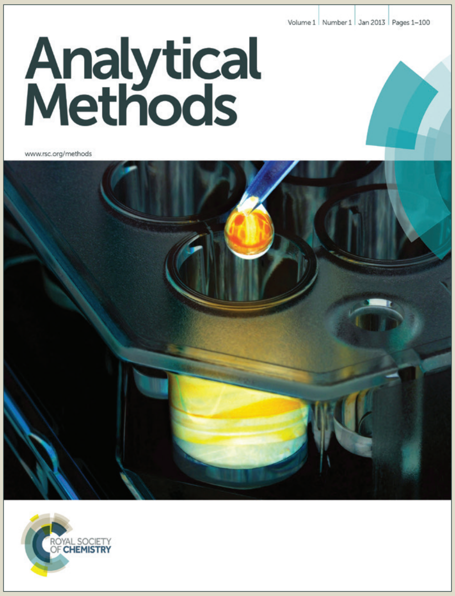
Analytical Methods

Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Analytical Methods

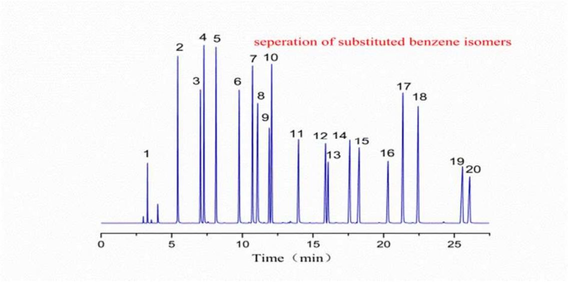
www.rsc.org/methods

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

A stationary phase for gas chromatography DFP-15 was synthesized, with great potential in the analysis of substituted benzene and PAHs.



Analytical Methods RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl grafted polysiloxane as stationary phase of gas chromatography

Pengchao Zhao, Lei Liu, Miao Yu, Na Niu, Bo Wu*, Guangbao Wang

In this work, a new polycyclic phenyl grafted polysiloxane called DFP-15 (15.1% 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl) was synthesized by the Diels-Alder reaction of tetraphenyl cyclopentadienone monomer containing trifluoromethyl with methyl vinyl polysiloxanes composed by 18% methyl vinyl, 82% dimethyl, and another one DFP-8 was also prepared for the purpose of comparison. Then the thermo stability of the product was evaluated by thermogravimetric (TG) test and the result revealed that both of the DFP had similar thermal stability, which began to decompose slightly at 380 ºC. Subsequently, the copolymers were coated on fused silica capillary columns used as stationary phase by static coating and characterized, respectively. The column efficiency of DFP-15 column was 3960 plates/m (k=1.90, naphthalene), and that of the other one was 3740 plates/m (k=1.74, naphthalene). The excellent film-forming ability in the inner surface of fused-silica capillary columns was proved by the analysis of Grob reagent. Furthermore, the selectivity of the novel stationary phases for analytes, including substituted benzene isomers and polycyclic aromatic hydrocarbons was evaluated. The present work suggests that both of the stationary phases have great potential for further development and application.

1. Introduction

With over sixty years' development, capillary column technology has been relatively mature. Work of searching and developing new stationary phase of gas chromatography becomes increasingly difficult. Analytical Chemistry specially stressed the urgency of researching and developing new and high selective stationary phase in gas chromatography overview in 2008 and 2010, hoping to see another upsurge of the development of stationary phase of gas chromatography [1, 2]. Currently, it's difficult to cater to the analysis demand of increasing complicated samples (in particularly environmental pollutants) due to the shortage of capillary products of stationary phase in gas chromatography with high selectivity and sound usability under both high and low temperatures and of over medium polarity [3].

In the researches of high temperature resistant stationary phase with medium polar, introducing polarizable phenyl group to polysiloxane is a commonly seen mean [4, 5], with the phenyl group content (note: referring to the ratio between mole number of phenyl group and mole number of polymer Si-O chain) between 5%～150%. Introducing low content of phenyl group has limited contribution to the polarity and selectivity of stationary phase, but has better usability of chromatography; while introducing high content of phenyl group will be conducive to strengthening the polarity and selectivity, but will lead to stiffness to the stationary phase structure, and weakens its coating performance and usability under low temperature [6, 7].

M. L. Lee at al. introduced bicyclic group with large polarizability such as xenyl, naphthyl and diphenyl ether, etc. to increase the polarity and separation selectivity [8-10], their features are: (i) The contribution of the two benzene rings (biphenyl) connected by single bond equals to the sum of two separate benzene rings in terms of increasing the polarity, while the contribution of the condensed nucleus (naphthalene) reduces. (ii) Introducing polar group such as ether group, methoxy group and cyano group to conjugate ring, which will bring higher separation selectivity while increasing the polarity of stationary phase. (iii) The synthetic route of stationary phase synthesizes monomers with functional group before condensing with silicone monomers containing dimethyl. The molecular weight of the polymer obtained is not high enough due to the influence of steric effect of functional group, which affects the temperature tolerance of the polymer. Then Mayer and his research group synthesized 75% diphenyl, 25% dimethyl polysiloxane to act as the high temperature stationary phase, where the column temperature could reach 400 ºC [6]. Later, they prepared 50% n-octyl methyl, 50% diphenyl polysiloxane, this stationary phase had special selectivity and the excellent performance with low polarity [11].

