °C (lit:18 108.0-111.0 °C). The BH2 synthesis route was similar to that of the BH1 (13.2 g, 84.1% yield), mp 165.2-165.6 °C (lit:19 165-166 °C).

2.2.2 Synthesis of 1,2-di(4-methoxyphenyl)ethane-1,2dione (BED1) and 1,2-di(3, 4,5-trimethoxyphenyl)ethane-1,2dione (BED2). BED1 was synthesized by oxidizing BHE1 (6.3 g, 23.0 mmol) using anhydrous cupric sulphate (0.6 g, 3.0 mmol) and ammonium nitrate (2.0 g, 24.0 mmol) in 35.0 mL of 80% acetic acid. The reaction was refluxed at 110 °C for 90 min. The product appeared as a solid yellow mass after cooling. After extensively washing with distilled water, the product was recrystallized from ethanol to provide pure BED1 (4.8 g, 76% yield) as yellow crystals, mp 132.0–133.0 °C (lit:¹⁸ 130–133 °C). The BED2 synthesis route was similar to that of the BED1 (7.8 g, 87.1% yield), mp 192.2–192.9 °C (lit:¹⁹ 192–193 °C).

2.2.3 Synthesis of 3,4-di(4-methoxyphenyl)-2,5-diphenylcyclopentadienone (BD1) and 3,4-di(3,4,5-trimethoxy phenyl)-2,5-diphenylcyclopentadienone (BD2). BD1 was synthesized by the reaction of BED1 (5.4 g, 20.0 mmol) and 1,3-diphenylacetone (4.6 g, 22.0 mmol) in 20.0 mL of dry ethanol. When the mixture was heated near its boiling point, 5.0 mL of KOH ethanol solution (3.0 mol L⁻¹) was added dropwise. The reaction was heated to reflux at 75 °C for a further 30 min. The abovementioned solution was cooled to room temperature and filtered to obtain the crude product. The product was then re-crystallized with ethanol to obtain the desired BD1 (5.4 g, 64.3% yield) as a red-brown solid powder, mp 238.0–239.5 °C. The BD2 synthesis route was similar to that of BD1 (7.4 g, 61.7% yield), mp 165.2–165.9 °C. The BD1 and BD2 structures were analyzed by ¹H NMR and FT-IR.

BD1. ¹H NMR (CDCl₃, 400 MHz, δ_{ppm}): 3.81 (d, 6H, OCH₃); 6.72–6.76 (d, 4H, Ar-H); 6.85–6.89 (m, 6H, Ar-H); 7.23–7.28 (d, 8H, Ar-H). FT-IR (KBr, ν/cm^{-1}): 3105.8 [ν (C–H)]; 1879.6 [ν (C= O)]; 1247.9 [ν (C–O)]; 815.2, 764.5 [ν (Ar-H)].

BD2. ¹H NMR (CDCl₃, 400 MHz, δ_{ppm}): 3.47 (s, 12H, 4OCH₃); 3.86 (s, 6H, 2OCH₃); 6.63–6.65 (d, 4H, Ar-H); 7.19–7.25 (m, 4H, Ar-H); 7.28–7.32 (d, 6H, Ar-H). FT-IR (KBr, ν/cm^{-1}): 3009.6 [ν (C–H)]; 1708.9 [ν (C=O)]; 1240.2, 1126.4 [ν (C–O)]; 846.7, 734.8 [ν (Ar-H)].

2.2.4 Synthesis of MTP and TMP. The MTP and TMP were prepared through a Diels–Alder reaction between cyclopentadienone and methyl vinyl polysiloxanes (MVP). Accordingly, 20% vinyl content of the MVP side chain was obtained according to a literature method.²⁰ MVP (7.0 g, containing 18.3 mmol vinyl of the side chain) and BD1 (8.8 g, 20.0 mmol) were added to a dry four-necked round bottom flask containing 50.0 mL of dry diphenyl ether. The mixture was heated at 240 °C for 72 h under nitrogen atmosphere. The color of the solution

changed from dark brown to yellow with a large number of bubbles. The polymerization reaction was terminated when bubbles were no longer observed in the reaction vessel. After distilling the solvent, the product was dissolved in 5.0 mL of toluene and precipitated with 25.0 mL of methanol. The step was repeated five times to remove the low molecular weight polymer and unreacted BD1. Subsequently, MTP was obtained as a clear, pale brown gum (3.2 g, 22% yield) after evaporating the solvent under vacuum. The TMP synthesis route was similar to that of the MTP (4.5 g, 26% yield). The MTP and TMP structures were analyzed by ¹H NMR and FT-IR.

