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High temperature stationary phase of polysiloxane containing *N,N'*-bis(diphenylsilyl) tetramethylcyclodisilazane for gas chromatography

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An alternate copolymer (P(BPTMC)-*alt*-ODMS) constructed from *N,N'*-bis(diphenyl-silyl) tetramethylcyclodisilazane (BPTMC) and oligo-dimethylsiloxane (ODMS) segments was synthesized and coated on the inside of fused-silica capillary columns to evaluate their properties as stationary phase in gas chromatography. The thermal stability, selectivity, column efficiency, and working range of these capillary columns were characterized. The obtained results indicated that such produced columns exhibited better separation efficiency than commercial ones with high thermal stability and low column bleeding. The upper working temperature can reach up to 400 °C, which resulted in high-quality GC analysis of polyethylene pyrolysis products, petroleum, and aromatic hydrocarbon mixtures. The influence of BPTMC content on the thermal stability and polarity of the stationary phase was also investigated.

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Introduction

High-temperature gas chromatography (HTGC) is suitable for analyzing high molecular weights with thermal stability and high efficiency.¹ The most important component of such a GC instrument is the chromatographic column, the heart of which is a stationary phase that determines the thermal stability and selectivity of the GC capillary column. A stationary phase with high thermal stability is required to obtain high column temperature. Considering these motivations, modified polysiloxanes, including poly-*m*-carborane-siloxane (Dexsil series) and silphenylene-modified polysiloxane, which are obtained by replacement of the oxygen atoms of the backbones using arylene ($-C_6H_4-$)²⁻⁴ and carborane ($-CB_{10}H_{10}C-$),^{1,5-8} have been adopted as high temperature stationary phases (HTSP) for several decades.⁹⁻¹⁴ These two types of stationary phases are commonly used as HTSP in GC.¹⁵ Despite withstanding temperatures of up to 400 °C to 480 °C,¹ the Dexsil series polysiloxanes are only applied to separate non-polar and weakly polar substances.^{2,3} In addition, the decaborane used for fabricating the Dexsil series is highly toxic. Regarding silphenylene-modified polysiloxane, which has higher polarity than poly-*m*-carborane-siloxane because of the introduction of a phenyl group, the maximum operating temperature can only be controlled in the range of 380 °C to 400 °C.¹⁵ Therefore, fabricating a stationary phase with both high thermal stability and polarity is significant.

Recent years, some new materials as GC stationary phases with high thermal and mechanical stability have been reported, especially for carbon nanotubes (CNTs) and metal-organic frameworks (MOFs). In 2005, Mitra reported the first application of self-assembled CNTs in long capillary tubes used for gas chromatography columns.¹⁶ Later, through catalytic chemical vapor deposition process, they synthesized the self-assembled, single-walled carbon nanotubes and used it as high temperature stationary phases with no column bleed or other instability at temperatures around 425 °C.¹⁷ In 2010, Yan group fabricated the first MOF-coated capillary column (MIL-101) as stationary phase for high-resolution capillary GC separation and achieved a baseline separation of *p*-xylene, *o*-xylene, *m*-xylene, and ethylbenzene within 1.6 min.¹⁸ Then Yan group focused on the molecular sieving effect of MOFs (ZIF-7, ZIF-8,¹⁹ and UIO-66 (ref. 20)) with different pore window size and pore size. With narrow pore windows (~ 3.4 Å) and larger pores (~ 11.4 Å), zeolitic imidazolate framework-8 (ZIF-8) demonstrates a high capability in sieving linear alkanes from branched alkanes and offers high resolution GC separation of linear alkanes from each other according to boiling points.¹⁹

Cyclodisilazane, a compound with relatively high polarity, was synthesized by Fink and exhibited good thermal stability, with a decomposition temperature up to 500 °C.²¹ Breed prepared an oligomer of cyclodisilazane and siloxane,²² and the resulting decomposition temperature was still above 450 °C. Notably, a series of alternate copolymers synthesized by Xie's group using hydroxyl cyclodisilazane and α,ω -diethylin (or dimethylamino) dimethyl polysiloxane presented good thermal endurance and good solubility in organic solvents such as