Generally, the separation property of stationary phase will be improved if single phenyl substituent group is replaced by concentrated benzene rings. Furthermore, increasing the rings of polycyclic aromatic hydrocarbon connected by single bonds, and trying to improve the molecular weight and viscosity of the polymer will improve its polarity, selectivity, film-forming property and high-and-low temperature resistant property. In addition, introducing polarity substituent group such as trifluoromethyl, etc. to benzene ring on the side chain of polycyclic phenyl group will provide more abundant function mechanism for various polar and nonpolar compound molecules containing unsaturated double bonds, with their polarity strengthened and selectivity becoming better.

In this paper, the addition reaction of 3,4-2(4-trifluoromethyl phenyl) -2,5-diphenylcyclopentadienone and methyl vinyl polysiloxanes with different vinyl contents was carried out in diphenyl ether solution, getting the grafted polysiloxane containing 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl group as the stationary phase of gas chromatography. The coated fused silica capillary columns with this newly synthesized polymer were evaluated for their column efficiency, polarity, working temperature range and selectivity. Apart from separating general hydrocarbons, this new polymer also has excellent separation selectivity for environmental pollutants such as substituted benzene mixtures, polycyclic aromatic hydrocarbons and its substituendum isomer by relying on its mighty polarizable force and π-π interaction among solutes and the stationary phase.

2. Experimental

2.1 Polymer synthesis

The reaction scheme for the preparation of DFP is shown in Fig.1. Unless otherwise specified, all reagents and other testing compounds used in this study are of analytical grade (Sinopharm Chemical Reagent limited corporation, China).

2.1.1 Synthesis of 3,4-2(4-trifluoromethyl phenyl) -2,5-diphenylcyclopentadienone

Firstly, 3,4-2(4-trifluoromethyl phenyl) -2,5-diphenylcyclopentadienone was synthesized according to Ref. [12]. 11.4 g (0.033 mol) 4,4'-ditrifluoromethylbenzil and 6.9 g (0.033 mol) 1,3-Diphenylacetone was dissolved in stirred ethanol (50.0 mL) under nitrogen atmosphere. 5 ml KOH ethanol solution (1/5, w/V) was added dropwise into the solution which was heated near boiling. The reaction was continued for 45 min. Afterwards the mixture was filtered after cooling. Then the crude product was re-crystallized in the solvent mixture of ethanol/toluene (V/V=1:1) to obtain bright black crystals with a yield of 78%.

2.1.2 Procedure for the preparation of DFP

Methyl vinyl polysiloxanes with different vinyl contents of 10%, 18% were synthesized according to Ref. [13]. Then DFP was prepared through a reaction between 3,4-2(4-trifluoromethyl phenyl) -2,5-diphenylcyclopentadienone and methyl vinyl polysiloxanes [14, 15]. The products were named DFP-8, DFP-15 according to the content of the 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl group, respectively. An appropriate amount of methyl vinyl polysiloxanes and 3,4-2(4-trifluoromethyl phenyl) -2,5-diphenylcyclopentadienone, e.g., 5.00 g polysiloxanes (containing 0.0118 mol vinyl) and 5.63 g (0.0108 mol) 3,4-2(4-trifluoromethyl phenyl) -2,5-diphenylcyclopentadienone for the synthesis of DFP-15, (Specifically, a small percent of vinyl group was retained in each polymer mixture in order to facilitate cross-linking, as described in the Ref. [16]) were dissolved in diphenyl ether (50.0 mL) and heated at 230 ºC for 48 h under nitrogen protection. The polymerization reaction was terminated when the bubbles stopped evolving. Then the solution was poured into a separatory funnel and precipitated with 50 ml methanol. For purification the product was dissolved in 10 ml toluene and precipitated with 25 ml methanol. This step was repeated three times. Finally the solvent was removed by evaporating under vacuum to give a clear, pale yellowish gum. The yield of DFP-15 was about 74% while that of DFP-8 was close to 80%.

2.2 Capillary preparation

Fused silica capillary tubes (30 m length, i.d. 0.32 mm, manufactured in laboratory) were prepared according to the procedures reported previously [17, 18]. Two pieces of the tubes were purged with nitrogen at 250 ºC for 2 h after consecutively rinsed with 10% (w/V) sodium hydroxide in ethanol, deionized water, 12% dilute hydrochloric acid (w/w), deionized water and methanol (15 mL each) at room temperature. After washing with 1,3-dimethyl-1,1,3,3-tetraphenyl-disilazane in dichloromethane (10%, w/V), these tubes were dried under nitrogen at room temperature for 2 h to remove the residual solvent in the column. Then both ends of capillary column were sealed by flame and deactivated at 380 ºC by high temperature silylation for 2 h. After that, the tubes were rinsed with methanol (15 ml) and purified under nitrogen at 250 ºC for 2 h once again. Then the column A and B were statically coated with solution of 0.3% (w/V) of DFP-15 and DFP-8 in dichloromethane which also contained a certain amount of dicumyl peroxide (DCP) for cross-linking (about 2% (w/w) of the amount of stationary phase present in the coating solution) respectively and finally, conditioned under a flow of nitrogen from 50 ºC to 160 ºC (isothermal for 2 h) at 2 ºC $\min^{-1}$, then 2 ºC $\min^{-1}$ to 365 ºC (isothermal for 12 h). Film thickness of both columns was about 0.24 μm calculated according to Ref. [19].