MTP. ¹H NMR (CDCl₃, 400 MHz, δ_{ppm}): 3.63–3.66 (d, 6H, OCH₃); 5.78–5.98 (d, 3H, CH=CH₂); 6.40–6.48 (d, 4H, Ar-H); 6.62–6.71 (d, 4H, Ar-H); 7.11–7.28 (d, 11H, Ar-H); peaks at 0.09 ppm were attributed to C–H on Si atoms in the skeleton of polysiloxane. FT-IR (KBr, ν/cm^{-1}): 3057.7 [ν (Ar-H)]; 2962.9, 1515.6 [ν (C–H)]; 1410.8 [ν (CH=CH₂)]; 1134.6 [ν (C–O)]; 1096.4, 1016.6 [ν (Si–O–Si)].

TMP. ¹H NMR (CDCl₃, 400 MHz, δ ppm): 3.38–3.41 (d, 6H, 2OCH₃); 3.65–3.72 (d, 12H, 4OCH₃); 5.95–6.07 (d, 3H, CH=CH₂); 7.30–7.39 (d, 4H, Ar-H); 7.41–7.49 (m, 11H, Ar-H). Peaks at 0.15 ppm were attributed to C–H on Si atoms in the polysiloxane skeleton. FT-IR (KBr, ν/cm^{-1}): 3109.6 [ν (Ar-H)]; 2989.5, 1515.6 [ν (C–H)]; 1400.2 [ν (CH=CH₂); 1184.3 [ν (C–O)]; 1069.0, 1021.2 [ν (Si–O–Si)].

The 3,4-di(4-methoxy phenyl)-2,5-diphenyl phenyl content in MTP was 17.0% calculated from the ratio of the integral at δ 6.40–7.28 ppm (attributed to Ar-H in the multiphenyl moiety) to that at about δ 0.09 ppm (attributed to Si–CH₃). The contents of the remaining vinyl groups were determined to be 2.9% calculated from the ratio of the integral at δ 5.78–5.98 ppm (attributed to Si–vinyl) to that at about δ 0.09 ppm (attributed to Si–CH₃) based on the ¹H NMR spectra.²¹ Using the similar calculation method, the 3,4-di(3,4,5-trimethoxy phenyl)-2,5-diphenyl phenyl content in TMP was 16.9%. The remaining vinyl groups were 3.1%.

2.3 Preparation of capillary column

Prior to coating, the capillary tubes were rinsed with 5 mL of dichloromethane and purged with a continuous stream of N₂ at 260 °C for 1 h. The columns were then statically coated with 0.80% (w/v) MTP and TMP solution containing 4% (w/w) dicumylperoxide of MTP or TMP as a radical initiator. Both of the coated capillary columns had a film thickness of 0.50 µm. The capillary columns were then conditioned under a constant flow of nitrogen from 40 °C (maintained for 0.5 h) to 160 °C at 1 °C min⁻¹ (maintained for 2 h) and followed to 360 °C at 1 °C min⁻¹ (maintained for 24 h). The 15 m TMP columns were treated at 370 °C for 24 h. The prepared MTP and TMP columns (30 m \times 0.25 mm) were called columns I and II, respectively. The prepared MTP and TMP columns (15 m \times 0.25 mm) were called columns A and B, respectively.

3. Results and discussion

3.1 Column efficiency

Table 1 shows the chromatographic properties of the two columns. The column efficiencies determined at liner velocity

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of 8 cm s⁻¹ were 3412 and 3606, respectively. A part of the vinyl remained (about 3%) to facilitate crosslinking, which was caused by the BD1 and BD2 with large volumes not fully reacting with the vinyl on the polysiloxane side chain. The degree of crosslinking was more than 80%, thereby showing a good crosslinking capacity of the two new stationary phases.²²

3.2 Molecular polarizability

The dispersive and dipole-induced dipole interactions between solutes and stationary phases were related to the deformation of

the electron cloud of the functional groups. The increased polarizability of side group can enhance the dipole–induced dipole interactions of the stationary phases with polar analytes as well as their dispersive interactions with non-polar analytes. We calculated the polarizabilities of several multiphenyl groups according to ref. 23 (Table 2). As shown, the introduction of the multiphenyl–phenyl moiety greatly increased the polarizabilities of the polysiloxanes. Additionally, the TMP with six methoxy-substituted groups were the most polarizable, the dipole–induced dipole and dispersive interactions of the TMP