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toluene.^{23–26} Meanwhile, P(BPTMC)-*alt*-ODMS (an alternate copolymer constructed by *N,N'*-bis(diphenyl-silyl) tetramethylcyclodisilazane (BPTMC) and oligo-dimethylsiloxane (ODMS) segments) has been found to show good filming ability as a commercial stationary phase, exhibiting almost the same temperature tolerance as *m*-carborane-siloxane,^{27,28} making it suitable to act as stationary phase in HTGC. However, to the best of our knowledge, the use of P(BPTMC)-*alt*-ODMS as GC stationary phase has not been reported yet. No similar commercial stationary phase has also been reported.

In addition, compared to the above high temperature stationary phases, such as Dexsil series, silphenylene-modified polysiloxane, and silylphenylene ether-modified polysiloxane, the polysilazane studied in this paper has a novel structure. It is characterized in that: (1). rigid block unit (*N,N'*-bis(diphenyl-silyl) tetramethylcyclodisilazane) has a rational structure: volume of constitutional unit of cyclodisilazane is smaller than that of carborane, but four phenyl groups on it play an important role in increasing polarity of a stationary phase while it can be inferred that its CP index is higher than Dexsil-300; plus, its volume and rigidity exceed those of silylphenylene and silylphenylene ether, making for increase in temperature resistance performance; (2). the degree of polymerization of siloxane oligomer is three, thus cyclization degradation of copolymer can be effectively reduced. When the siloxane polymerization degree is four or above, the temperature resistance performance of stationary phase will be weakened.

Based on these reasons, an alternate copolymer, P(BPTMC)-*alt*-ODMS, has been synthesized and used as HTSP. Elemental analysis, ¹H nuclear magnetic resonance spectroscopy (¹HNMR), infrared spectroscopy (IR), and thermo-gravimetric analysis (TGA) have been used to characterize the polymer composition and structure. The coated fused silica capillary columns with the polymer are evaluated on their selectivity, polarity, inertness, separation efficiency, and bleeding. Moreover, the applications of such columns on the analysis of polyethylene pyrolysis products, petroleum, and aromatic hydrocarbon mixtures are described. The obtained results reflect a great potential of the P(BPTMC)-*alt*-ODMS in practical applications, such as stationary phases for HTGC.

Experiment

Reagents and apparatus

Dimethyldichlorosilane, diphenyldichlorosilane, hexamethylcyclotrisilazane, and diethylamine were all of analytical grade and purchased from Beijing Chemical Works (Beijing, P. R. China). 1,3-Dimethyl-1,1,3,3-tetraphenyl-disilazane (>99.5%) was purchased from Shandong Kunrong Chemical Engineering Company (Jinan, P. R. China). The test mixture for the polar capillary column was prepared according to the method described by Grob *et al.*^{29,30} Five Rohrschneider–McReynolds standards (benzene, 2-pentanone, 1-nitropropane, 1-butanol, and pyridine) were obtained from Fluka (Buchs, Switzerland). Petroleum samples were obtained from Shengli Oil Field (Dongying, P. R. China). Polycyclic aromatic hydrocarbons were prepared by mixing various chemically pure reagents together.

Polyethylene pyrolysis products as chromatographic separation sample were prepared as follows: 100 g polyethylene was placed into a 500 mL round bottom flask with air condenser under N₂ protection. After heating to 600 °C to 650 °C, the C–C bonds in alkyl chains were broken randomly, and the products were collected. After 30 min, approximately 85 g of product was obtained.

