NJC

ROYAL SOCIETY
OF CHEMISTRY

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c9nj04918e

1,4-Diphenyltriphenylene grafted polysiloxane as a stationary phase for gas chromatography

Li Xu, Jianchun Bai, Aiqin Du, Zaixiao Yang and Bo Wu *

Received 28th September 2019,
Accepted 5th December 2019

DOI: 10.1039/c9nj04918e

rsc.li/njc

In this work, 1,4-diphenyltriphenylene-grafted (14.2%) polysiloxane (DPTP) was successfully synthesized and statically coated on capillary columns as a stationary phase for gas chromatography. The DPTP columns exhibited excellent efficiencies of 3646 plates m^{-1} for a 30 m column and 3125 plates m^{-1} for a 10 m column, as evidenced by naphthalene measurements at 120 °C, which demonstrated the good film-forming ability of DPTP. Thermogravimetric analysis showed that the weight of DPTP is reduced by 2% at 380 °C. Separation of the polyethylene pyrolysis product indicated that the maximum allowable operating temperature of the DPTP column is 360 °C. The moderate polarity of the DPTP column was investigated in terms of McReynolds constants. The DPTP column was utilized to separate analytes, including aromatic isomers, fatty acid esters, ethers, polycyclic aromatic hydrocarbons and their derivatives, and nitrogenous heterocyclic compounds, on the basis of the column's strong π–π stacking, dipole-induced dipole, and dispersion interactions with solutes. In general, the DPTP column offers great potential as a novel stationary phase for separating various analytes due to its special structure and remarkable separation performance.

1. Introduction

Gas chromatography has been widely applied in analysis, especially in food,[1] drug,[2] environment,[3] and petrochemical industries,[4] because of its excellent characteristics, which include a wide range of applications, rapid analysis, small sample size, and high sensitivity. Gas chromatographic stationary phases have been intensively developed over the last few decades, and new stationary phases have been gradually replacing traditional materials. For instance, carbon nanotubes,[5,6] graphene,[7,8] and metal–organic frameworks[9,10] have emerged as novel gas chromatographic stationary phases exhibiting special retention behaviors due to their unique structures and properties.

Previous studies have been carried out on polysiloxane stationary phases, which have good film-forming ability, low vapor pressure, small viscosity coefficients, and high thermal stability.[11] Continuous developments in gas chromatography have been focused on the separation of complex compounds possessing similar structures and polarities, and high boiling points and molecular weights, thereby increasing the performance requirements of gas chromatographic stationary phases. Therefore, the development of stationary phases with good separation efficiency, high temperature resistance, and excellent selectivity is an urgent problem that should be addressed by researchers to meet increasing demands for separation and analysis.

According to some reports,[12–15] the separation selectivity of aromatic ring-grafted polysiloxane toward polar substances, especially aromatic compounds, largely depends on the polarizability of aromatic rings. Increasing the polarizability of aromatic rings plays an extremely important role in improving the separation selectivity of the stationary phase. For example, Martin synthesized a single phenyl-substituted methylphenylpolysiloxane stationary phase and demonstrated that the introduction of phenyl groups improves the stability and separation selectivity of the material.[16] A number of gas chromatographic stationary phases with different polarities and properties have been subsequently obtained by introducing different numbers of aromatic rings into the polysiloxane backbone or side chains. Lee *et al.* synthesized polysiloxane stationary phases containing biphenyl or naphthyl groups, and these phases showed excellent separation performance for aminophenanthrene isomers by promoting enhanced dipole-induced dipole interactions. However, because these stationary phases could only be used below 280 °C, their applications were severely limited.[17] Based on the work by Lee *et al.*, Naikwadi synthesized a side-chain liquid crystalline polysiloxane, the structure of which includes four phenyl rings; this stationary phase exhibited high thermal stability and selectivity for separating isomeric compounds, including polychlorinated dibenzo-*p*-dioxins and polycyclic aromatic hydrocarbons (PAHs), due to the presence of a fused-ring aromatic system on the side-chains.[18] In general, replacing a single phenyl group with concentrated multiple aromatic rings improves the polarizability of the stationary phase, resulting in remarkable chromatographic separation performance.

College of Chemistry and Chemical Engineering, Shandong University, 27 Shanda South Road, 250100, China. E-mail: wubo@sdu.edu.cn

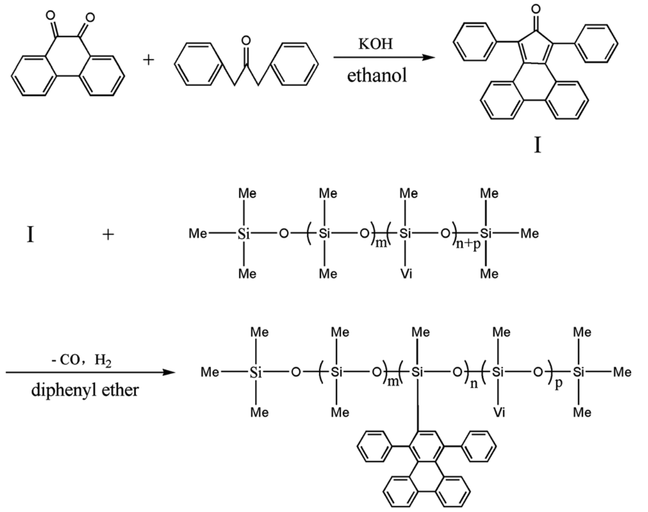

Fig. 1 Reaction scheme for the preparation of DPTP.

In this work, 1,4-diphenyltriphenylene grafted polysiloxane (DPTP) was synthesized (Fig. 1) according to ref. 19 and utilized as a gas chromatographic stationary phase to systematically evaluate its chromatographic performance. The proposed DPTP stationary phase was expected to show good separation for aromatic isomers, PAHs and their derivatives, and heterocyclic compounds on account of π–π stacking and dipole-induced dipole interactions originating from the rigid coplanar structure of the 1,4-diphenyltriphenylene group.

The composition and structure of the stationary phase were characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. McReynolds constants and Abraham solvation parameters were used to evaluate the polarity of DPTP and interaction between DPTP and analytes. Finally, the application of DPTP in the analysis of aromatic isomers, fatty acid esters, ethers, PAHs and their derivatives, and nitrogenous heterocyclic compounds was investigated.

2. Experimental

2.1 Reagents and equipment

Phenanthrenequinone was purchased from Zhengzhou Alpha Chemical Co. Ltd (Zhengzhou, China). All reagents used were of analytical grade. A polyethylene pyrolysis product and a Grob test mixture were prepared on the basis of ref. 20 and 21, respectively. Fused-silica capillaries (10 and 30 m, i.d. 0.25 mm) were produced from the fiber level (SiO_2; 99.999% purity) with a drawing machine in our laboratory. A commercial DB-17 column was purchased from Agilent Technologies for comparison. Chromatographic analyses of all analytes, except that of the polyethylene pyrolysis product, were performed on a 30 m column; analysis of the pyrolysis product was conducted on a 10 m column.