Table 1 Chromatographic properties of the MTP and TMP columns at 120 $^\circ\text{C}$									
Column	Stationary	Dimension L	n	Coating efficiency ^a	Degree of crosslinking ^b				
	phase	(m) × i.d. (mm)	(plates per m)	(%)	(%)				
I	MTP	30 imes 0.25	3412	69.2	80.5				
II	TMP	30 imes 0.25	3606	73.7	82.3				

 a Coating efficiency calculated through a formula according to ref. 20. b Degree of cross-linking calculated from the capacity factor after rinsing with 5 mL of dichloromethane divided by that of the column tested before.²¹

Table 2 Molecular polarizabilities of several aromatic compounds



Table 3 McReynolds constants of the MTP and TMP

Stationary phase	Χ'	Y'	Z'	U'	S'	Sum of ΔI	CP index
МТР	109	160	164	162	157	752	17.8
TMP	121	170	168	173	162	794	18.8
OV-11 ^a	102	142	145	219	178	786	18.6
^a Data obta	ined fro	om ref.	24.				

with solutes would be significantly increased. Thereby, TMP is expected to exhibit much better chromatographic selectivity for a number of applications.

3.3 McReynolds constants

The McReynolds constants were quantitatively measured to investigate the polarity of the novel stationary phases. Table 3 shows the determined data. Accordingly, the elution sequence of the five probe compounds on the prepared columns was as follows: Y' (*n*-butanol) \rightarrow X' (benzene) \rightarrow Z' (2-pentanone) \rightarrow U' $(1-nitropropane) \rightarrow S'$ (pyridine). The CP indexes of the MTP (17.0% 3,4-di(4-methoxy phenyl)-2,5-diphenyl phenyl) and the TMP (16.9% 3,4-di(3,4,5-trimethoxy phenyl)-2,5-diphenyl phenyl) were 17.8 and 18.8, respectively. This result suggested their medium polarity. The polarity of the new stationary phases was quite close to that of the OV-11 (35% diphenyl-65% dimethyl polysiloxane).²⁴ The X', Y', and Z' values of the TMP and the MTP were higher than those of the OV-11, which demonstrated their stronger dispersive and H-bond interactions with the solutes. The higher polarity of the TMP compared with that of the MTP indicated that the TMP could provide a stronger retention for polar compounds like *n*-butanol.

3.4 Abraham system constants of the MTP and TMP

Table 4 shows the Abraham system constants. Each value represented an interaction. The numerical value reflected the strength of the interaction as follows: $e - p - \pi$ and $n - \pi$ electron, s – dipole–induced dipole, a – H-bond alkaline, b – H-bond acid, and l – dispersive interactions.²⁵ As shown in Table 4, the MTP and the TMP exhibited strong molecular interactions with

solutes *via s*, *a*, and *l*, but non H-bond acid (b = 0). It also could be observed that the MTP and the TMP showed slightly higher *s* and *l* values and much higher *a* values than DB-35, which suggested that the tetraphenyl–phenyl moieties with concentrated benzene rings as the polysiloxane side chain increased the polarizabilities of the side chain. Therefore, the dipole– induced dipole, dispersive, and H-bond alkaline interactions between the stationary phases and the solutes were enhanced. In addition, every value (*s*, *l*, and *a*) of the TMP was higher than the MTP, which proved that introducing more methoxy polar groups on the tetraphenyl–phenyl moiety side chain was favorable in improving the selectivity of the stationary phases.

3.5 Separation performance

The separation performance of the columns was evaluated by the GC separation of the Grob test mixtures. Fig. 2 shows the chromatogram for the separation of the Grob test mixtures on columns I and II. From an elution perspective, the two columns exhibited guite similar retention behaviors. As shown, (a) both columns achieved baseline separation. The peaks were symmetrical, except octanol, which indicated that the new stationary phases exhibited good wettability on the inner surface of the columns and the new columns had high column efficiency. (b) The tailing factors of octanol in columns I and II were equal to 1.09 and 1.07, respectively. This finding suggested slight H-bonded reversible adsorption. The area of peak 8 (2ethylhexanoic acid) was reduced on both columns, which indicated the irreversible acid-base adsorption. (c) Nonanal (bp 191.5 °C) and 1-octanol (bp 195.2 °C) had lower boiling points than C_{11} (bp 196.0 °C). However, they were eluted after C_{11} , which was attributed to the columns with moderate polarity and stronger interaction with the polar compounds than the nonpolar compounds. (d) 2,6-Dimethylphenol was eluted before 2,6-dimethylaniline, thereby revealing that the two new columns had stronger retention for alkaline than acidic compounds.