The chemical structure and composition of the synthesized copolymer were analyzed by ¹H NMR and FT-IR spectroscopic methods. The molecular weight and distribution were determined and calculated against the polystyrene standard by gel permeation chromatography (Waters 515 HPLC) at room temperature. Toluene was used as eluent at a flow rate of 0.35 mL min^{−1}. The glass transition temperature of the copolymer was measured using differential scanning calorimetry (Pyris 7, Perkin-Elmer Instruments, Norwalk, CT). Elemental analysis was performed by a Vario EI III elemental analyzer (Elementar, Germany).

Synthesis of P(BPTMC)-*alt*-ODMS stationary phase and characterization

P(BPTMC)-*alt*-ODMS were prepared according to the procedures described in Fig. 1.^{23,24} *N,N'*-Bis(chlorodimethylsilyl)-tetramethylcyclodisilazane (II) was produced from hexamethylcyclotrisilazane (I) based on previously reported methods.^{21,23} The reaction was conducted at 220 °C using compound I-to-dimethyldichlorosilane molar ratio of 1 : 1.8. *N,N'*-Bis(chlorodiphenylsilyl) tetramethylcyclodisilazane (III) was therefore synthesized from II,²³ with a reaction temperature of 320 °C and molar ratio of II to diphenyldichlorosilane of 1 : 2.2. Afterward, a mixture of 10.9 g (0.02 mol) *N,N'*-bis(hydroxydiphenylsilyl) tetramethylcyclodisilazane (IV) was obtained from the hydrolysis of III, and 7.0 g (0.02 mol) α,ω -bis(diethylamino)-dimethylsiloxane (prepared according to literature^{23,24}) was stirred at 120 °C under nitrogen for over 10 h.

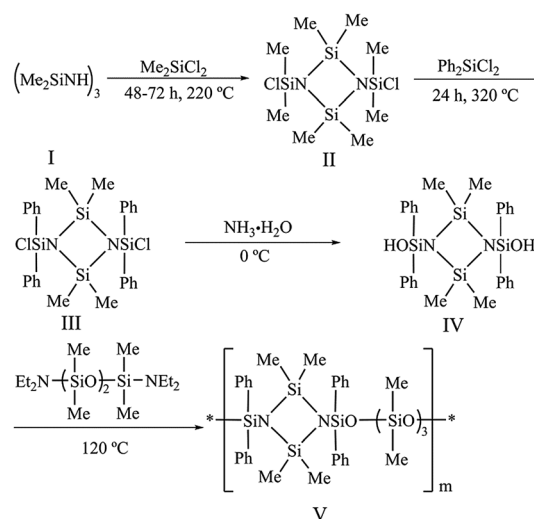


Fig. 1 Condensation reaction of cyclodisilazane with polysiloxane to obtain P(BPTMC)-*alt*-ODMS.

When no Et₂NH can be detected, the target polymers (V) were collected. Such products were dissolved in toluene and precipitated with methanol of five volume times. This procedure was repeated for five times to remove any small molecular polymer. After evaporation of the solvent under vacuum, an opaque, white, highly viscous polymer with a yield of approximate 75% was obtained. ¹H NMR(CDCl₃, 300 MHz, 25 °C, δ ppm): 0.137 [s, 18H, (CH₃)₆], 0.158 [s, 12H, (CH₃)₄], 7.374 to 7.560 [m, 20H, (C₆H₅)₄]; FT-IR (KBr, ν/cm⁻¹): 3070.0 [ν(Ar-H)], 1580.2, 1124.7 [ν(Ar-C=O)], 2961.7, 1428.9, 800.5 [ν(C-H)], 1093.3 [ν(Si-O-Si)], 1021.5, 842.2 [ν(Si-N)]; M_n: 1.42 × 10⁵, M_w/M_n: 1.98. T_g: -42.8 °C; elemental analysis (%), calculated (for C₃₄H₅₀Si₇N₂O₄, %): C, 54.64; H, 6.74; N, 3.75. Found: C, 54.25; H, 6.82; N, 3.81.