A DPX-300 NMR spectrometer (Bruker, Bremen, Germany), LCT-2 TGA analysis instrument (Beijing Optical Instrument Factory, Beijing, China), FTIR-8400S spectrometer (Shimadzu Corporation, Kyoto, Japan) and MS50 mass spectrometer (British Karasto Company, London, UK) were employed to characterize the intermediates and ultimate products. Chromatographic evaluations were performed on a Shimadzu GC-2014 gas chromatograph (Shimadzu Corporation, Kyoto, Japan) with a split/splitless injection system and a flame ionization detector. Nitrogen (N_2, 99.999% purity) served as the carrier gas. All chromatographic evaluations were accomplished under the same split ratio (30 : 1).

2.2 Synthesis of the DPTP polymer

2.2.1. Synthesis of 1,3-di(phenyl)cyclopenta[*l*]phenanthren-2-one (chemical formula: $C_{29}H_{18}O$). Phenanthrenequinone (10.5 g, 0.0504 mol) and dibenzyl ketone (10.8 g, 0.0514 mol) were dissolved in 100.0 mL of absolute ethanol under heating and continuous stirring in a N_2 atmosphere. When the mixture began to boil, 3.00 mL of 3.60 mol L^{-1} KOH in ethanol solution was added dropwise to it. The color of the mixture changed from orange to dark green, and the reaction was continued for another 30 min, during which large quantities of solids were precipitated from the solution. The mixture was cooled in an ice bath, and the solids were filtered. The crude product was recrystallized from ethanol/toluene (V : V = 3 : 2) to produce 15.3 g of black crystals with a yield of 79.3%. FTIR (KBr, ν/cm^{-1}): 3055.95 [ν(Ar–H)]; 1692.11 [ν(C=O)]; 1591.59, 1483.95 [ν(C=C)]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 6.93–7.80 (m, Ar–H, 18H). ESI-MS *m/z* for $(C_{29}H_{18}O + H)^+$, calcd: 383.1431; found: 383.1437.

2.2.2 Synthesis of the DPTP stationary phase. According to ref. 22, polymethylvinylsiloxane containing 19.0% vinyl groups were synthesized through ring-opening polymerization of octamethylcyclotetrasiloxane and tetramethyltetravinylcyclotetrasiloxane. The DPTP polymer was obtained by the Diels–Alder reaction of 1,3-di(phenyl)cyclopenta[*l*]phenanthren-2-one and polymethylvinylsiloxane. The synthetic process was as follows. Polymethylvinylsiloxane (5.00 g, including 0.0124 mol vinyl) with 50.0 mL of diphenyl ether as a solvent was added to a four-necked flask under a N_2 atmosphere. The polymethylvinylsiloxane was completely dissolved in diphenyl ether under heating conditions, after which a slight excess of 1,3-di(phenyl)cyclopenta[*l*]-phenanthren-2-one (5.40 g, 0.0141 mol) was added to it. The mixture was continuously reacted at 220 °C for 48 h. A large number of bubbles were produced, and the color of the mixture gradually turned from brown to yellow during the reaction. The reaction was considered complete when bubble formation was no longer observed. The solvent was removed under vacuum distillation, and the residue was dissolved in 10.0 mL of toluene and precipitated with 30.0 mL of methanol. This step was repeated four times. The solvent was evaporated, and DPTP (6.50 g, 78.5%) was obtained as a transparent yellow viscous liquid. FTIR (KBr, ν/cm^{-1}): 3058.29 [ν(Ar–H)]; 2962.32, 1603.81, 800.80 [ν(C–H)]; 1408.77, 1594.26 [ν(Si–C=C)]; 1093.73, 1019.22 [ν(Si–O–Si)]. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.02–8.42 (m, Ar–H, 19H). The peaks at 5.97 and 0.03 ppm corresponded to vinyl and C–H on Si atoms, respectively.

2.3 Preparation of capillary columns

Prior to static coating, 5.0 mL of dichloromethane was flushed into 10 and 30 m fused-silica capillaries. The columns were then maintained at 260 °C for 1 h with continuous N_2. Subsequently, 0.8% (W/V) DPTP, including dicumyl peroxide (4% of the weight of DPTP) in dichloromethane, was statically coated on the capillary columns. Dicumyl peroxide served as a free radical initiator to accelerate cross-linking.[23] The columns were conditioned from 40 °C to 160 °C at a rate of 1 °C min^{-1}; this condition was maintained for 2 h. Then, the temperature was increased to 360 °C at a rate of 2 °C min^{-1} and held for 10 h to remove low-molecular weight polymers. All operations of programing temperature were conducted under N_2 flow. The columns were coated with films with a thickness of 0.5 μm, which was calculated on the basis of ref. 24.

3. Results and discussion

3.1 Polymer characterization by NMR spectroscopy

^{1}H NMR results revealed that 14.2% 1,4-diphenyltriphenylene was grafted to the polysiloxane side-chains. The grafting rate was obtained by calculating the ratio of the integral at 7.027–8.421 ppm (corresponding to Ar–H of the 1,4-diphenyltriphenylene group) to the integral at 0.098 ppm (corresponding to Si–CH_3). The calculated ratio of the integral at 5.983 ppm (corresponding to Si–CH$=$$CH_2$) to the integral at 0.098 ppm showed that DPTP contains 4.8% vinyl groups. Groups with large steric hindrance restrict the reaction from being completed, leading to a small amount of vinyl available for cross-linking.

3.2 Thermal stability of the DPTP stationary phase

Thermogravimetric analysis was carried out to assess the thermal stability of the DPTP stationary phase. DPTP was conditioned from 50 °C to 700 °C at 10 °C min^{-1} under helium. Fig. 2 shows a weight loss of 2% in DPTP at 380 °C. The presence of 1,4-diphenyltriphenylene, which presents large steric hindrance, effectively prevents DPTP from undergoing cyclization and rearrangement degradation at high temperatures.[25] Therefore, the thermal stability of DPTP was significantly improved compared with that of polydimethylsiloxane.

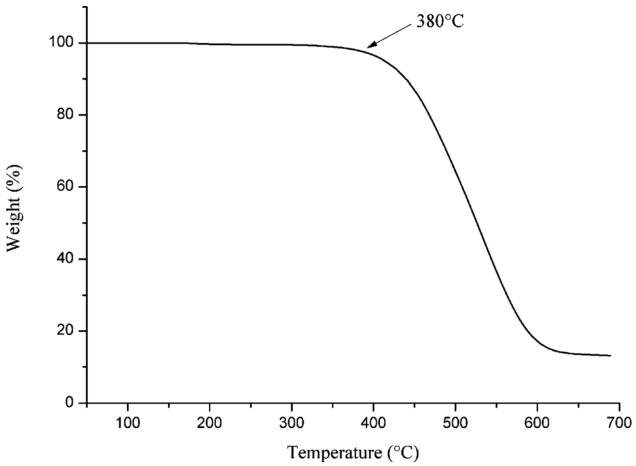

Fig. 2 TGA analysis of the DPTP polymer.

