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Fluoro-substituted tetraphenyl–phenyl grafted polysiloxanes as highly selective stationary phases for gas chromatography

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ABSTRACT

In this work, two new types of polycyclic aromatic grafted polysiloxanes, namely, 3,4-bis(4-fluoro phenyl)-2,5-diphenyl polysiloxane (FPP) and 3,4-bis(3,4,5-trifluoro phenyl)-2,5-diphenyl polysiloxane (TFPP), were synthesized and statically coated onto capillary columns as stationary phases for gas chromatography (GC). Based on their McReynolds constants, both columns exhibited moderate polarity. The efficiencies of the FPP and TFPP columns were 3316 ($k = 3.96$, naphthalene; 0.25 mm inner diameter) and 3768 ($k = 4.14$, naphthalene; 0.25 mm inner diameter) plates/m, respectively. The thermostability of the polymers was tested by thermogravimetric analysis (TGA), and results revealed that both TFPP and FPP began to decompose slightly at 380 °C. Separation of polyethylene pyrolysis products showed that the upper working temperature of the two columns can reach up to 360 °C. Relying on their unique polarizable characteristics in combination with other types of interactions, such as H-bond acceptor, dipole-dipole, and dispersive interactions, the newly synthesized polarizable stationary phases offered unique selectivity for aromatic isomers and substituted benzenes. A slight separation difference between TPP and TFPP was observed. TFPP also exerted excellent selectivity for polycyclic aromatic hydrocarbons, fatty acid esters, and fatty alcohols. Overall, FPP and TFPP demonstrated considerable potential for further applications because of their unique structures and outstanding separation performance.

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1. Introduction

Different types of stationary phases with specific selectivity, such as poly(ethylene glycol), ionic liquids [1–3], and metal-organic frameworks [4–6], have been developed to meet a wide range of analytical demands in gas chromatography (GC). A number of commercially available and laboratory-made stationary phases are made up of functionalized polysiloxanes, which feature chemical inertness, wide temperature operating ranges, and good film-forming abilities [7–9]. For instance, Peaden et al. [10] first used non-extractable methylphenylpolysiloxanes with different phenyl concentrations as a GC stationary phase in 1982. This polymer contained 4% vinyl, was conducive to cross-linking, and could be used up to 400 °C; however, its poor low-temperature usability limited its development. Then, functionalized polysiloxanes containing polarizable side groups, such as biphenyl, dicyanobiphenyl, methoxyphenyl, and naphthyl, were synthesized by Lee et al. [11–13]; while the products obtained achieved superior selectivity in a variety of aromatic isomer separations, these stationary phases could only be used below 280 °C because of their low molecular

weight, which is related to the polymerization method used for their synthesis. Significant improvements to similar polysiloxanes were made by Mayer [14], who synthesized 75% diphenyl and 25% dimethylpolysiloxane as a stationary phase for high-temperature, high-selectivity GC. This phase offered good selectivity and high inertness even at temperatures as high as 400 °C.

A previous study showed that introduction of phenyl to polysiloxanes can improve their thermal stability and polarity and promote resistance to oxidation [11–13]. However, working with complex samples, such as polycyclic aromatic hydrocarbons (PAHs), remains challenging because these samples feature large amounts of congeners/isomers and, in some cases, high boiling points. This challenge has prompted researchers to develop stationary phases that can achieve separation of complex samples with a wide polarity range and endure high column temperatures.

Inspired by the research of Lee, we confirmed in a recent study that the selectivity of polycyclic aromatic grafted polysiloxanes for polar compounds, especially aromatic isomers with similar chemical structures, markedly depends on the polarizability of multiphenyl–phenyl groups [15]. Introducing polar substituent groups, such as trifluoromethyl, to multiphenyl–phenyl groups improved the polarity and selectivity of the resultant stationary phases [16]. Thus, in this paper, we introduced a higher concentration of benzene rings in the functional groups attached to the