Preparation of capillary column

The fused-silica capillary column (produced in our laboratory, with a polyimide outside coating stable up to a high temperature of 420 °C) was treated according to the procedures described.^{4,10} The tubes with inner diameter of 0.25 mm were filled with 10% (w/v) sodium hydroxide in ethanol solution, with capillary length at 20 m to 30 m. The tubes were kept for 24 h and consecutively rinsed with water, dilute hydrochloric acid (1/3, v/v), water, and methanol (15 mL each). The tubes were then dried under nitrogen at 250 °C for 2 h. After washing with 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazane in dichloromethane (10%, w/v), the tubes were dried under nitrogen at room temperature for 2 h to remove the residual solvent in the column. Both ends of the capillary column were sealed and deactivated at 420 °C for 2 h. Afterward, the tubes were rinsed with 5 mL dichloromethane and dried under nitrogen at 250 °C for 2 h. The column was coated with a 0.5% (w/v) solution of the P(BPTMC)-*alt*-ODMS in dichloromethane as stationary phase with a film thickness of 0.31 μm using a static coating method. Finally, the capillary column was conditioned at 50 °C for 0.5 h under a flow of nitrogen, and the temperature was elevated to 400 °C at a rate of 2 °C min⁻¹ and maintained for 10 h.

Capillary evaluation

All analyses were performed on a Varian-3400 gas chromatograph (Varian company, USA) equipped with a flame ionization detector (FID) and N2000 chromatographic data handling system (Zhejiang University, Hangzhou, China). High purity nitrogen (>99.999%) was used as carrier gas. The test mixtures were introduced by capillary split injection at an injection split ratio of 30 : 1. The split injector and detector working temperatures were 20 °C higher than the final column temperature.

Column efficiency was evaluated for naphthalene at 120 °C by the number of theoretical plates. The Kovats retention indices of five Rohrschneider–McReynolds standards (benzene, 2-pentanone, 1-nitropropane, 1-butanol, and pyridine) were measured at 120 °C. Stationary phase polarity was expressed by Rohrschneider–McReynolds index, which was obtained from the sum of the five Rohrschneider–McReynolds constants minus those from squalane.^{31,32} The average polarity of the stationary phase was expressed as CP index, which was obtained from the sum of the first five Rohrschneider–McReynolds

constants, divided by the sum of the Rohrschneider–McReynolds constants of OV-275 (4215), and multiplied by 100.⁸

The upper working temperature was determined by evaluating the inertness and separation efficiency of the capillary column with the test mixtures after conditioning up to 400 °C. The capillary column (length, 30 m; i.d., 0.25 mm; and film thickness, 0.31 μm) coated with Dextsil-300 (purchased from Ohio Valley Specialty Company, Marietta, Ohio, USA) was prepared using the same procedures.

Results and discussion

Thermal stability of P(BPTMC)-*alt*-ODMS

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of P(BPTMC)-*alt*-ODMS. The 10 mg sample was heated from 40 °C to 700 °C at a rate of 10 °C min⁻¹ under helium. As shown in Fig. 2, the polymer started to decompose slightly above 400 °C and significantly after 480 °C, consistent with the literature.²³ Such high thermal stability resulted from the bulk unit of polymer constructed by the connection between the rigid planar four-member ring structure of BPTMC and two silicon atoms with two phenyls to form an organized copolymerized microstructure. The main chain had three dimethylpolysiloxane monomers. Steric hindrance would restrict the formation of cyclic oligomers, and the rearrangement degradation of polymer can only occur at high temperature.