3.6 Thermal stability of MTP and TMP

The TGA test was conducted to evaluate the thermal stability of the stationary phases. The temperature was increased at a rate

Fable 4 Abraham system constant of the MTP and TMP									
Stationary phase	Temperature (°C)	С	е	S	а	b	l	n	R^2
MTP	80	-2.688	-0.063	0.787	0.628	0	0.651	30	0.99
	100	-3.033	-0.027	0.713	0.539	0	0.602	31	0.99
	120	-2.983	0.020	0.670	0.473	0	0.564	33	0.99
TMP	80	-2.543	-0.090	0.807	0.694	0	0.659	30	0.99
	100	-2.613	-0.046	0.765	0.626	0	0.618	31	0.99
	120	-2.677	0.012	0.693	0.561	0	0.575	33	0.99
DB-35 ^{<i>a</i>}	80	-2.381	0.009	0.758	0.378	0	0.630	61	0.99
	100	-2.460	0.036	0.701	0.326	0	0.577	66	0.99
	120	-2.536	0.074	0.640	0.277	0	0.536	66	0.99

^a Data obtained from ref. 26.



Fig. 2 GC separation of the Grob test mixtures on columns I and II. Conditions: the temperature was increased from 40 °C to 150 °C at 3 °C min⁻¹. Carrier gas velocity: 12 cm s⁻¹. The injection and detector temperatures are both 200 °C. Peaks: 1: hexane, 2: trichloromethane, 3: 2,3-butanediol, 4: decane, 5: undecane, 6: 1-octanol, 7: nonanal, 8: 2-ethylhexanoic acid, 9: 2,6-dimethylphenol, 10: 2,6-dimethylaniline, 11: methyl decanoate, 12: methyl undecanoate, 13: dicyclohexylamine, and 14: methyldodecanoate.

of 10 °C min⁻¹ from 50 °C to 700 °C under helium protection. Fig. 3 showed that the MTP began to lose weight at 390 °C and significantly after 450 °C. Meanwhile, the TMP began to lose weight at 410 °C and significantly after 460 °C. These findings were attributed to the five benzene rings connected with a single bond on the polysiloxane side chains. These benzene rings enhanced steric hindrance, reduced the molecular chain spiraling trend, and effectively prevented the polysiloxane cyclization and rearrangement degradations at high temperature. The thermal stability of the TMP was slightly better than that of the MTP, which could attribute to the more methoxy groups on TMP, further increased its space steric hindrance.

Separations of the polyethylene pyrolysis products were performed to demonstrate the temperature resistance of the new columns. Fig. 4 showed that the polyethylene pyrolysis products had a baseline separation with nice peak shapes on columns A and B. The maximum operating temperatures of the new columns were 360 $^{\circ}$ C and 370 $^{\circ}$ C, respectively, when the

columns still owned satisfactory column efficiencies and separation performances. An obvious baseline drift on column A was also observed at 360 $^{\circ}$ C, while this phenomenon was significantly improved on column B.



Fig. 3 TGA curves of the synthesized MTP and TMP polymers.



Fig. 4 GC separation of the polyethylene pyrolysis products on columns A and B. Conditions: column A: the temperature is increased from 100 °C for 2 min to 360 °C at 16 °C min⁻¹ (maintained for 10 min); column B: the temperature is increased from 100 °C for 2 min to 370 °C at 16 °C min⁻¹ (maintained for 10 min). Carrier gas velocity: 13 cm s⁻¹. The injection and detector temperatures are both 400 °C. The components of the peaks not listed in the chromatogram are hydrocarbons with increased carbon number.