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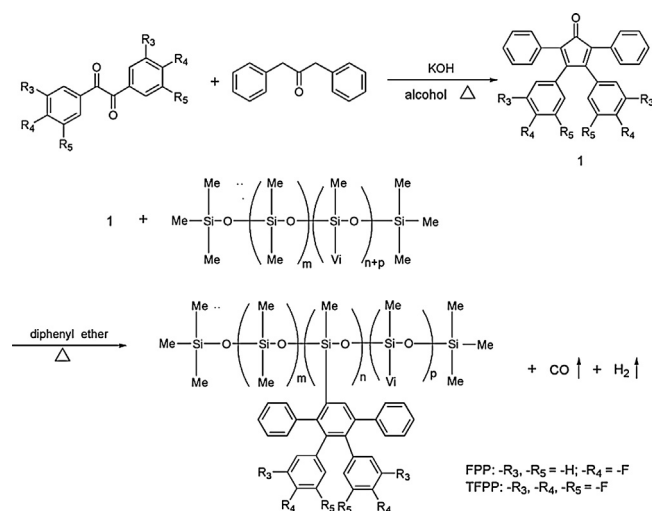


Fig. 1. Reaction scheme for the preparation of FPP and TFPP.

polysiloxane backbone. The respective average molecular polarizability values of 1,4-diphenyl-2,3-di(4-fluoro phenyl)-phenyl and 1,4-diphenyl-2,3-di(3,4,5-trifluoro phenyl)-phenyl are 48.1 and 46.9 Å³ [calculated according to Ref. [17]; the slightly lower polarizability of 3,4-bis(3,4,5-trifluoro phenyl)-2,5-diphenyl polysiloxane (TFPP) in comparison with that of 3,4-bis(4-fluoro phenyl)-2,5-diphenyl polysiloxane (FPP) is caused by the increased availability of fluorine groups with strong electronegativity in the former], which are considerably higher than those of benzene (10.40 Å³) and biphenyl (20.05 Å³). These results demonstrate that the new phases can possess better chromatographic selectivity with lower concentration than conventional phases. The presence of bulky mobile π -bonding electrons in multiphenyl-phenyl grafted polysiloxanes also presents significant advantages over previously reported phases in terms of strong π -stacking interactions.

Based on these aforementioned points, two novel functionalized polysiloxanes, namely, FPP and TFPP, were synthesized in this work. ¹H nuclear magnetic resonance spectroscopy (¹H NMR), infrared spectroscopy (IR), and thermo-gravimetric analysis (TGA) were used to characterize polymer structure and heat resistant properties of the products. McReynolds and Abraham system constants were determined to characterize the molecular interactions of the FPP and TFPP stationary phases with a number of analytes. Moreover, a comparative study between the FPP and TFPP columns was conducted by separation experiments of Grob test mixtures, aromatic positional isomers, and substituted benzenes. TFPP was further tested chromatographically through separation of PAHs, fatty acid esters (FAEs), and fatty alcohols. TFPP and FPP demonstrated good potential use as stationary phases for GC because of their excellent thermal stability and high selectivity.

2. Experiment

2.1. Materials and equipment

GC separation was conducted on a Shimadzu GC-2014C gas chromatograph (Shimadzu Corporation, Kyoto, Japan) fitted with a flame ionization detector (FID) and a split/splitless injection system. Nitrogen (N₂, 99.99% purity) was employed as the carrier gas, and the injection split ratio was 30:1. A DPX-300 NMR spectrometer (Bruker, Bremen, Germany), Nicolet 870 FT-IR spectrometer (Magna550), and LCT-2 TGA system (Beijing Optical Instrument Factory, Beijing, China) were used to characterize the prepared stationary phases. Column efficiencies were determined by using naphthalene at 120 °C.