Selectivity

The chromatogram of Grob reagents for our assembled capillary column is shown in Fig. 3. The Grob test mixture was well-separated and the peaks were nearly symmetrical, indicating that P(BPTMC)-*alt*-ODMS possesses good coating property. Compared with Dextsil-300 coated fused-silica capillary column, P(BPTMC)-*alt*-ODMS coated ones can yield less tailing and improved peak shapes.¹⁴

The elution order of analytes was consistent with that of OV-17, except for am, which eluted after E11, as shown in Fig. 3.³⁰ This result indicates a similar retention capability to analytes

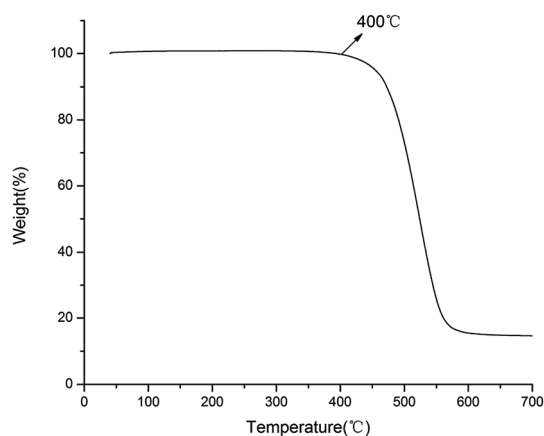


Fig. 2 TGA analysis for the P(BPTMC)-*alt*-ODMS. Temperature from 40 to 700 °C at a heating rate of 10 °C min⁻¹ under helium.

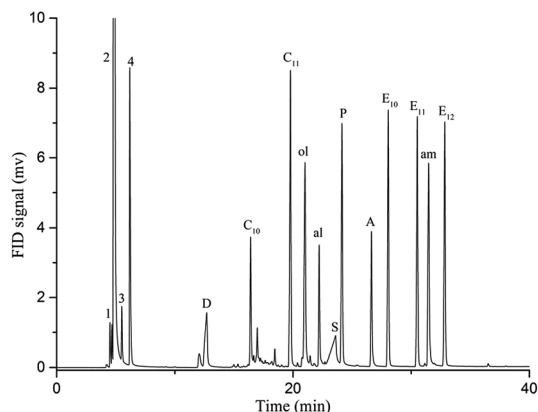


Fig. 3 Grob test chromatogram of P(BPTMC)-alt-ODMS coated capillary column after thermal treatment at 400 °C. Capillary length 30 m, film thickness 0.31 μm , i.d. 0.25 mm. Temperature program: from 30 °C (kept for 5 min), then to 240 °C at 6 °C min^{-1} . 10 cm s^{-1} nitrogen linear velocity. Peaks: 1 = 3-methylpentane (bp, 64 °C), 2 = *n*-hexane (bp, 69 °C), 3 = methyl-cyclopentane (bp, 72 °C), 4 = chloroform (bp, 61 °C), D = 2,3-butanediol, C₁₀ = decane, C₁₁ = undecane, ol = octanol, al = nonanal, S = 2-ethylhexanoic acid, P = 2,6-dimethylphenol, A = 2,6-dimethylaniline, am = dicyclohexylamine, E₁₀–E₁₂ = methyl ester of decanoic, undecanoic, and dodecanoic acid.

between P(BPTMC)-alt-ODMS and OV-17. However, this elution order is considerably different from that of Dexsil-300.¹⁴ The tailing factor (TF) of ol with a relatively high peak is small and equal to 1.16, which reflects the lack of hydrogen bond formation between the H atom of ol and the N atom of BPTMC because of the big steric effect of its nearly planar quadrilateral structure. In other words, the first class adsorption in the chromatographic column is exceptionally weak.²⁹ The small peak height of al, however, denotes the existence of a second class absorption of chromatographic column. Similar to component A, S is also an acid that has a wider peak shape and tailing, which should be attributed to overloading. The Trennzahl (TZ) indexes of E₁₀/E₁₁ and E₁₁/E₁₂ are 23.8 and 21.6, with an average of 22.7, disclosing that the chromatographic column coated with P(BPTMC)-alt-ODMS has extremely high separation efficiency.

Polarity

To investigate the general influence of the BPTMC unit on the polarity of the column, both the Rohrschneider–McReynolds constant and the CP-index of P(BPTMC)-alt-ODMS have been quantitatively measured, and the results are listed in Table 1. For comparison, certain data related to Dexsil-300, (34.5% bis(methylsilyl)-*m*-carborane, 65.5% dimethylsiloxane

copolymer⁵) which has a similar structure to P(BPTMC)-alt-ODMS, have also been listed in Table 1.