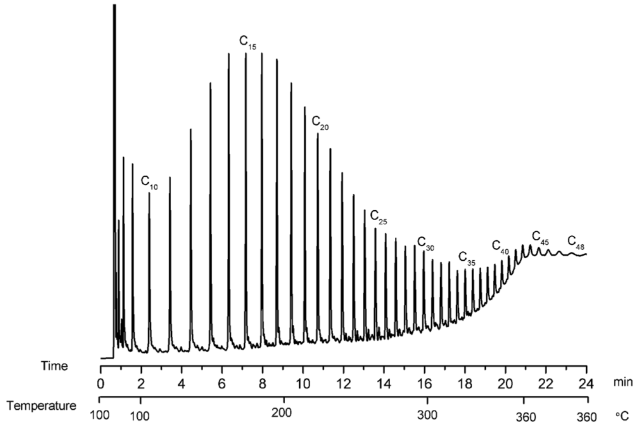

Fig. 3 Chromatogram of the polyethylene pyrolysis product on the DPTP column (10 m × 0.25 mm). Conditions: the temperature was increased from 100 °C (maintained for 2 min) to 360 °C (maintained for 4 min) at 14 °C min^{-1}. Carrier gas velocity: 14 cm s^{-1}. The injection and detector temperatures were both 400 °C.

The polyethylene pyrolysis product was separated on the 10 m DPTP column to further characterize the thermal stability of DPTP, and the related chromatogram is displayed in Fig. 3. Baseline separation was achieved with sufficiently sharp symmetrical peaks. The DPTP column retained noteworthy column efficiency and separation performance until 360 °C. The thermogravimetric analysis and polyethylene pyrolysis product separation results thus confirm that the high-temperature resistance of DPTP enables the separation of high-boiling point substances.

3.3 Column efficiency of DPTP

Column efficiencies of 3646 and 3125 plates m^{-1} were observed by determining naphthalene at 120 °C with the 30 and 10 m columns, respectively. The coating efficiencies of DPTP in the 30 and 10 m columns were calculated in accordance with ref. 23 to be 78.3% and 75.4%, respectively. Moreover, the crosslinking degrees of DPTP, which were obtained by calculating the ratio of the capacity factors before and after the DPTP columns were rinsed with 5 mL dichloromethane,[26] were 81.2% (30 m) and 79.6% (10 m). These findings show that DPTP has good film-forming and cross-linking abilities. Golay curves were created by evaluating naphthalene at different linear velocities to describe the relationship between the height equivalent of a theoretical plate and linear velocity. Fig. 4 reveals that the optimal linear velocities of the 30 and 10 m columns range from 8 cm s^{-1} to 15 cm s^{-1}.

3.4 McReynolds and Abraham system constants of the DPTP columns

McReynolds constants[27] were quantitatively measured to investigate the polarity of DPTP. Five probe compounds were eluted on the prepared DPTP column in the following sequence: Y' (n-butanol) → X' (benzene) → Z' (2-pentanone) → U' (1-nitropropane) → S' (pyridine). As demonstrated in Table 1, the DPTP column has moderate polarity with a CP index of 17.3. The McReynolds constants of DPFP[13] and OV-11,[27] the side-chain groups of which are 7,10-diphenylfluoranthene and benzene, respectively,

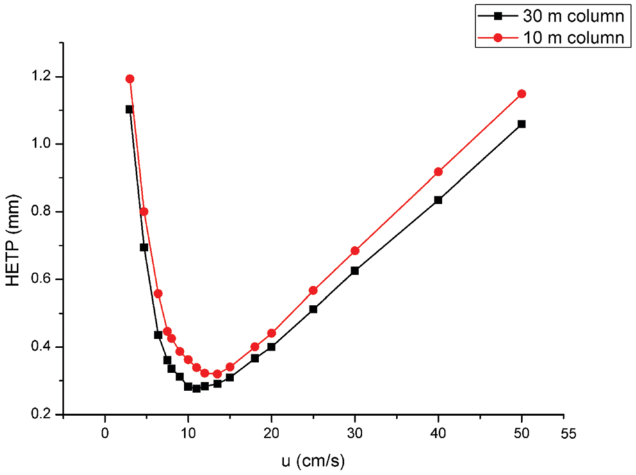

Fig. 4 Golay curves of the DPTP capillary columns.

Table 1 McReynolds constants of DPTP, DPFP and OV-11

Column	X'	Y'	Z'	U'	S'	Sum	CP index
DPTP	121	139	153	182	138	733	17.3
DPFP[13]	118	136	142	178	135	704	16.7
OV-11[27]	102	142	145	219	178	786	18.6

are presented in Table 1 to analyze the factors affecting the polarity. As computed in accordance with ref. 28, the average molecular polarizability values of benzene, 7,10-diphenylfluoranthene, and 1,4-diphenyltriphenylene are 10.40, 44.79, and 48.26 Å^3, respectively. Table 1 shows that the values of the five characteristic constants of DPTP (containing 14.2% 1,4-diphenyltriphenylene) are slightly larger than those of 7,10-diphenylfluoranthene-grafted (15.9%) polysiloxane (DPFP), although the grafting amount of the former is slightly smaller than that of the latter. These results reveal that different structures of the grafting groups significantly influence the interaction between the stationary phase and the analyte. 1,4-Diphenyltriphenylene, which is a rigid coplanar group, promotes π–π stacking, dipole-induced dipole, and dispersion interactions to a certain extent with increasing average molecular polarizability. The polarity of DPTP is smaller than that of OV-11 (35% phenyl-methyl polysiloxane), although the average molecular polarizability of benzene is only 10.40 Å^3. Therefore, the polarizability of the grafting group and the grafting amount jointly affect the polarity of the stationary phases.

Table 2 Abraham system constants of DPTP and DPFP

Stationary phase	Temperature (°C)	Interaction parameter c	e	s	a	b	l	n	R^2
DPTP	80	−2.376	0.021	0.743	0.612	0	0.669	32	0.99
	100	−2.425	0.050	0.670	0.533	0	0.643	31	0.99
	120	−2.501	0.093	0.564	0.383	0	0.587	31	0.99
DPFP[13]	80	−2.927	0.013	0.733	0.603	0	0.663	39	0.99
	100	−3.001	0.020	0.666	0.492	0	0.658	39	0.99
	120	−2.996	0.091	0.559	0.379	0	0.608	39	0.99

Abraham system constants[29,30] were applied to determine individual intermolecular interactions between DPTP and the analytes. The results are shown in Table 2; here, c represents the phase ratio of a given column, e represents n–π/π–π interactions, s represents dipole interactions, a represents hydrogen-bond basicity, b represents hydrogen-bond acidity, and l represents dispersion interactions. The results revealed that dipole-induced dipole interactions (s) are the main interactions occurring between DPTP and the analytes, followed by dispersion interactions (l). Nearly all interaction parameters of DPTP were larger than those of DPFP. Thus, large rigid coplanar groups containing delocalized electrons significantly improve the interactions, especially n–π/π–π and dipole-induced dipole interactions, between DPTP and the analytes. Furthermore, DPTP has considerable potential for separating polarizable compounds, such as aromatic compounds, *via* dipole-induced dipole and dispersion interactions, which is in accordance with the McReynolds constants obtained.