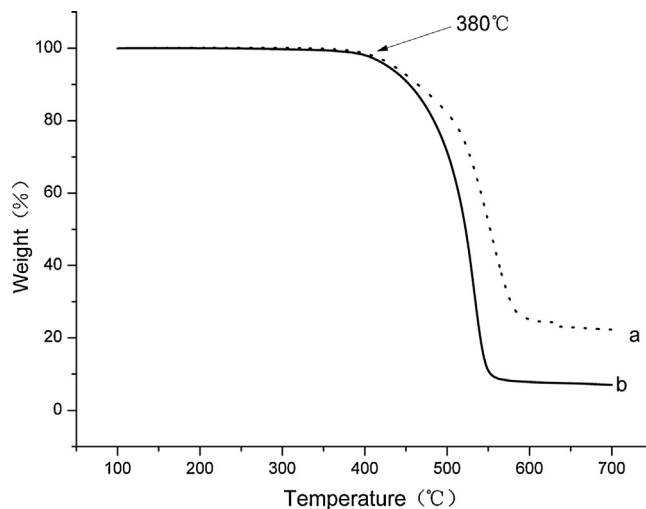


Fig. 2. TGA analysis of the (a) FPP and (b) TFPP polymers. The temperature was increased from 50 °C to 700 °C at a heating rate of 10 °C min⁻¹ under helium protection.

All of the chemicals used in this work, except for several synthetic raw materials, were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). The compounds 1,2-bis(4-fluoro phenyl)-1,2-ethanedione and 1,2-bis(3,4,5-trifluoro phenyl)-1,2-ethanedione were synthesized as described in Ref. [18]. A Grob test mixture was prepared according to the method described by Grob et al. [19,20]. Fused silica capillary tubes (30 m × 0.25 mm i.d.) were produced in our laboratory from fiber-level (SiO₂, 99.999% purity) raw tubes by using a self-made drawing machine. A commercial DB-17 capillary column (30 m × 0.25 mm i.d.; film thickness, 0.50 μm) was purchased from Agilent Technologies. A 3,4-2(trifluoromethyl phenyl)-2,5-diphenylphenyl grafted polysiloxane (TMPP) column was prepared as described in Ref. [16].

2.2. Preparation of FPP and TFPP polymers

FPP and TFPP polymers were synthesized via the Diels–Alder reaction, as shown in Fig. 1.

2.2.1. Synthesis of 3,4-bis(4-fluoro phenyl)-2,5-diphenyl cyclopentadienone (FPC) and 3,4-bis(3,4,5-trifluoro phenyl)-2,5-diphenyl cyclopentadienone (TFPC)

FPC was synthesized as follows: A certain amount of 1,2-bis(4-fluoro phenyl) ethane-1,2-dione (12.2 g, 0.050 mol) and 1,3-diphenylacetone (10.5 g, 0.050 mol) were dissolved in 60.0 mL of ethanol under nitrogen protection. Then, 6.0 mL 5 mol/L KOH in ethanol (0.030 mol KOH) was gradually dropped into the mixture over a period of 1 h. Afterward, the solution was continuously refluxed at 78 °C for 30 min and then filtered after cooling to yield bright black crystals. The crude product was recrystallized with ethanol-hexane solvent (v:v = 1:1), and 18.2 g of 3,4-di(4-fluoro phenyl)-2,5-diphenyl cyclopentadienone was obtained (yield, 86.3%). The product was confirmed by FT-IR and ¹H NMR. FT-IR (KBr, ν /cm⁻¹): 3068.6 [ν (Ar-H)]; 1723.9 [ν (C=O)]; 1243.5 [ν (C-F)]; 854.3 and 701.4 [ν (C-H)]. ¹H NMR(CDCl₃, 300 MHz, δ ppm): 7.33–7.48 (d, 8H), 7.19–7.27 (m, 6H), 6.93–6.96 (d, 4H).

TFPC was synthesized from 1,2-bis(3,4,5-trifluoro phenyl)-1,2-ethanedione and 1,3-diphenylacetone in a similar manner (yield, 84.7%). FT-IR (KBr, ν /cm⁻¹): 3071.6 [ν (Ar-H)]; 1714.6 [ν (C=O)]; 1616.1 [ν (Ar-C=C)]; 1239.5 [ν (C-F)]; 868.6 and 694.9 [ν (C-H)]. ¹H

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