Table 1 shows the middle polarity of P(BPTMC)-alt-ODMS where the stationary phase is notably higher than that of Dexsil-300, reflecting a serious impact on the polarity by BPTMC units.

The overall polarity based on reference data is plotted against the diphenyl content of dimethyl-diphenyl-polysiloxanes in Fig. 4, where a nearly linear relationship can be observed. The graph and the CP-index of P(BPTMC)-alt-ODMS show that the BPTMC units displayed an average polarity corresponding to 25% diphenyl and 75% dimethyl-polysiloxane. The polarity of Dexsil-300, however, only reached to the extent of 11% diphenyl and 89% dimethyl-polysiloxane. From the structure of P(BPTMC)-alt-ODMS, the content of BPTMC unit was measured to be about 25% in the polymer, which means that a BPTMC unit acts like one with only a single diphenylsiloxy group in chromatographic separation. In fact, one BPTMC unit has two diphenylsiloxy groups. Therefore, the diphenylsiloxy groups of the polymer have less effect on chromatographic separation, which may be caused by the considerable steric hindrance that prevents the interaction between planar phenylene groups and analytes.

Column efficiency

The separation efficiency of the P(BPTMC)-alt-ODMS column was evaluated by the number of theoretical plates. The column had 4620 theoretical plates per m, which is a distinctly higher value than that of the Dexsil-300 column (3465 plates per m). This result indicates that the GC stationary phase using P(BPTMC)-alt-ODMS

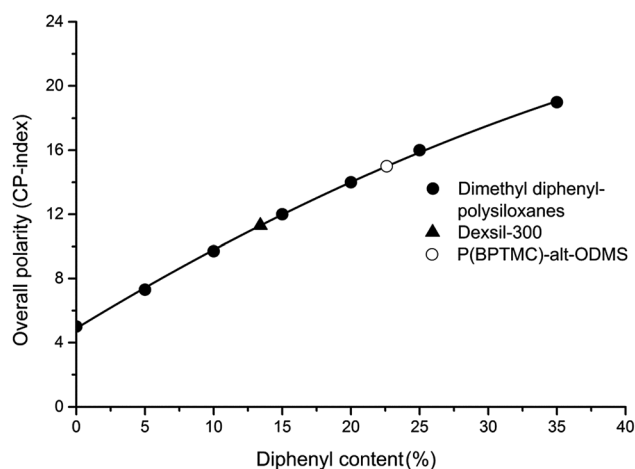


Fig. 4 Plot of CP-index versus diphenyl content of dimethyl diphenyl-polysiloxanes,¹⁰ and the equivalent diphenyl contents of P(BPTMC)-alt-ODMS and Dexsil-300.

Table 1 Rohrschneider–McReynolds constants and the CP-index of P(BPTMC)-alt-ODMS and Dexsil-300

	Benzene	<i>n</i> -Butanol	2-Pentanone	Nitropropane	Pyridine	Rohrschneider–McReynolds constant	CP-index
P(BPTMC)-alt-ODMS	72	97	119	178	165	631	15.0
Dexsil-300 (ref. 30)	47	80	103	148	96	474	11.3

Table 2 Column bleed of P(BPTMC)-*alt*-ODMS and Dexsil-300 at different temperatures

Stationary phases	Relative bleed ^a (mV)		
	360 °C	380 °C	400 °C
P(BPTMC)- <i>alt</i> -ODMS	0.40	0.81	1.28
Dexsil-300	0.38	0.71	1.05
Empty capillary column	0.03	0.04	0.05

^a The relative column bleed (in mV) was the bleed at the final temperature minus the bleed at 60 °C.¹⁰

has a good film-forming property on the inner surface of fused silica, as well as high separation efficiency.