2.3 Capillary evaluation

All columns were tested in the Varian-3400 Gas Chromatography (Varian company, USA) equipped with a flame ionization detector (FID) operated at least 20 ºC over the final oven temperature, refrigeration system of oven column and N2000 chromatographic data processing system (Zhejiang University, Hangzhou, China). High purity helium was used as carrier gas with a linear velocity of 10 cm/s. Evaluation was made with respect to column efficiency, polarity, selectivity for Grob test mixtures, surface inertness, bleeding, and operating range of the capillary columns. The column efficiency was expressed as the number of theoretical plates per meter for naphthalene. The polarity was evaluated by measuring the

McReynold's Constants of the first five standards. And the relative column bleed was calculated as the bleed at a given temperature minus bleed at 60 ºC, similar to Ref. [11].

3. Results and discussion

3.1 Polymer characterization by NMR spectroscopy

1H NMR spectra of DFP in CDCl3 was recorded with a DRX 400 spectrometer (Bruker Analytische Messtechbik, Germany) at ambient temperature. Based on the data of 1H NMR, the content of the 3,4-2(trifluoromethyl phenyl group)-2,5-diphenyl phenyl-methyl group in DFP-15 and DFP-8 were about 15.1%, 8.2%, respectively. The chemical compositions of 2.9%, 1.8% remaining vinyl groups in DFP were roughly calculated from the integration value of the 1H NMR spectra, which was in a good agreement with the theoretical calculation.

3.2 Columns efficiency

The efficiencies of the columns were measured isothermally with naphthalene at 120 ºC and were expressed as the number of theoretical plates per meter. And meanwhile in order to demonstrate the durability of the DFP columns, the column efficiency and capacity factors of naphthalene had been detected for one hundred injections under the same experimental conditions, see Table 1 [20]. The average column efficiency of DFP-15 column was 3960 plates/m (k=1.90±0.13, naphthalene), and that of DFP-8 was 3740 plates/m (k=1.74±0.08, naphthalene). It was found that of value of k only varied slightly after hundreds of injections which indicated that the films were not altered during the chromatographic separations, thus the columns could endure long-term use. In the meantime, more than 80% of the coating efficiency of the new stationary phases suggested that it had a good film-forming ability, which is consistent with the gummy properties of the DFP-15. And as the content of 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl increases, the stationary phase could provide the selectivity improvement significantly, but it was found that when the content of 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl group was up to 20% in polymer, a solid instead of a gum product at room temperature was obtained. The prepared solid polymer was not suitable for low temperature chromatographic separation, which was consistent with the results reported previously [8].

3.3 Columns polarity

The Kováts retention indices of the first five standards benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine were quantitatively measured at 120 ºC applying split injection with a ratio of 30: 1 [21]. The average polarity of the stationary phase was expressed as CP-index calculated from the sum of the first five Rohrschneider–McReynolds constants divided by the sum of the Rohrschneider–McReynolds constants of OV-275 multiplied by 100 [22, 23]. Table 2 lists the Rohrschneider-McReynolds constants and the overall polarity on four different columns [11, 22]. This CP-index indicates that DFP-15 has a similar polarity compared to OV-17 column (50% dimethyl, 50% diphenyl-polysiloxane) exhibiting a CP-index at 20.5, while the overall polarity of DFP-8 is similar to 24% diphenyl, 76% dimethylpolysiloxane [11, 18]. Therefore, increasing the content of 3,4-2(trifluoromethyl phenyl group)-2,5-diphenyl phenyl group has a significant effect on the overall polarity and the individual interactions.

Additionally, each Rohrschneider-McReynolds standard interacts with the stationary phase in a particular way: X’ (benzene)- dispersive interactions; Y’ (1-butanol)- proton donor and acceptor capabilities plus dipolar interactions; Z’ (2-pentanone)- dipolar interactions plus weak proton acceptor, but not proton donor capabilities; U’ (1-nitropropane)- dipolar interactions; and S’ (pyridine)- strong proton acceptor capabilities [20]. Strong Rohrschneider-McReynolds constants for proton donor and proton acceptor indicate that the DFP-15 column could provide strong retentions for polar compounds. As a result, The DFP-15 could have an excellent selectivity for polar and easily polarizable analytes, including substituted benzene mixtures and polycyclic aromatic hydrocarbons.

3.4 Selectivity and surface inertness

As showed in Fig. 2, the Grob test chromatogram on the column DFP-15 was presented for evaluating the selectivity of stationary phase and surface inertness of the column. The elution order and elution pattern of Grob test mixtures on the DFP-15 column demonstrated a similar selectivity in comparison to SOP-50 (50% dimethyl, 50% diphenylpolysiloxanes) [24]. Additionally, it was noted that all compounds were well separated with symmetry peaks except the peak shapes of 1-octanol (ol) which is prone to reversible adsorption. However, it was interesting to calculate that the tailor factor of 2,3-butanediol (D) was close to 1.15 on the DFP-15 column, indicating that the impact of the interaction of hydrogen bond between the fluorine atoms on the side chain and the hydroxyl was not so severe. Meanwhile, the reduced peak areas of the dicyclohexylamine (am) indicated that a minor irreversible acid–base adsorption may take place at relatively low temperature.

3.5 Column bleed and operating range

In order to evaluate the thermal stability of DFP, thermogravimetric (TG) tests were carried out on a LCT-2 TGA analysis instrument (Beijing Optical Instrument Factory, Beijing, China) [25, 26]. 25 mg sample was heated from 40 ºC to 700 ºC at a rate of 10 ºC min^{-1} under condition of dynamic nitrogen atmosphere. The result revealed that both of the DFP had similar initial decomposition temperature, which began to decompose slightly at 380 ºC. However, with temperature increasing, DFP-8 began to show weight-loss more dramatically, e. g., When the decomposition of DFP reached 20% of the original quality, the temperature of DFP-8 was much lower than DFP-15 by 30 ºC, see Fig. 3. It could be concluded that the thermal stability of DFP was affected by the polycyclic phenyl group with the huge steric-hindrance effect which was conformed in Ref. [8]. And in spite of the content of phenyl group in DFP-15 was twice as large as that of DFP-8 approximately, the total amount of phenyl group in polysiloxane compared to dimethyl was so insignificant that both of the DFP had the approximate initial decomposition temperature.