Table 5 The separation of o-, m-, and p-disubstituted benzene isomers on the columns

	Temperature (°C)	Column	Peak order	k			α	
Analyte				k_1	k_2	k_3	$\alpha_{2/1}$	$\alpha_{3/2}$
Xylene	80	Ι	p, m, o	1.342	1.440	1.614	1.073	1.121
		II	p, m, o	1.472	1.596	1.992	1.084	1.248
		TFPP	p, m, o	1.131	1.204	1.451	1.065	1.205
Cresol	120	Ι	o, p, m	1.319	1.479	1.703	1.121	1.152
		II	o, p, m	1.401	1.612	1.875	1.151	1.163
		TFPP	o, p, m	1.125	1.293	1.488	1.149	1.151
Nitrochlorobenzene	160	Ι	<i>m</i> , <i>o</i> , <i>p</i>	1.036	1.239	1.570	1.196	1.267
		II	m, o, p	1.160	1.404	1.952	1.210	1.391
		TFPP	m, o, p	1.097	1.310	1.476	1.194	1.127
Cyanobenzaldehyde	160	Ι	p, o, m	1.219	1.299	1.392	1.066	1.071
		II	p, o, m	1.257	1.360	1.478	1.082	1.087
	150	TFPP	p, o, m	1.237	1.322	1.412	1.069	1.068
Nitrotoluene	160	Ι	o, m, p	0.823	1.007	1.191	1.223	1.183
		II	o, m, p	0.809	0.994	1.187	1.229	1.194
		TFPP	o, m, p	0.701	0.852	0.947	1.215	1.112
Nitroaniline	200	Ι	o, m, p	0.672	0.925	1.612	1.411	1.896
		II	o, m, p	0.723	1.020	1.934	1.411	1.896
		TFPP	o, m, p	0.761	1.031	1.689	1.355	1.638



Fig. 5 Chromatograms of substituted benzenes on the columns I, II, TFPP and DB-17. Conditions: temperature was isothermal at 130 °C. Carrier gas velocity: 12 cm s⁻¹. The injection and detector temperatures were both 200 °C. Peaks: 1: 2-chlorotoluene; 2: 3-chlorotoluene; 3: 3-chlorotoluene; 4: 1,3,5-trimethylbenzene; 5: 1,3,5-trimethylbenzene; 6: *tert*-butylbenzene; 7: mercaptobenzene; 8: 1,3-dichlorobenzene; 9: 1,4-dichlorobenzene; and 10: 1,2,3-trimethylbenzene.

3.7 Applications of the capillary columns

Based on the structures of the stationary phases and the analysis results of Sections 3.3 and 3.4, the stationary phases can be reasonably expected to have a preferential selectivity for the easily polarizable analytes with large aromatic π -conjugated structures, polar compounds, and weak polar compounds. Therefore, analytes, such as several *o*-, *m*-, and *p*-disubstituted benzene isomers, MAHs, and aromatic mixtures were used to evaluate the chromatographic selectivity and retention behaviors of the stationary phases. Fig. 5–7 show the corresponding GC chromatograms.

3.7.1 Separation of the o-, m-, and p-disubstituted benzene isomers. The isothermal separations of the o-, m-, and p-disubstituted benzene isomers were performed to examine the separation performance of the new stationary phases. Table 5 shows the chromatographic parameters of the MTP, TMP and TFPP (fluoro-substituted tetraphenyl-phenyl grafted polysiloxanes)27 columns. The two new columns exhibited excellent selectivity for both polar and weakly polar aromatic isomers. For the separation of *m*- and *p*-xylenes, both columns showed obvious superiority over previously reported phases, such as OV-1701 (7% cyanopropyl, 7% phenyl-polysiloxane),³ in which mand *p*-xylenes were co-eluted ($\alpha = 1$). Owing to the contribution of methoxy-riched groups, the separation factors (α) of most isomers were larger on TMP than on MTP and TFPP. Such a result suggested the participant of methoxy groups could improve the selectivity for closed isomers.

The methoxy-rich polysiloxanes generally exhibit a unique blend of polar and polarizable characteristics because they are based on substituted polycyclic aromatics. Polar methoxy groups on the stationary phases can significantly increase the polarizability of the side chain and produce dispersive, acidbase, and dipole-induced dipole interactions. A more complex of substituted benzene mixture with similar boiling points was separated on TMP, MTP, TFPP and DB-17 columns (Fig. 5). As shown, all components were baseline resolved on TMP but could not done on TFPP and DB-17 columns, indicating that the participant of methoxy groups played an important function in separating closely related aromatic isomers.