Working range

To test the column low-temperature chromatographic separation performance, 3-methylpentane (bp, 64 °C) and methylcyclopentane (bp, 72 °C), with boiling points near to that of *n*-hexane (bp, 69 °C), were added to the Grob test mixture. As expected, good separation could be realized at 30 °C, indicating that the minimum allowable operating temperature (MiAOT) of the column should be controlled below 30 °C. The reason is that the low T_g (−42.8 °C) of P(BPTMC)-*alt*-ODMS results in a low MiAOT when used as stationary phase for GC. The column bleeding of P(BPTMC)-*alt*-ODMS and Dexsil-300 under the same conditions (length, 15 m; i.d., 0.25 mm; film thickness, 0.31 μm) is respectively determined at 360 °C, 380 °C, and 400 °C without any injection, with the results listed in Table 2. Meanwhile, the bleeding from the empty column was also measured. The table shows that the high temperature performance of P(BPTMC)-*alt*-ODMS column is similar to that of Dexsil-300, and its maximum operating temperature is controlled near 400 °C in the present study.

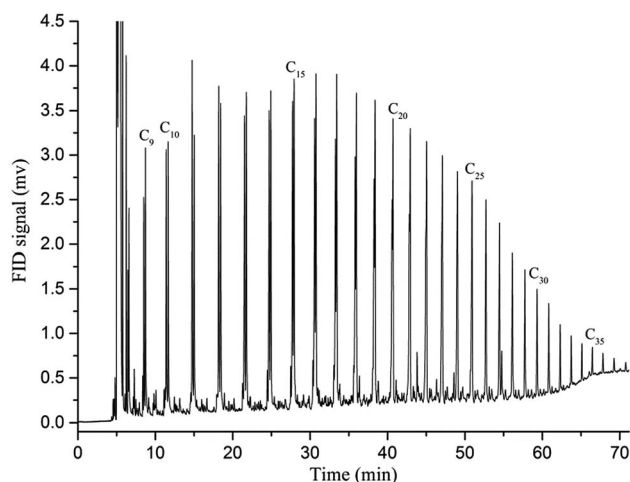


Fig. 5 Chromatogram of polyethylene pyrolysis product with P(BPTMC)-*alt*-ODMS as stationary phase. Capillary length 30 m, film thickness 0.31 μm, i.d. 0.25 mm. Temperature program: from 60 °C (kept for 5 min), then to 370 °C (kept for 5 min) at 5 °C min^{−1}, 12 cm s^{−1} nitrogen linear velocity.

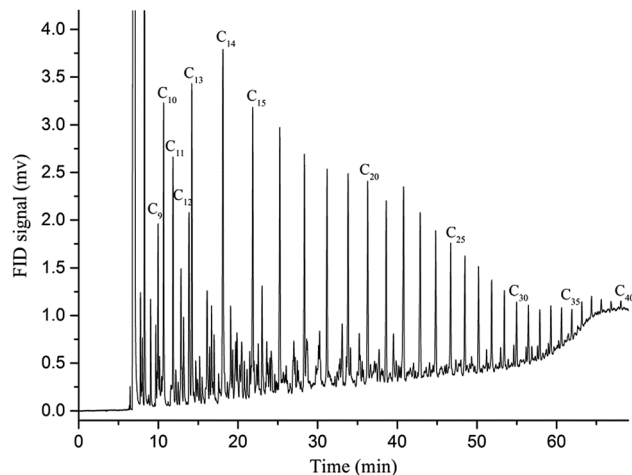


Fig. 6 Chromatogram of petroleum components with P(BPTMC)-*alt*-ODMS as stationary phase. Capillary length 30 m, film thickness 0.31 μm, i.d. 0.25 mm. Temperature program: from 50 °C (kept for 5 min), then to 400 °C (kept for 5 min) at 6 °C min^{−1}, 12 cm s^{−1} nitrogen linear velocity.