The computed McReynolds and Abraham system constants confirm that the introduction of 1,4-diphenyltriphenylene groups, which is characterized by a rigid coplanar structure containing polyphenyl and a large π-conjugated group, could enhance the π–π stacking, dipole-induced dipole, and dispersion interactions between DPTP and various analytes.

3.5 Selectivity, repeatability and reproducibility of the DPTP column

As shown in Fig. 5, the Grob mixture was analyzed to evaluate the comprehensive performance of the chromatographic columns, including their column efficiency, adsorption activity, and acid–base properties. All substances expressed baseline separation with sharp symmetrical peaks, except for peak S. The leading peak of 2-ethylhexanoic acid (peak S) resulted from overloading.[31] 2,6-Dimethylaniline (peak A) revealed a longer retention time

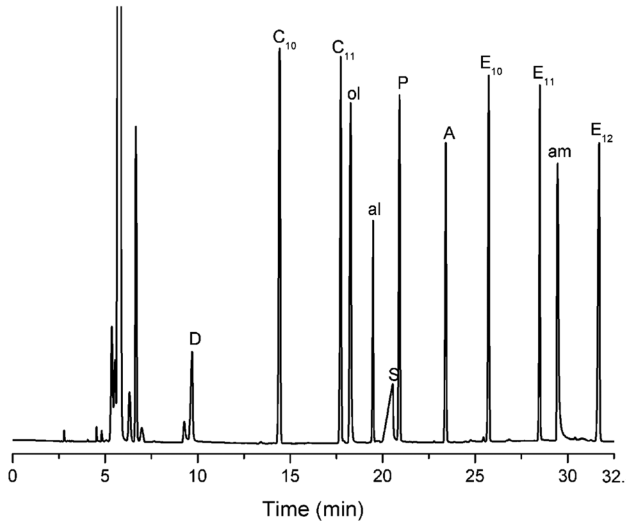

Fig. 5 Chromatogram of the Grob test mixture on the DPTP column. Conditions: the column temperature was increased from 40 °C to 170 °C at 4 °C min^{-1}. Carrier gas velocity (N_2): 10 cm s^{-1}. The injection and detector temperatures were both 220 °C. Peaks: (D) 2,3-butanediol; (C_{10}) decane; (C_{11}) undecane; (ol) *n*-octanol; (al) nonanal; (S) 2-ethylhexanoic acid; (P) 2,6-dimethylphenol; (A) 2,6-dimethylaniline; (E_{10}) methyl decanoate; (E_{11}) methyl undecanoate; (am) dicyclohexylamine; (E_{12}) methyl dodecanoate.

Table 3 Repeatability and reproducibility of the DPTP column

	Month-to-month (*n* = 6)		Column-to-column (*n* = 3)	
Analytes	Mean (min)	RSD (%)	Mean (min)	RSD (%)
Heptane	5.532	0.15	5.545	2.63
Butyl acetate	6.087	0.43	6.099	3.82
Chlorobenzene	6.943	0.22	6.951	2.83
Bromobenzene	7.963	0.10	7.972	2.57
Octanol	9.836	0.38	9.833	4.32
p-Cresol	11.114	0.51	11.128	3.30
Acetophenone	12.038	0.13	12.047	2.37

than 2,6-dimethylphenol (peak P), thus indicating that the DPTP column retains alkaline analytes more strongly than acidic analytes. Undecane and *n*-octanol have similar boiling points (195.6 °C and 194.0–195.0 °C, respectively). However, the retention time of *n*-octanol was noticeably longer than that of undecane. Thus, DPTP has stronger retention capacity for alcohols than alkanes with identical boiling points.

Column repeatability and reproducibility after a long-term use were obtained by separating several analytes of different classes at 120 °C. As shown in Table 3, the relative standard deviations (RSD%) of the retention time were below 0.51% for month-to-month and 4.32% for column-to-column, demonstrating good repeatability and reproducibility of the DPTP column.

3.6 Application of the DPTP column

The DPTP stationary phase could interact with analytes through π–π stacking, dipole-induced dipole, and dispersion interactions because of its special structure. Therefore, multiple analytes, including substituted benzene and a series of isomers, FAEs, ethers, PAHs, nitrogenous heterocyclic compounds and diesel, were used to evaluate the chromatographic performance of the DPTP stationary phase. The corresponding chromatograms are shown in Fig. 6–12.

3.6.1. Separation performance of DPTP for substituted benzene and a series of isomers. As seen from the results of the McReynolds and Abraham system constants of DPTP, 1,4-diphenyltriphenylene could improve the stationary phase's dipole-induced dipole interactions with polar substances and π–π stacking effects with aromatic substances. Fig. 6 and 7 show the chromatograms of substituted benzene and a series of isomers. A comparison of the separation effects of the DPTP and DB-17 columns on substituted benzene is illustrated in Fig. 6. Baseline separation was observed for all substances on the DPTP column, particularly *p*-xylene (peak 4, b.p. 137.0–138.0 °C), *m*-xylene (peak 5, b.p. 139.3 °C), and *o*-xylene (peak 6, b.p. 144.4 °C), which were co-eluted on the DB-17 column. As seen in Fig. 7, a series of isomers, including butanol, pinene, nitroaniline, and cyanobenzaldehyde, were effectively separated *via* enhanced sensitive dipole-induced dipole and π–π interactions. Based on these tests and the analytical results, the DPTP stationary phase may be an ideal candidate for separating a variety of isomers.

