



7,10-Diphenylfluoranthene grafted polysiloxane as a highly selective stationary phase for gas chromatography



Xue Han, Huan Wang, Xinxin He, Bing Wang, Bo Wu*

College of Chemistry and Chemical Engineering, Shandong University, 27 Shanda South Road, 250100, China

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ABSTRACT

A novel 7,10-diphenylfluoranthene grafted polysiloxane (DPFP) was synthesized and statically coated on a fused-silica capillary column. High column efficiency (3864 plates per m) was achieved for naphthalene at 120 °C. Thermo-gravimetric analysis showed that the DPFP polymer began to decompose at 380 °C. The chromatogram of polyethylene pyrolysis products indicated that the maximum allowable temperature of the DPFP column could reach 360 °C. By relying on its specific π - π stacking and dipole-induced dipole interactions with aromatic solutes, the DPFP stationary phase achieved excellent resolution for substituted benzene and aromatic hydrocarbons with satisfactory peak shapes, as well as showed superiority to current stationary phases that failed to resolve some critical pairs. Moreover, DPFP also showed good selectivity and resolving ability for Grob test mixtures, fatty acid esters, and ethers.

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1. Introduction

Capillary gas chromatography (GC) is extensively used in the field of analysis. For GC stationary phases, polysiloxanes, poly(ethylene glycol), ionic liquids, and macrocyclic derivatives are widely used traditional stationary phases. Currently, some new materials that serve as GC stationary phases with high resolution and thermal stability have been reported, such as carbon nanotubes [1,2], metal-organic frameworks [3–8], and graphene sheets [9]. 7,10-Diphenylfluoranthene grafted polysiloxane (DPFP) differs greatly from any of the aforementioned GC stationary phases in both chemical structure and molecular interactions with solutes, and may exhibit different retention behavior for GC separations. Thus, the feasibility of DPFP as a stationary phase for capillary GC may be worth exploring.

7,10-Diphenylfluoranthene is characteristic of a large aromatic π -conjugated system that contains mobile π -bonding electrons and may acquire dipole moments when composed into polar molecules. The DPFP with unique structure is expected to interact selectively with specific analytes *via* dipole-induced dipole and π - π stacking interactions. Lee introduced a bicyclic group with large polarizability, such as diphenyl, naphthyl, and diphenyl ether, to enhance dipole-induced dipole interactions with solutes

[10–12]. While these phases can achieve good resolution for closely related polar isomers, they can only endure column temperatures below 280 °C as they are limited by their polymerization methods. Our group has synthesized a series of polycyclic aromatic grafted polysiloxanes in recent studies [13–15], and has found that stationary phases with enhanced-polarizability functional groups offers improved selectivity for a number of applications.

However, working with critical pairs such as anthracene/phenanthrene remains a challenge because these two compounds possess exactly the same polarizability and quite similar boiling points. Compared to phases synthesized in our previous studies [13–15], the planarized biphenyl structure of 7,10-Diphenylfluoranthene leads to a larger delocalized π -electron system. Consequently, the DPFP stationary phase is expected to have better separation performance for critical pairs with large aromatic π -conjugated structures.

On the basis of these aforementioned points, a novel DPFP was synthesized and used as a stationary phase. ¹H nuclear magnetic resonance spectroscopy (¹H NMR), infrared spectroscopy (IR), and thermo-gravimetric analysis (TGA) were used to characterize the polymer. McReynolds and Abraham system constants were used to characterize the polarity and molecular interactions between DPFP stationary phase and solutes. A comparative study among DPFP, 3,4-(2(trifluoromethyl phenyl)-2,5-diphenyl phenyl grafted polysiloxane (DFP, containing 15.6% 3,4-(2(trifluoromethyl phenyl)-2,5-diphenyl phenyl groups), and DB-17 column was conducted by separating analytes containing π units. The DPFP separation per-

* Corresponding author.

E-mail address: wubo@sdu.edu.cn (B. Wu).