Application

The gas chromatograms of the separations of polyethylene pyrolysis product and petroleum components using P(BPTMC)-*alt*-ODMS columns are illustrated in Fig. 5 and 6, respectively. Good chromatographic separation performance with low bleeding rate can be achieved with practical samples, where the polyethylene pyrolysis products, alkane and alkene with

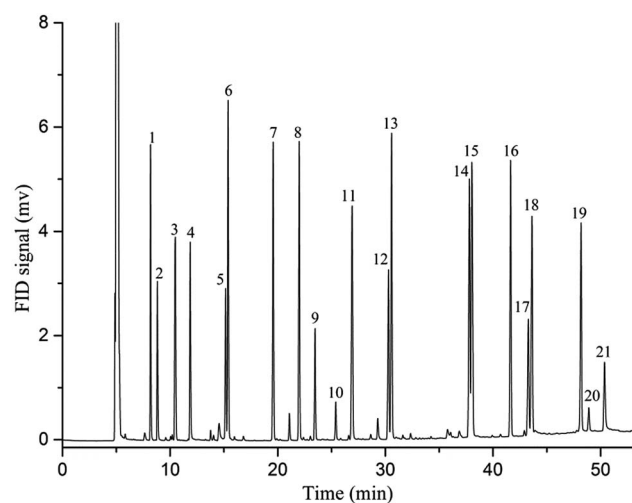


Fig. 7 Chromatogram of aromatic hydrocarbon mixtures with P(BPTMC)-*alt*-ODMS as stationary phase. Capillary length 30 m, film thickness 0.31 μm, i.d. 0.25 mm. Temperature program: from 120 °C (kept for 5 min), then to 320 °C at 4 °C min^{−1}, 12 cm s^{−1} gas nitrogen linear velocity. Peaks: (1) acetophenone; (2) indene; (3) naphthane; (4) naphthalene; (5) 2-methylnaphthalene; (6) 1-methylnaphthalene; (7) 8-hydroxyquinoline; (8) biphenyl; (9) 1-nitronaphthalene; (10) 2,2'-dihydroxybiphenyl; (11) 5-acenaphthenol; (12) 3,5-dinitrophenol; (13) 2,2'-methylenebiphenyl; (14) phenanthrene; (15) anthracene; (16) benzil; (17) anthraquinone; (18) triphenylmethane; (19) 1,8-naphthalic anhydride; (20) chrysene; (21) 1,4-dibenzoylbenzene.

identical carbon numbers, can be separated. Compared with Dextsil-300 and despite the slightly weak thermal stability of the column, the good separation characteristics and column efficiencies of P(BPTMC)-*alt*-ODMS make the column especially suitable as stationary phases in HTGC for analyzing non-polar alkane mixtures with high boiling point.

To test the capability of P(BPTMC)-*alt*-ODMS column for separating polycyclic aromatic hydrocarbons, the chromatogram of aromatic hydrocarbon mixtures was measured, with the results shown in Fig. 7. Excellent separation ability of the column for polar phenols containing a hydroxyl group and polycyclic aromatic hydrocarbons can be observed, reflecting its advantage in separating polar aromatic mixture as stationary phase.

Conclusion

P(BPTMC)-*alt*-ODMS is a novel stationary phase for gas chromatography and has several beneficial properties in chromatographic separation.

(I) The increased thermal stability caused by introducing the BPTMC unit to the backbone resulted in increased glass transition temperature. The operating temperature is between 30 °C and 400 °C.

(II) BPTMC unit acts such as diphenylsiloxy group in chromatographic separation. The stationary phase using P(BPTMC)-*alt*-ODMS thus possesses higher middle polarity than Dextsil-300.

(III) P(BPTMC)-*alt*-ODMS is easy to coat in the capillary column, which imparts high column efficiency.

(IV) Such stationary phase is suitable for separating nonpolar alkanes and polar aromatic compounds.

In summary, the use of P(BPTMC)-*alt*-ODMS as stationary phase for HTGC exhibit great potential in practical applications.

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