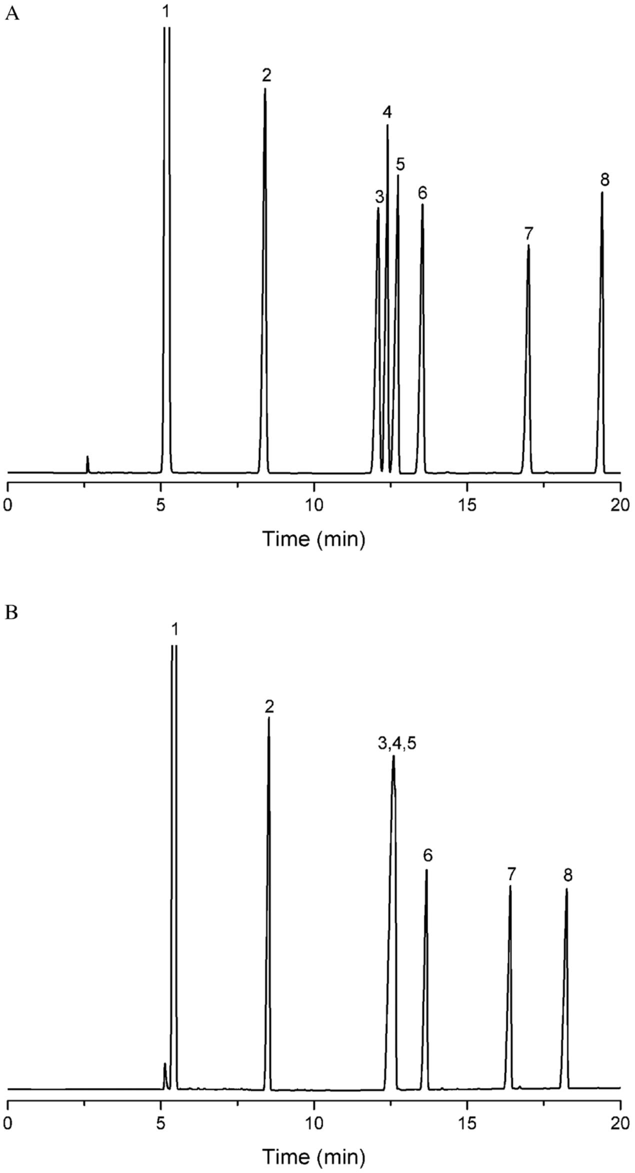

Fig. 6 Chromatograms of substituted benzene on the DPTP (A) and DB-17 (B) columns. Conditions: the temperature was increased from 60 °C to 140 °C at 4 °C min^{-1}. Carrier gas velocity: 10 cm s^{-1}. The injection and detector temperatures were both 220 °C. Peaks: (1) benzene; (2) toluene; (3) ethylbenzene; (4) *p*-xylene; (5) *m*-xylene; (6) *o*-xylene; (7) *tert*-butylbenzene; and (8) *n*-butylbenzene.

3.6.2. Separation performance of DPTP for FAEs. As shown in Fig. 8, the FAEs composed of polar and nonpolar compounds were directly separated on the DPTP column with good selectivity. The figure also shows that the retention time of unsaturated FAEs was longer than that of saturated FAEs, such as butyl formate (peak 6, b.p. 107.0 °C)/ethyl acrylate (peak 7, b.p. 99.4 °C), ethyl butyrate (peak 9, b.p. 120.0–121.0 °C)/ethyl methacrylate (peak 11, b.p. 119.0 °C), and methyl laurate (peak 27, b.p. 262.0 °C)/ethyl 10-undecenoate (peak 28, b.p. 259.0 °C). Propyl propionate (peak 10, b.p. 122.0 °C–124.0 °C) and ethyl methacrylate (peak 11, b.p. 119.0 °C) achieved baseline separation on the DPTP column but were co-eluted on the DPFP column (Fig. 8 in ref. 13). These findings may be due to the improved dipole-induced dipole interactions between the C=C double bond of the unsaturated FAEs and the DPTP stationary phase, which strengthens the retention behavior of the latter for unsaturated FAEs. The elution time of benzyl acetate (peak 25, b.p. 213.0 °C)

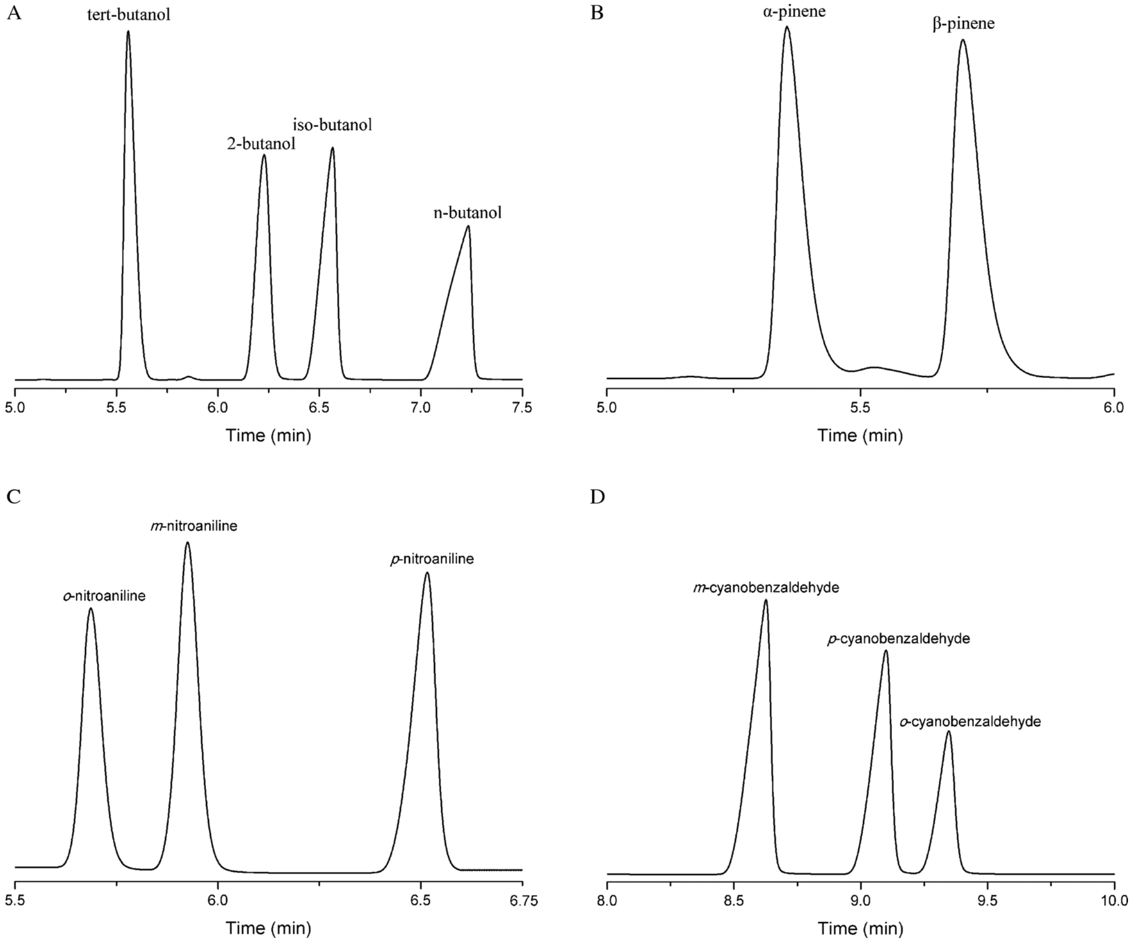

Fig. 7 Chromatograms for separation of (A) butanol isomers, (B) pinene isomers, (C) nitroaniline isomers (D) cyanobenzaldehyde isomers at 80 °C, 180 °C, 300 °C and 240 °C, respectively. The solvents for them were ether and their N_2 linear velocity was 13 cm s^{-1}. The injection and detector temperatures were 220 °C for A and B, 340 °C for C and 300 °C for D.

was later than that of 2-(2-ethoxyethoxy)ethyl acetate (peak 23, b.p. 219.0 °C). This result could be due to the π–π stacking interactions between benzene moieties in benzyl acetate and concentrated aromatic rings in the DPTP stationary phase. In addition, ethyl cyanoacetate (peak 24, b.p. 206.0 °C) was eluted after 2-(2-ethoxyethoxy)ethyl acetate (peak 23, b.p. 219.0 °C). The sensitive dipole-induced dipole interaction between $-C\equiv N$ and the DTPP stationary phase may be a reasonable explanation for this finding.