3.7.2 Separation of MAHs. Fig. 6 illustrates the GC separation of MAHs on columns I and II. A similar retention behavior can also be observed. As shown, column I has a little lower separation ability than column II. For example, the separation of the two analytes, namely, 1,2,4-trimethylbenzene (peak 7 bp 169 °C) and 1,3-dichlorobenzene (peak 8 bp 172 °C), significantly improved on column II. The elution order of chlorobenzene (peak 3) and ethylbenzene (peak 4) on column I is the opposite of that on column II, which was possibly because column II had higher *s* (dipole–induced dipole) than the MTP stationary phase and interacted more strongly with chlorobenzene than with ethylbenzene.

3.7.3 Separation of aromatic mixtures. The aromatic compounds were separated on columns I, II, and DB-17 to obtain a better understanding of the separation property of the analytes with large aromatic π -conjugated structures on the new columns. Fig. 7 shows that all the aromatic compounds

achieved baseline separation with sharp and symmetric peak shapes on columns I and II. The separation ability of column II was better than that of column I, which indicated that introducing methoxy groups favored the improvement of the chromatographic resolution of the stationary phase. Meanwhile on the DB-17, most of the analytes were well separated except for the separation of 1,2-dihydroacenaphthylene (peak 10, bp 279 °C) and 2-ethoxynaphthalene (peak 11, bp 282 °C). This phenomenon may be attributed to the polarizable multiphenyl moiety as appended functional groups to the polysiloxanes. Compared with benzene and biphenyl, the multiphenyl moiety used in this study was more polarizable. The increased polarizability of MTP and TMP can enhance the dipole-induced dipole and π - π stacking interactions with aromatic solutes. In addition, slight bleeding with a baseline drift at 320 °C on column DB-17 was observed. Columns I and II showed a smooth



Fig. 6 GC separations of MAHs on columns I and II. Conditions: the temperature is increased from 80 °C (maintained for 5 min) to 230 °C at 5 °C min⁻¹. Carrier gas velocity: 10 cm s⁻¹. The injection and detector temperatures are both 250 °C. Peaks: 1: benzene, 2: toluene, 3: ethylbenzene, 4: chlorobenzene, 5: *m*-xylene, 6: *p*-chlorotoluene, 7: 1,2,4-trimethylbenzene, 8: 1,3-dichlorobenzene, 9: nitrobenzene, 10: 2,6-difluorobenzonitrile, 11: 1,4-dibromobenzene, 12: 2-nitrotoluene, 13: *p*-nitrotoluene, 14: *p*-nitroethylbenzene, 15: 1-chloro-2-nitrobenzene, 16: 1-bromo-4-nitrobenzene, 17: 1,4-dichloro-2-nitrobenzene, 18: 5-nitro-1,3-dimethyl benzene, 19: 1-methyl-2,4-dinitrobenzene, and 20: 1-chloro-2,4-dinitrobenzene.



Fig. 7 GC separations of aromatic mixtures on columns I, II, and DB-17. Conditions: the temperature was increased from 100 °C (maintained for 5 min) to 320 °C at 6 °C min⁻¹. Carrier gas velocity: 10 cm s⁻¹. The injection and detector temperatures were both 350 °C. Peaks: 1: benzene, 2: decahydronaphthalene, 3: tetralin, 4: naphthalene, 5: 1benzothiophene, 6: 1-methylnaphthalene, 7: biphenyl, 8: 8-hydroxyquinoline, 9: diphenylmethane, 10: 1,2-dihydroacenaphthylene, 11: 2ethoxynaphthalene, 12:1,4-naphthoquinone, 13: dibenzyl ether, 14: 1nitronaphthalene, 15: 4-hydroxybiphenyl, 16: phenanthrene, 17: benzil, 18: triphenylmethane, 19: phenanthrenequinone, 20: fluoranthene, 21: pyrene, 22: 1-hydroxy anthraquinone, 23: tetraphenylmethane, and 24: 1,8-dihydroxy anthraquinone.

baseline and a nice separation for the analytes, which indicated that the new columns can be used for analysing samples with high boiling points.

4. Conclusions

This work described a synthesis method for the MTP and TMP polymers. Good coating ability, high column efficiency, and excellent thermal stability were exhibited when these polymers were used as GC stationary phases. The Abraham system constants showed that the dipole–induced dipole, dispersive, and H-bond alkaline interactions are the main interactions between stationary phases and solutes. The better chromatographic separation performance of the TMP than that of the MTP could attribute to the different contents of methoxy groups on the tetraphenyl–phenyl moiety. The good selectivity for analytes, including substituted benzene mixture, aromatic isomers, and aromatic mixtures, indicated that the MTP and the TMP had great potential in analyzing environmental pollutants and were worthy of further development and application.

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