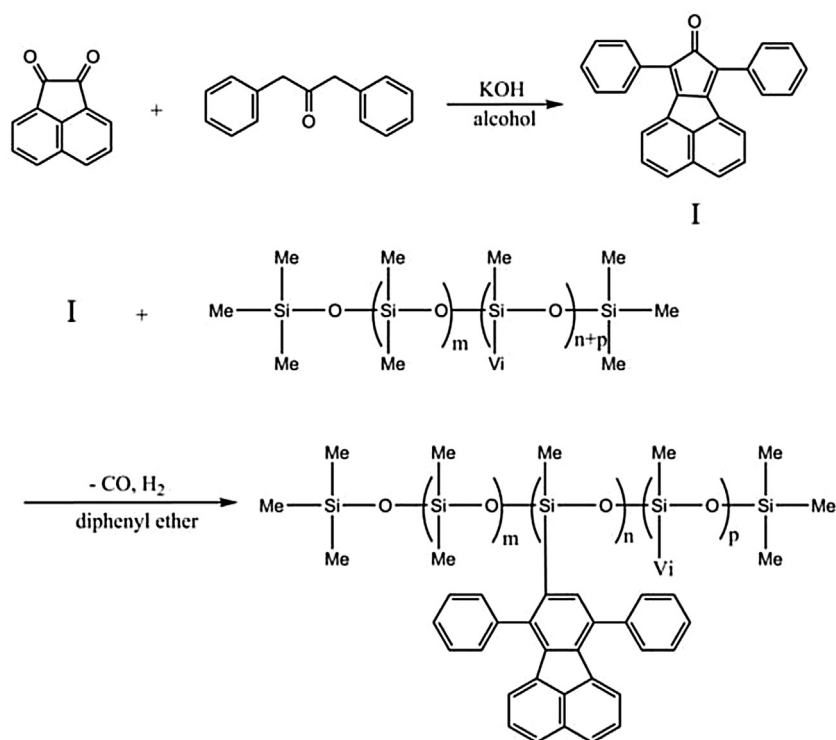


Fig. 1. Reaction scheme for preparation of DPFP.

formance was also further investigated using Grob test mixture, aromatic hydrocarbons, fatty acid esters (FAEs), and ethers. Moreover, separation repeatability of DPFP capillary column was also evaluated and the results indicated that the DPFP column could withstand long-term use.

2. Experiment

2.1. Reagents and apparatus

Acenaphthaquinone was purchased from Wuhan Yuancheng Technology Development Co. Ltd. (Wuhan, China). 1,3-Diphenylacetone and diphenyl ether were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All reagents and other testing compounds, except FAEs and ethers (industrial grade), were of analytical grade. Polyethylene pyrolysis products were prepared as described in ref. [16]. Fused-silica capillaries (0.25 mm I.D.) were produced in our laboratory [15]. Diphenyl-phenyl polysiloxane (DPPP, containing 16.1% diphenyl-phenyl groups) and DFP columns (30 m × 0.25 mm I.D.; 0.50 μm film thickness) were prepared according to ref. [13] and ref. [14] respectively. Commercial DB-17 column (30 m × 0.25 mm I.D.; 0.50 μm film thickness) was purchased from Agilent Technologies. All separations were performed on 30 m-long columns, except for polyethylene pyrolysis products, which were separated on a 12 m-long column.

Shimadzu GC-2014 gas chromatograph (Shimadzu Corporation, Kyoto, Japan) equipped with a split/splitless injection system and a flame ionization detector was used to perform all GC measurements. Nitrogen (N₂, 99.99% purity) was employed as carrier gas. The injection split ratio was 30:1. Bruker Avance-400 NMR spectrometer (Bruker, Switzerland), FTIR-8400S (Shimadzu Corporation, Kyoto, Japan), and LCT-2 TGA analysis instrument (Beijing Optical Instrument Factory, Beijing, China) were used to characterize the synthesized polymer.

2.2. DPFP polymer

2.2.1. Synthesis of

7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one (DPC) [17]

DPC was synthesized by a double Knoevenagel condensation reaction of acenaphthaquinone (5.46 g, 0.03 mol) and dibenzyl ketone (6.93 g, 0.033 mol) in 50.0 mL absolute ethanol under nitrogen atmosphere. When the solution was brought to reflux, KOH (1.0 g) in 5.0 mL ethanol was added dropwise into the solution. Afterward, the reaction was heated to reflux at 78 °C for a further 45 min, and then the mixture was filtered after cooling. The crude product was re-crystallized using ethanol/toluene solvent mixture (v/v = 3:2) to obtain a pure, dark-brown crystal DPC (8.3 g, 78%). FTIR (KBr, ν/cm^{-1}): 3059.6 [$\nu(\text{Ar-H})$]; 1720.8 [$\nu(\text{C=O})$]; 1569.6, 1509.3 [$\nu(\text{C=C})$]. ¹H NMR (CDCl₃, 400 MHz, δ ppm): 7.26–8.08 (m, Ar-H, 16H).

2.2.2. Procedure for DPFP preparation

Polymethylvinylsiloxane with 20% vinyl was synthesized as described in ref. [18]. DPC (4.27 g, 0.012 mol) and polymethylvinylsiloxane (5.00 g, containing 0.010 mol vinyl) were added to a dry, four-necked flask containing 20.0 mL diphenyl ether. The solution was heated at 220 °C for 38 h under N₂ atmosphere, and a yellow viscous product appeared with numerous bubbles. Polymerization was stopped when bubbles were no longer observed. After distilling the solvent, the resultant was dissolved in 10 mL toluene, and then washed with 25 mL methanol to precipitate the product. The step was repeated for three times. After the residual solvent evaporated under vacuum, DPFP was obtained as a transparent, light yellow, high-viscosity gum (13.83 g, 78.0%). FTIR (KBr, ν/cm^{-1}): 3074.8 [$\nu(\text{Ar-H})$]; 2958.4, 1604.2, and 806.2 [$\nu(\text{C-H})$]; 1410.6 and 1596.7 [$\nu(\text{Si-CH=CH}_2)$]; 1072.6 and 1023.2 [$\nu(\text{Si-O-Si})$]. ¹H NMR (CDCl₃, δ ppm): 6.46–7.69 (m, Ar-H, 17H). Peaks at 5.96 and 0.086 ppm were attributed respectively to vinyl and C–H on Si atoms in a polysiloxane skeleton.

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