Additionally, the column bleed was measured by programming the DFP column at 340 ºC and 360 ºC for 30 min, respectively, see Table 3. The bleeding of DFP-8 column at 360 ℃ was found to be about 50 pA, which was double that of DFP-15 column at the same temperature with 24 pA of baseline drift. Consequently, the results mean that the DFP-15 could endure high temperature up to 360 ºC while 340 ºC of the maximum allowable temperature (MAOT) about DFP-8 is obtained. However, compared to the MAOT of 50% dimethyl, 50% diphenyl-polysiloxane with similar polarity such as SOP-50 [24, 27], that of DFP-15 doesn't reach a satisfactory state which could be attributed to introducing a small amount of 3,4-2(trifluoromethyl phenyl group)-2,5-diphenyl phenyl group on the side chain of polysiloxane is weaker than the introduction of phenyl with reference to enhancing thermal stability concerned with the cyclization degradation of polysiloxane.

Besides the MAOT, the minimum allowable operating temperature (MiAOT) which is defined as that temperature according to Ref. [28], where the column efficiency is the half of its original value at elevated temperatures of the capillary, was determined by analysing the homologous series of n-alkanes in the range of 0 ºC to 150 ºC. As the glass transition temperature of the polymer increases with the increasing of phenyl group and degree of crosslinking, a minimum allowable operating temperature of 18 ºC which is consistent with the glass transition temperature [6], was observed for DFP-15, higher than that of DFP-8 by 10 ºC. And compared to the capillary columns with similar or even much lower polarity [28, 29], the polymer kept high viscosity status of gum under ambient temperature with lower MiAOT which could be attributed to the benzene ring on the side chain connected by single bond is highly concentrated, and all the phenyl groups can rotate freely while having large conjugated degree.

3.6 Applications of the capillary columns

Fig. 4 illustrates the separation of three disubstituted benzene isomers on DFP-15 column by temperature programming. And the capacity factors (k) and relative retention factors (α) listed in Table 4 show that all tested positional isomers, such as the difficult-to-separate m, p-xylene isomers are well separated, which exhibits evident advantages over SOP-50-Octyl column [11]. Comparing the relative retention factors of each group of isomers, it could also be seen that the separation results for the stronger polarity, or easily polarized benzene isomers such as nitroaniline, are better than that of isomers with weaker polarity such as xylene, which might be attributed to dipole-dipole interaction and induced force between the solutes and 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl group of the stationary phase.

Meanwhile, Fig. 5 illustrates the chromatogram of polycyclic aromatic hydrocarbons (PAHs) on DFP-15 column in which the baseline separation could be achieved for 1-methylnaphthalene and 2-methylnaphthalene. And the elution order of the compounds was according to their boiling points and the increasing polarizable force. Additionally, since most of these PAHs are serious environmental pollutants, the DFP-15 column could be widely used for the determination of these pollutants.

Furthermore, the chromatograms of two substituted benzene mixtures on the DFP-15 column are also displayed in Fig. 6, in which it can be found that the aromatic positional isomers, such as dichlorobenzene, trimethylbenzene, dinitrochlorobenzene and so on, are well separated with sharp symmetrical peaks. A noticeable phenomenon is that a shift of the 1-fluoro-2,4-dinitrobenzene, which is more retarded by the trifluoromethyl compared to the separation results of another stationary phase (20% tetraphenyl phenyl polysiloxane, not list here) synthesized in laboratory in which the peak of 1-fluoro-2,4-dinitrobenzene is between p-nitrobromobenzene (14) and diphenylmethane (15). And the baseline separation of all components including the disubstituted and trisubstituted benzene isomers was achieved within 30 min in Fig. 6 (A). Therefore, due to the participation of 3,4-2(trifluoromethyl phenyl)-2,5-diphenyl phenyl group, separation of all single components in complex samples such as substituted benzene mixtures may be accomplished within a single run. So, in conclusion, fused silica capillary column coated with DFP-15 is recommended for the analysis of substituted benzene mixtures and polycyclic aromatic hydrocarbons (PAHs) and can be applied in environmental analysis [30].

4. Conclusions

This work describes a synthesis method of polycyclic phenyl grafted polysiloxane (DFP-15 and DFP-8). When these polymers are used as novel GC stationary phases, it exhibit good coating ability and higher column efficiency. Moreover, the average polarity of stationary phases shows that increasing the content of 3,4-2(trifluoromethyl phenyl group)-2,5-diphenyl phenyl group has a significant effect on the overall polarity of the DFP stationary phases. In addition, the good selectivity for analytes including substituted benzenie mixtures and polycyclic aromatic hydrocarbons indicates the DFP-15 has a great potential in the analysis of environmental pollutants for further development and application.

Acknowledgements

This project was supported by The National Natural Science Foundation of China (No. 21275090) and the National Science Foundation for Fostering Talents in Basic Research of the National Natural Science Foundation of China (No.J1103314).

References

[1] F. L. Dorman, J. J. Whiting, J. W. Cochran, J. Gardea-Torresdey, Anal. Chem., 2008, 80, 4487-4497.