3.6.3. Separation performance of DPTP for ethers. Ethers were separated on the DPTP column to evaluate the separation ability of DPTP for resolving weak polar substances. As can be seen in Fig. 9, all compounds demonstrated effective separation with sharp chromatographic peaks. The analytes (except for some specific compounds) were eluted in the order of an increasing boiling point. The retention time of anisole (peak 15, b.p. 155.5 °C) was longer than that of bis(2-methoxyethyl)ether (peak 14, b.p. 162.0 °C), likely due to the presence of π–π stacking interactions between the DPTP stationary phase and anisole. Moreover, the elution sequences of dibutyl ether (peak 11, b.p. 142.0 °C–143.0 °C) and ethylene glycol diethyl ether (peak 13, b.p. 121.4 °C) were reversed on the DPTP and DPFP columns (Fig. 9 in ref. 13), possibly because 1,4-diphenyltriphenylene serves as a functional group that enhances dipole-induced dipole interactions with ethylene glycol diethyl ether. As seen from these findings, the DPTP stationary phase differs from the traditional stationary phase by virtue of the former's π–π stacking and dipole-induced dipole interactions with analytes. Thus, DPTP is suitable for separating weak polar substances.

3.6.4. Separation performance of DPTP for PHAs. High-boiling-point PAHs are widely found in food and environmental contaminants.[32,33] The proposed DPTP was used to separate PAHs. As observed in Fig. 10, 22 components were separated with well-shaped peaks within 42 min on the DPTP column. In particular, 2-methylnaphthalene (peak 4, b.p. 241.0–242.0 °C) and 1-methylnaphthalene (peak 5, b.p. 240.0–243.0 °C) were successfully separated on the DPTP column, thereby indicating the material's advantageous separation capability for certain isomers of PAHs. Moreover, 4-nitrobiphenyl (peak 14, b.p. 340.0 °C), anthracene (peak 16, b.p. 342 °C), and phenanthrene (peak 17, b.p. 340.0 °C), which have similar boiling points, revealed baseline separation. The elution sequence of benzil (peak 15, b.p. 346.0–348.0 °C) and phenanthrene (peak 17, b.p. 340.0 °C) was against their boiling points. A possible reason for this finding is that the

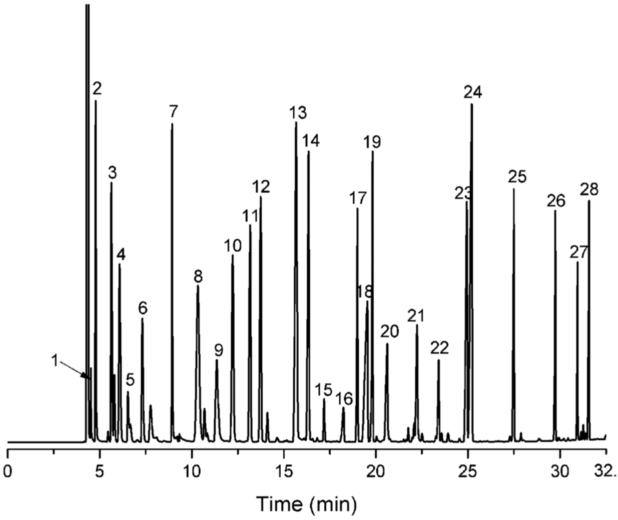

Fig. 8 Chromatograms of the separation of FAEs on the DPTP column. Conditions: the temperature was increased from 45 °C (maintained for 8 min) to 90 °C at 4 °C min^{-1}, and then to 250 °C at 12 °C min^{-1}. Carrier gas velocity: 12 cm s^{-1}. The injection and detector temperatures were both 320 °C. Peaks: (1) ethyl acetate; (2) vinyl acetate; (3) ethyl propionate; (4) propyl acetate; (5) ethyl propionate; (6) butyl formate; (7) ethyl acrylate; (8) isobutyl acetate; (9) ethyl butyrate; (10) propyl propionate; (11) ethyl methacrylate; (12) butyl acetate; (13) amyl acetate; (14) methyl crotonate; (15) butyl propionate; (16) isoamyl acetate; (17) *n*-propyl methacrylate; (18) allyl methacrylate; (19) butyl acrylate; (20) ethyl caproate; (21) propyl hexanoate; (22) 2-hydroxyethyl methacrylate; (23) 2-(2-ethoxyethoxy)ethyl acetate; (24) ethyl cyanoacetate; (25) benzyl acetate; (26) methyl decanoate; (27) methyl laurate; and (28) ethyl 10-undecenoate.

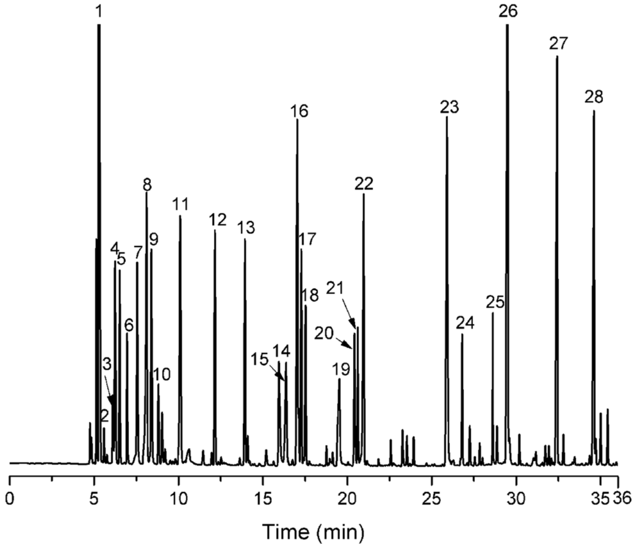

Fig. 9 Chromatograms of the separation of ethers on the DPTP column. Conditions: the temperature was increased from 50 °C (maintained for 5 min) to 240 °C at 6 °C min^{-1}. Carrier gas velocity: 10 cm s^{-1}. The injection and detector temperatures were both 320 °C. Peaks: (1) diethyl ether; (2) ethyl vinyl ether; (3) tetrahydrofuran; (4) isopropyl ether; (5) 2,3-dihydrofuran; (6) 2-methyltetrahydrofuran; (7) ethyl propenyl ether; (8) 1,2-dimethoxyethane; (9) allyl ether; (10) 1,4-dioxane; (11) dibutyl ether; (12) ethylene glycol monomethylether; (13) ethylene glycol diethyl ether; (14) bis(2-methoxyethyl)ether; (15) anisole; (16) ethylene glycol monobutyl ether; (17) isopentyl ether; (18) dibutylsulfide; (19) dichloroisopropyl ether; (20) 2,2′-oxybis-ethanomonoethylether; (21) 2-ethoxyethyl ether; (22) 2-(2-ethoxyethoxy)ethyl acetate; (23) diethylene glycol monobenzyl ether; (24) 4-methoxyphenol; (25) diphenyl ether; (26) 2-nitroanisole; (27) ethyl naphthylether; and (28) benzyl ether.