[2] F. L. Dorman, J. J. Whiting, J. W. Cochran, J. Gardea-Torresdey, Anal. Chem., 2010, 82, 4775-4785.

[3] E. Kaal, H. G. Janssen, J. Chromatogr. A, 2008, 1184, 43-60.

[4] G. A. Eiceman, J. Gardea-Torresdey, E. D. Overton, F. Dorman, Anal. Chem., 2004, 76, 3387-3394.

[5] J. A. Yancey, J. Chromatogr. Sci., 1994, 32, 403-413.

[6] B. X. Mayer, P. Zöllner, E. Lorbeer, H. Kählig, J. Sep. Sci., 2002, 25, 60-66.

[7]J. Buijten, L. Blomberg, K. Markides, W. Rauter, J. Chromatogr. A, 1982, 237, 465-468.

[8] M. L. Lee, J. C. Kuei, N. W. Adams, B. J. Tarbet, M. Nishioka, B. A. Jones, J. S. Bradshaw, J. Chromatogr. A, 1984, 302, 303-318.

[9] A. Malik, S. L. Reese, S. Morgan, J. S. Bradshaw, M. L. Lee, Chromatographia, 1997, 46, 79-84.

[10] J. S. Bradshaw, N. W. Adams, R. S. Johnson, J. High Resol. Chromatogr., 1985, 8, 678-683.

[11] B. X. Mayer, H. Kählig, W. Rauter, Analyst, 2003, 128, 1238-1242.

[12] A. Friedman, W. Gugig, L. Mehr, E. I. Becher, J. Org. Chem., 1959, 24, 516-520.

[13] S. Y. Feng. Silicone Polymers and Their Applications, ed. J. Zhang, M. J. Li, Q. Z. Zhu, Chemical Industry Press, Beijing, 2004, pp. 79-80.

[14] O. Grummitt, R. S. Klopper, C. W. Blenkhorn, J. Am. Chem. Soc., 1942, 64, 604-607.

[15] G. W. Goodall, W. Hayes, Chem. Soc. Rev, 2006, 35, 280-312.

[16] S. R. Lipsky, W. J. McMurray, J. Chromatogr. A, 1982, 239, 61-69.

[17] B. X. Mayer, W. Rauter, G. Rauchbauer, C. Tomastik, H. Bangert, J. Sep. Sci., 2004, 27, 335-342.

[18] B. X. Mayer, H. Kählig, W. Rauter, J. Chromatogr. A, 2004, 1042, 147-154.

[19] J. L. Anderson, D. W. Armstrong, G. T. Wei, Anal. Chem., 2005, 77, 6453-6462.

[20] X. Sun, Y. Zhu, P. Wang, L. Jing, C. Y. Wu, J. Xing, J. Chromatogr. A, 2011, 1218, 833-841.

[21] T. Ganicz, W. A. Stańczyk, J. Chmielecka, J. Kowalski, Polym. Int., 2009, 58, 248-254.

[22] W. O. McReynolds, J. Sep. Sci., 1970, 8, 685-691.

[23] M. Petsch, B. X. Mayer, V. Söllner, Anal. Bioanal. Chem., 2005, 383, 322-326.

[24] B. X. Mayer, E. Lorbeer, J. High Resol. Chromatogr., 1995, 18, 504-506.

[25] K. P. Huang, T. K. Misra, G. R. Wang, B. Y. Huang, C. Y. Liu, J. Chromatogr. A, 2008, 1215, 177-184.

[26] X. Sun, C. Y. Wu, J. Xing, J. Sep. Sci., 2010, 33, 3159-3167.

[27] I. Hägglund, K. Janak, L. Blomberg, A. Bemgård, S. G. Claude, M. Lymann, R. Tabacchi, J. Chromatogr. Sci., 1991, 29, 396-402.

[28] B. X. Mayer, W. Rauter, Analyst, 2005, 130, 502-507.

[29] A. Bemgård, L. Blomberg, M. Lymann, S. Claude, R. TabacchiJ, High Resol. Chromatogr., 1988, 11, 881-890.

[30] R. Montes, M. Ramil, I. Rodriguez, E. Rubí, R. Cela, J. Chromatogr. A, 2006, 1124, 43-50.

Table 1. The chromatographic properties of DFP columns at 120 ºC.

Stationary phases	Dimensions length (m)×i.d. (mm)	A			B		**Degree of crosslinking (%)
		n (plates/m)	Capacity factor (k)	*CE (%)	n (plates/m)	Capacity factor (k)	
DFP-8	30×0.32	3740	1.74	84.3	3811	1.43	82.2
DFP-15	30×0.32	3960	1.90	91.1	4045	1.52	80

A) was tested before rinsing with 5 ml dichloromethane.

B) was tested after rinsing with 5 ml dichloromethane.

*abbreviation of coating efficiency

** Degree of crosslinking was calculated from the capacity factor after rinsing with 5 ml dichloromethane divided by that of column tested before.

Table 2. The McReynolds constants and overall polarity expressed as CP-index of stationary phases.

Stationary phase	Benzene (X′)	n-Butanol (Y′)	2-Pentanone (Z′)	1-Nitropropane (U′)	Pyridine (S′)	Sum	CP-index
DFP-8	82.0	130.0	138.0	160.0	132.0	642.0	15.4
DFP-15	112.0	162.0	166.0	184.0	150.0	774.0	18.6
SPB-20[11]	67.0	116.0	117.0	174.0	131.0	605.0	14.5
OV-17[22]	119.0	158.0	162.0	243.0	174.0	856.0	20.5

Table 3. Column bleed* at 340 and 360 ˚C and operating range of DFP.

Stationary phase	MAOT (˚C)	MiAOT (˚C)	Relative bleed/pA	
			340 ˚C	360 ˚C
DFP-8	340 ˚C	8 ˚C	15	50
DFP-15	360 ˚C	18 ˚C	14	24

* The relative column bleed (in picoampere, pA) is calculated as the bleed at a given temperature minus bleed at 60 ˚C.

Table 4. The separation of o-, m-, p-disubstituted benzene isomers on the DFP-15.

Analyte	T(˚C)	Peak order	capacity factor (k)			Relative retention(α)	
			k_o	k_m	k_p	α_1^*	α_2^*
Xylene	90	o,m,p	0.248	0.623	0.701	2.51	1.12
Cresols	120	o,m,p	0.560	0.756	0.945	1.35	1.25
Nitrotoluene	130	o,m,p	1.075	1.361	1.534	1.27	1.13
Nitrochlorobenzene	160	m,o,p	1.250	1.015	1.435	1.23	1.15
Nitroaniline	180	o,m,p	0.859	1.171	1.948	1.36	1.66

*α_1 is the ratio of the relative retention of the second peak to that of the first peak in one isomer group, α_2 is the ratio of the relative retention of the third peak to that of the second peak.

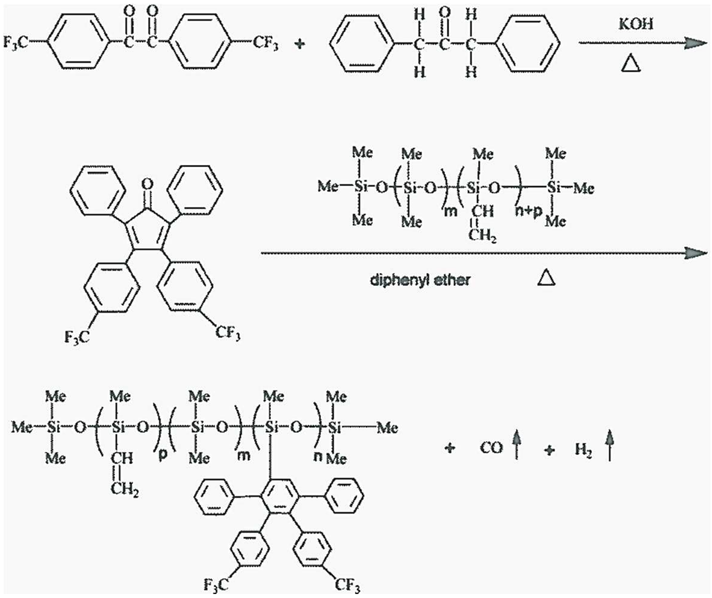


Fig. 1. Reaction scheme for the preparation of DFP

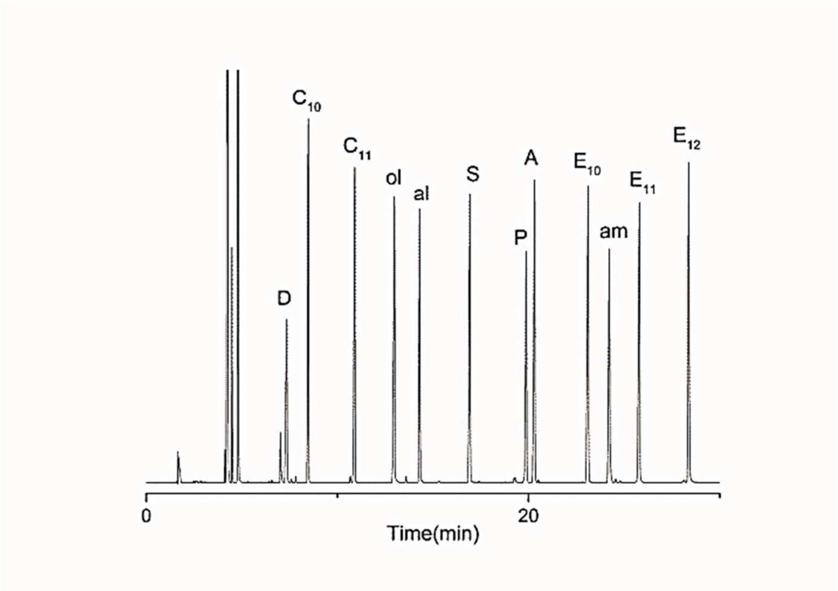


Fig. 2. Chromatogram of Grob test mixtures on the DFP-15 column. Capillary length 30 m, i.d. 0.32 mm, film thickness 0.24 μm. Temperature program: 50 ºC to 170 ºC at 4 ºC min^{-1}; 10 cm/s helium linear velocity. Peaks: D, 2, 3-butanediol; C_{10}, decane; C_{11}, undecane; ol, 1-octanol; al, nonanal; S, 2-ethylhexanoic acid; P, 2, 6-dimethylphenol; A, 2, 6-dimethylaniline; E_{10}, methyl decanoate; am, dicyclohexylamine; E_{11}, methyl undecanoate; E12, methyldodecanoate.