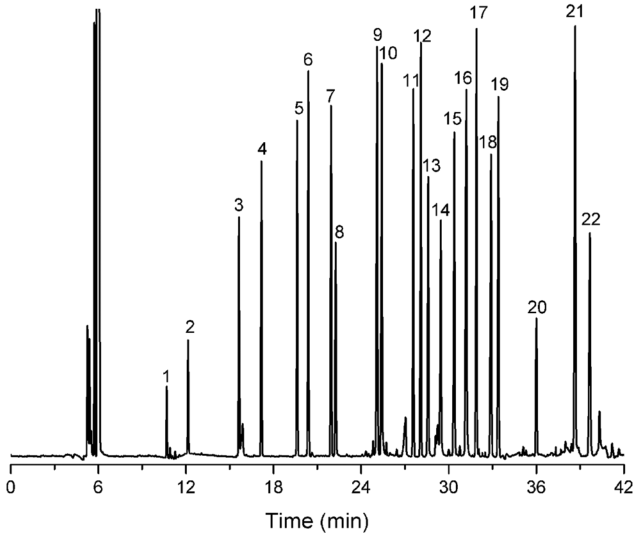

Fig. 10 Chromatogram of polycyclic aromatic hydrocarbons on the DPTP column. Conditions: the column temperature was increased from 80 °C to 290 °C at 5 °C min^{-1}. Carrier gas velocity: 10 cm s^{-1}. The injection and detector temperatures were both 340 °C. Peaks: (1) decahydronaphthalene; (2) tetralin; (3) naphthalene; (4) 2-methylnaphthalene; (5) 1-methylnaphthalene; (6) biphenyl; (7) di-benzyl ether; (8) 8-hydroxyquinoline; (9) acenaphthylene; (10) dihydroacenaphthylene; (11) naphthyl-ethyl ether; (12) fluorenone; (13) α-nitronaphthalene; (14) 4-nitrobiphenyl; (15) benzil; (16) anthracene; (17) phenanthrene; (18) phenanthrenequinone; (19) 1,8-dihydroxyanthracene-9,10-dione; (20) pyrene; (21) 1,2-benzanthracene; and (22) chrysene.

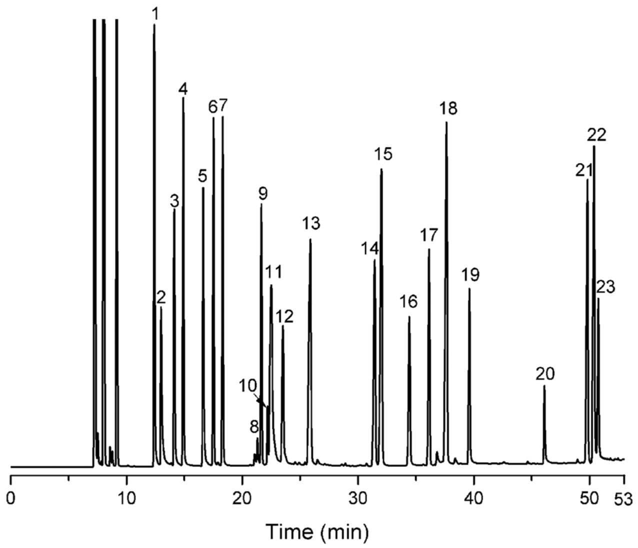

Fig. 11 Chromatograms of the separation of nitrogenous heterocyclic compounds on the DPTP column. Conditions: the temperature was increased from 50 °C (maintained for 8 min) to 320 °C at 6 °C min^{-1}. Carrier gas velocity: 8 cm s^{-1}. The injection and detector temperatures were both 380 °C. Peak: (1) piperidine; (2) pyridine; (3) morpholine; (4) α-picoline; (5) β-picoline; (6) 2,6-lutidine; (7) 2-ethylpyridine; (8) 3,5-lutidine; (9) 2,4,6-trimethylpyridine; (10) α-aminopyridine; (11) 1-methyl-2-pyrrolidone; (12) α-amino-3-methylpyridine; (13) benzothiazole; (14) quinoline; (15) isoquinoline; (16) 1-methyl-2-(3-pyridyl) pyrrolidine; (17) imidazole; (18) 8-hydroxyquinoline; (19) 2,2′-bipyridyl; (20) 4,4′-dimethyl-2,2′-dipyridyl; (21) carbazole; (22) β-naphthoquinoline; (23) benzimidazole.

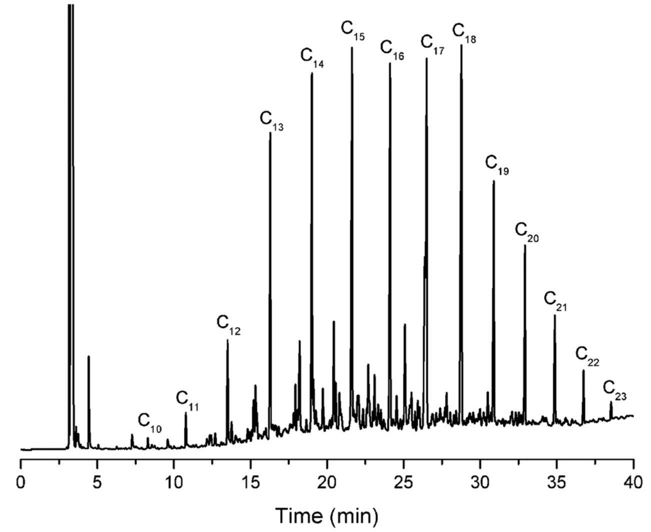

Fig. 12 Chromatogram of the separation of a kind of diesel on the DPTP column. Conditions: the temperature was increased from 80 °C to 320 °C at 6 °C min^{-1}. Carrier gas velocity: 15 cm s^{-1}. The injection and detector temperatures were both 380 °C.

electron-rich delocalized π-bonds of the polyphenyl ring structure of the 1,4-diphenyltriphenylene group enhance π–π stacking interactions between phenanthrene and the DPTP column.