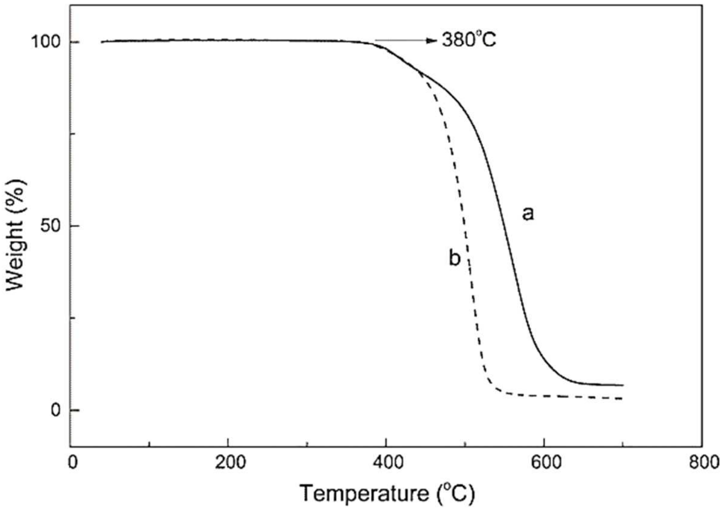


Fig. 3. TGA analysis for the (a) DFP-15 and (b) DFP-8. Temperature programmed from 40 ºC to 700 ºC at a heating rate of 10 ºC min^{-1}.

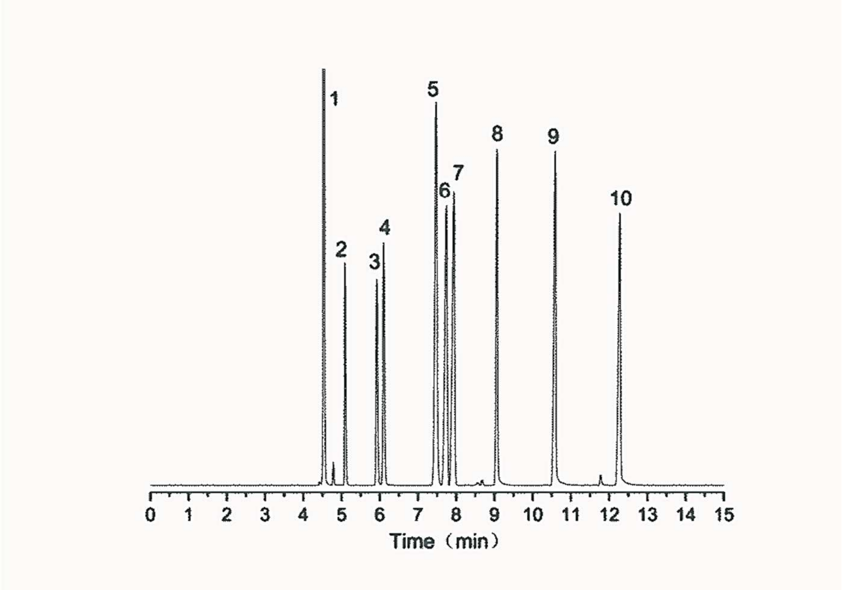


Fig. 4. Chromatogram of o-, m-, p-disubstituted benzene isomers on the DFP-15 column. Capillary length 30 m, i.d. 0.32 mm, film thickness 0.24 μm. Temperature program: 90 ºC to 200 ºC at 7 ºC min^{-1}; 10 cm/s helium linear velocity. Peaks: 1, benzene; 2, o-xylene; 3, m-xylene; 4, p-xylene; 5, o-nitrotoluene; 6, m-nitrotoluene; 7, p-nitrotoluene; 8, o-nitroaniline; 9, m-nitroaniline; 10, p-nitroaniline.

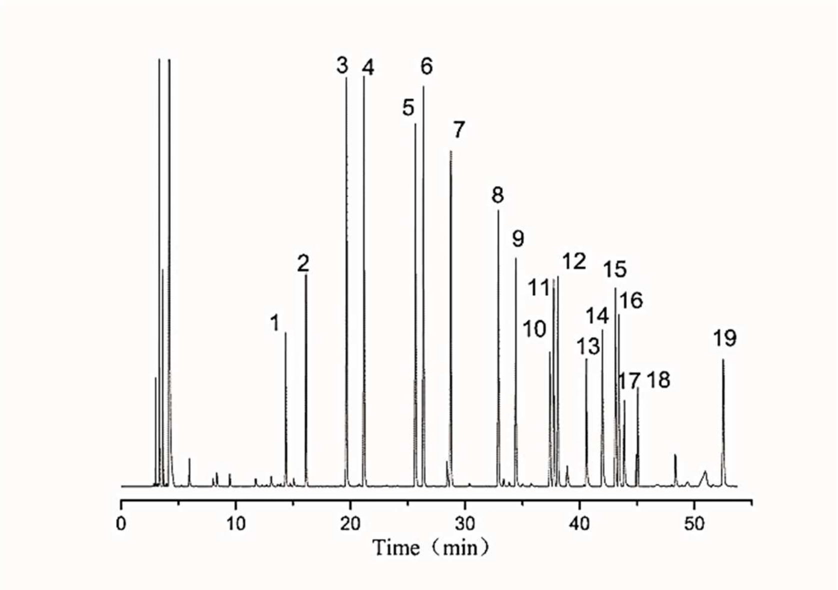


Fig. 5. Separation of polycyclic aromatic hydrocarbons on the DFP-15 column. Temperature program: from 50 ºC to 325 ºC at 5 ºC/min. 16 cm/s helium linear velocity. Peaks: 1, decahydronaphthalene; 2, tetralin; 3, naphthalene; 4, 2-methylnaphthalene; 5, 1-methylnaphthalene; 6, biphenyl; 7, 8-hydroxyquinoline; 8, dihydroacenaphthylene; 9, naphthyl ethyl ether; 10, phenanthrenequinone; 11, dibenzyl ether; 12, α-nitronaphthalene; 13, fluorenone; 14, phenanthrene; 15, benzil; 16, 4-nitrobiphenyl; 17, *β*-naphthol quinoline; 18, 1,8-dihydroxy anthraquinone; 19, pyrene.

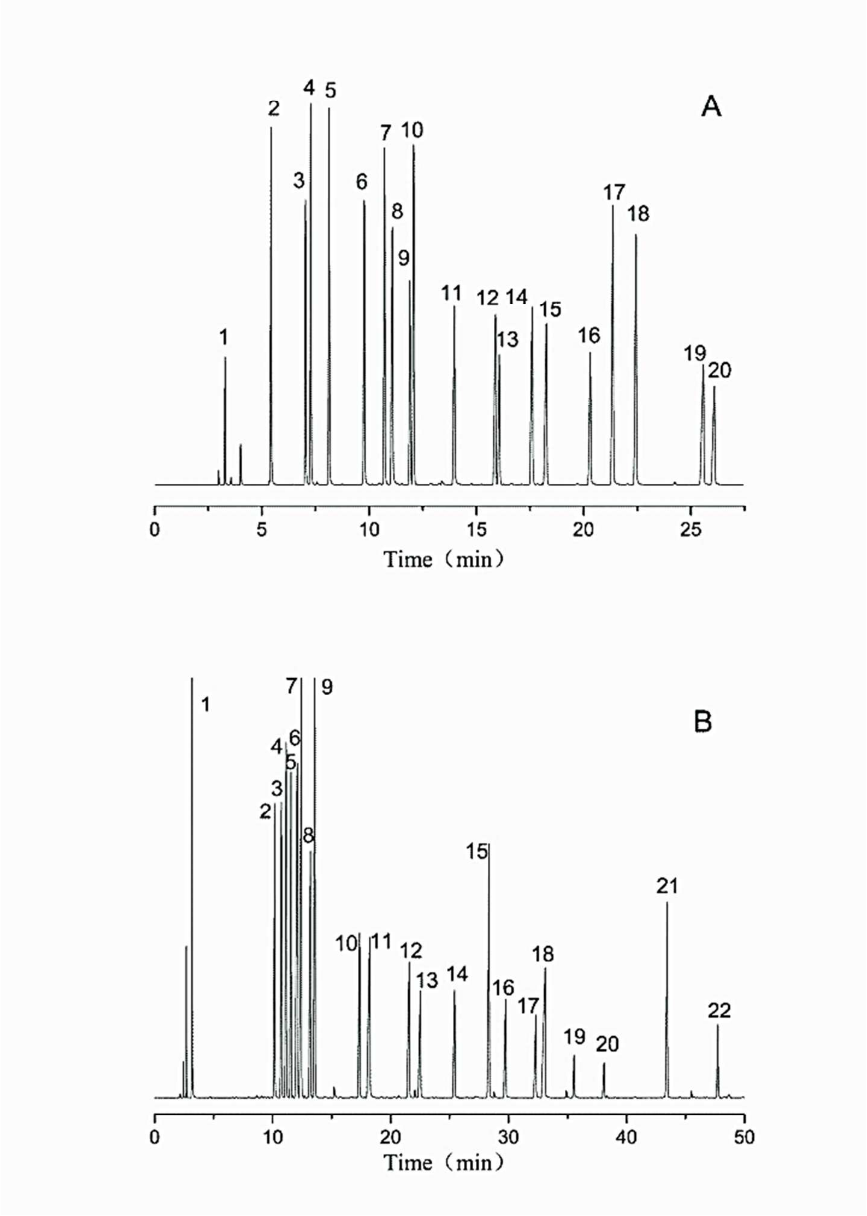


Fig. 6. Chromatograms of substituted benzenes (A) and (B) on the DFP-15 column. (A) Temperature program: from 70 ºC to 250 ºC at 6 ºC/min. 16 cm/s helium linear velocity. Peaks: 1, benzene; 2, toluene; 3, chlorobenzene; 4, ethylbenzene; 5, *m*-xylene; 6, *p*-methylchlorobenzene; 7, 1,2,4-trimethylbenzene; 8, m-dichlorobenzene; 9, butylbenzene; 10, nitrobenzene; 11, *o*-methylnitrobenzene; 12, *o*-ethylnitrobenzene; 13, p-dibromobenzene; 14, *p*-methylnitrobenzene; 15, *p*-nitrochlorobenzene; 16, *p*-nitrobromobenzene; 17, biphenyl; 18, diphenylmethane; 19, 1-methyl-2,4-dinitrobenznen; 20, 1-chloro-2,4-dinitrobenzene. (B) Temperature program: from 60 ºC to 310 ºC at 5 ºC/min. Peaks: 1, benzene; 2, 1,3,5-trimethylbenzene; 3, p-chlorotoluene; 4, tert-butylbenzene; 5, 1,2,4-trimethylbenzene; 6, p-isopropyltoluene; 7, n-butylbenzene; 8, p-dichlorobenzene; 9, o-dichlorobenzene; 10, enzyl cyanide; 11, α,α-dichlorotoluene; 12, p-nitrotoluene; 13, o-nitrochlorobenzene; 14, p-nitrobromobenzene; 15, diphenylmethane; 16, 4-nitrobenzyl chloride; 17, 2, 4-dinitrotoluene; 18, 1-chloro-2,4-dinitrobenzene; 19, 1-Chloro-3,4-dinitrobenzene; 20, 1-fluoro-2,4-dinitrobenzene; 21, 1-bromo-2, 4-dinitrobenzene; 22, triphenylmethane.