3.6.5. Separation performance of DPTP for nitrogenous heterocyclic compounds. N–π interactions between the lone pair electrons on N and the electron-rich π system of 1,4-diphenyltriphenylene enable the separation of nitrogenous heterocyclic compounds on the DPTP column. Fig. 11 displays the chromatographic separation of the nitrogenous heterocyclic compounds. Most of the components were effectively separated within 53 min, and sharp symmetrical peaks were obtained. Isomers such as α-picoline (peak 4, b.p. 128.0–129.0 °C)/β-picoline (peak 5, b.p. 143.0–144.0 °C), and quinoline (peak 14, b.p. 237.7 °C)/isoquinoline (peak 15, b.p. 242.2 °C) were separated well on the DPTP column. Moreover, the elution sequence of carbazole (peak 21, b.p. 355.0 °C) and β-naphthoquinoline (peak 22, b.p. 350.4 °C) was opposite their boiling points. This result may be attributed to the enhanced π–π stacking interactions between β-naphthoquinoline and the 1,4-diphenyltriphenylene group, which prolongs the retention time of the latter.

3.6.6 Separation performance of DPTP for the real sample. The *n*-alkanes in diesel have important influence on its combustion performance. To demonstrate the potential of the DPTP column for separating real samples, a kind of diesel was determined without any enrichment process. Fig. 12 presents the chromatogram of this diesel with good separation of *n*-alkanes. It could be seen from the results that 14 kinds of *n*-alkanes were detected in this diesel, which indicated that the DPTP column had potential application value in the field of oil analysis.

4. Conclusion

This work describes the synthesis of DPTP, which possesses a rigid coplanar structure containing a polarizable electron-rich polyphenyl group, and its performance as a novel gas chromatographic stationary phase. The analysis results demonstrated that DPTP exhibits good film-forming ability, high column efficiency, high thermal stability, and moderate polarity. In addition, the DPTP column revealed a unique retention behavior and remarkable separation performance for multiple isomers, FAEs, ethers, PAHs, heterocyclic aromatic hydrocarbons and diesel due to its enhanced π–π stacking, dipole-induced dipole, and dispersion interactions derived from the 1,4-diphenyltriphenylene group of the polysiloxane side-chain. In conclusion, DPTP deserves further study as a high-selectivity and temperature-resistant stationary phase that may address increasing demands for accurate separation in many fields.

Conflicts of interest

There are no conflicts to declare.

References

1 J. Y. Tian, *J. Food Compos. Anal.*, 2010, **23**, 475–479.
2 R. H. Alremeithi, M. A. Meetani and S. A. Khalil, *RSC Adv.*, 2016, **6**, 80576–80584.
3 S. R. Rissato, M. S. Galhiane, M. V. D. Almeida, M. Gerenutti and B. M. Apon, *Food Chem.*, 2007, **101**, 1719–1726.
4 S. G. Cong, F. Fang, T. Wei, S. Q. Liu, G. S. Jiang and J. Cai, *Mod. Chem. Ind.*, 2013, **33**, 128–133.
5 A. Speltini, D. Merli and A. Profumo, *Anal. Chim. Acta*, 2013, **783**, 1–16.
6 C. M. Hussain, C. Saridara and S. Mitra, *RSC Adv.*, 2011, **1**, 685–689.
7 X. H. Yang, C. X. Li, M. L. Qi and L. T. Qu, *RSC Adv.*, 2017, **7**, 32126–32132.
8 X. H. Yang, C. X. Li, M. L. Qi and L. T. Qu, *J. Chromatogr. A*, 2016, **1460**, 173–180.
9 J. R. Yang, S. M. Xie, H. Liu, J. H. Zhang and L. M. Yuan, *Chromatographia*, 2015, **78**, 557–564.
10 L. Fan and X. P. Yan, *Talanta*, 2012, **99**, 944–950.
11 C. F. Poole and S. K. Poole, *J. Chromatogr. A*, 2008, **1184**, 254–280.
12 X. Han, X. X. He, H. Wang, B. Wang and B. Wu, *J. Chromatogr. A*, 2016, **1449**, 118–128.
13 X. Han, H. Wang, X. X. He, B. Wang and B. Wu, *J. Chromatogr. A*, 2016, **1468**, 192–199.
14 X. Han, X. X. He, B. Wang and B. Wu, *RSC Adv.*, 2016, **6**, 109786–109792.
15 X. X. He, X. Han, W. Hang, B. Wang and B. Wu, *RSC Adv.*, 2016, **6**, 76514–76523.
16 A. T. James and A. J. Martin, *Biochem. J.*, 1952, **50**, 679–690.
17 P. A. Peaden, B. W. Wright and M. L. Lee, *Chromatographia*, 1982, **15**, 335–340.
18 K. P. Naikwadi and P. P. Wadgaonkar, *J. Chromatogr. A*, 1998, **811**, 97–103.
19 T. J. Ge, J. Zhang, S. X. Xiao and X. F. He, *New Chem. Mater.*, 2017, **45**, 97–100.

20 P. C. Zhao, Y. Y. Niu, M. Yu, N. Niu, H. Wang, X. X. He and B. Wu, *RSC Adv.*, 2015, **5**, 22399–22404.

21 K. Grob Jr, G. Grob and K. Grob, *J. Chromatogr. A*, 1978, **156**, 1–20.

22 S. Y. Feng, *Silicone Polymers and Their Applications*, Chemical Industry Press, 1st edn, 2004.

23 P. Ma, X. Cai, Y. Zhang, S. Wang, W. Dong, M. Chen and P. J. Lemstra, *Polym. Degrad. Stab.*, 2014, **102**, 145–151.

24 J. L. Anderson and D. W. Armstrong, *Anal. Chem.*, 2005, **77**, 6453–6462.

25 T. H. Thomas and T. C. Kendrick, *J. Polym. Sci. Pol. Phys.*, 1970, **8**, 1823–1830.

26 C. Ragonese, D. Sciarrone, P. Q. Tranchida, P. Dugo, G. Dugo and L. Mondello, *Anal. Chem*, 2011, **83**, 7947–7954.

27 W. O. McReynolds, *J. Chromatogr. Sci.*, 1970, **8**, 685–691.

28 K. J. Miller and J. Savchik, *J. Am. Chem. Soc.*, 1979, **101**, 7206–7213.

29 J. L. Anderson, J. Ding, T. Welton and D. W. Armstrong, *J. Am. Chem. Soc.*, 2002, **124**, 14247–14254.

30 M. H. Abraham, P. L. Grellier, D. Prior and J. J. Morris, *J. Phys. Org. Chem.*, 1989, **2**, 243–254.

31 K. Grob, G. Grob and K. Grob Jr, *J. Chromatogr. A*, 1981, **219**, 13–20.

32 S. K. Samanta, O. V. Singh and R. K. Jain, *Trends Biotechnol.*, 2002, **20**, 243–248.

33 B. Veyrand, A. Brosseaud, L. Sarcher, V. Varlet, F. Monteau, P. Marchand, F. Andre and B. L. Bizec, *J. Chromatogr. A*, 2007, **1149**, 333–344.