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Poly(3-hexylthiophene) stationary phase for gas chromatographic separations of aliphatic and aromatic isomers

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ABSTRACT

This work describes the investigation of utilizing a chain-typed thiophene-based π-conjugated polymer, *i.e.*, poly(3-hexylthiophene) (P3HT), as the stationary phase for gas chromatography (GC). The P3HT column was statically prepared and investigated for its column efficiency, polarity, separation performance, repeatability and thermal stability. As a result, it showed moderate polarity and column efficiencies of 3260, 3310 and 3790 plates/m for 1-octanol, naphthalene and *n*-dodecane, respectively. As evidenced, it exhibited high-resolution performance for aliphatic and aromatic isomers, including those critical pairs such as phenanthrene/anthracene and *p*-/*m*-benzenediol isomers. Moreover, it displayed stronger retention for alkanes, alcohols and phenols in comparison to the polysiloxane stationary phase with close polarity. Also, the P3HT column had good repeatability and reproducibility with the RSD values less than 0.05% for run-to-run, 0.17–0.54% for day-to-day and 2.7–5.2% for column-to-column, and good thermal stability up to 260 °C. This work demonstrates the promising future of the thiophene-based polymer and its derivatives in separation science.

1. Introduction

Polymeric materials with good film-forming ability and thermal stability are advantageous as the stationary phases for gas chromatography (GC). Among them, polysiloxane-based stationary phases are widely used in GC and offer wide selectivity by diversifying side-chains [1]. Introduction of large π-conjugated side-chains onto the polysiloxane Si—O—Si backbone achieved improved selectivity for various types of analytes, especially aromatic isomers [2–4]. Over the past decade, advanced materials with a large planar π-conjugated system, typically graphene-based materials, have attracted growing attention as GC stationary phases, which showed preferential retention for aromatics and good separations ability for different types of analytes [5–11]. However, the major problems with the graphene materials are the strong aggregation tendency of nanosheets, and prone to produce tailing peaks for polar analytes such as alcohols and phenols due to the residual oxygen-containing groups in the materials [7,9,11].

Regioregular poly(3-hexylthiophene) (P3HT) (Fig. 1A) is a chain-like π-conjugated polymer with the backbone composed of only thiophene units, each unit substituted with one flexible hexyl group at 3-position. It features high charge carrier mobility and ordered nanostructures and has been used as organic field effect transistors and solar cells [12–14], gas sensors for ammonia gas [15,16] and nitrogen dioxide [17]. Moreover, P3HT possesses satisfactory solubility in organic solvents, good film-forming ability and chemical/thermal stability [18,19]. Its unique structure and favourable physicochemical features offer its good potential in separation science, which interested us to explore its separation performance as a GC stationary phase.

Herein, we present the investigation of the GC separation performance of the P3HT polymer. To our knowledge, this is the first report of utilizing a thiophene-based chain-typed polymer with an armchair conformation in GC separations. After its column efficiency and polarity were determined, the P3HT column was investigated for its resolving ability and retention behaviours by employing analytes of varying types and their isomers in comparison to a polysiloxane column of close polarity. Moreover, the P3HT column was evaluated for its repeatability and thermal stability, and then was applied to determine isomer impurities in real samples from commercial vendors.

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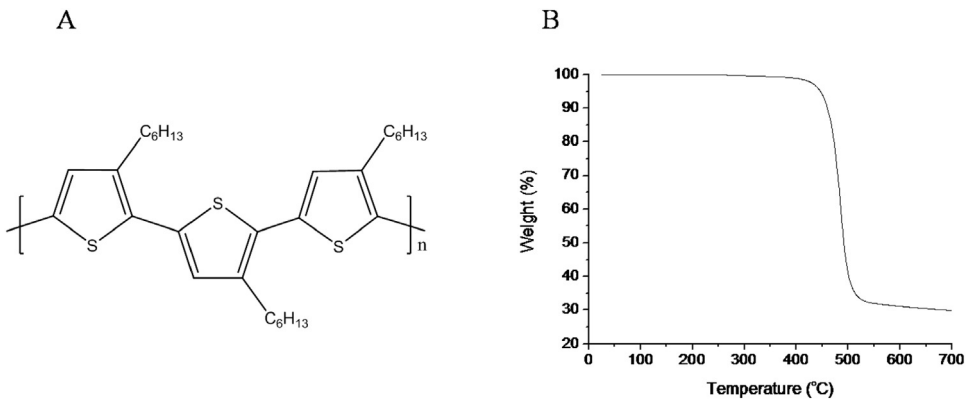

Fig. 1. (A) Structure of the regioregular P3HT polymer and (B) TGA curve of the P3HT polymer from 30 °C to 700 °C at 10 °C/min under nitrogen.

2. Experimental

2.1. Materials and instruments

All chemicals and reagents used in this work were at least of analytical grade and used as-received from commercial vendors. The regioregular poly(3-hexylthiophene) polymer (av. M. W. 20,000) was bought from Alfa Aesar (Shanghai, China). *n*-Decane, *n*-dodecane, *n*-pentadecane, 1-nonanol, nerol, geraniol, thymol, carvacrol, *α*-pinene, *β*-pinene, *m*-dibromobenzene, *o*-dichlorobenzene, *o*-diethylbenzene, *p*-diethylbenzene, *m*-diethylbenzene, *o*-chloronitrobenzene, 1-octanol, biphenyl, naphthalene, *p*-benzenediol, *m*-benzenediol, *o*-bromonitrobenzene, phenanthrene and anthracene were purchased from J&K. Scientific. Ltd. (Beijing, China). 1-Nitropropane, 2-pentanone, 2-heptanone, 1-butanol, *α*-naphthol, *β*-naphthol, 5-methyl-2-thiophenecarbaldehyde, 3-thiophenecarbaldehyde, 3-methyl-2-thiophenecarbaldehyde and cyclohexanone were purchased from Aladdin Industrial Corp. (Shanghai, China). Benzene, *n*-butylbenzene, 1-heptanol, pyridine, dichloromethane, chloroform and methanol were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). All test solutes were dissolved in dichloromethane. Untreated fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). A DB-35MS capillary column (10 m × 0.25 mm i.d., film thickness 0.25 μm) was purchased from Agilent Technologies (Palo Alto, USA) and used as a reference column.

GC separations were carried out on an Agilent 7890 A gas chromatograph (Palo Alto, USA), equipped with a split/splitless injector, a flame ionization detector (FID) and an autosampler. ChemStation software was used to process the chromatographic data. Nitrogen (99.999%) was used as the carrier gas. GC conditions are provided as follows except those specified in figure captions: flow rate of 1.0 mL/min, injection port 250 °C, injection volume of 0.20 μL, split ratio of 50:1, FID at 300 °C. A Shimadzu DTG-60AH thermal gravimetric analyzer (Kyoto, Japan) was used to measure the TGA curve of the P3HT polymer under the conditions from 30 °C to 700 °C at 10 °C/min under nitrogen.

2.2. Preparation of the P3HT capillary column

Prior to static coating, a bare fused-silica capillary column (10 m × 0.25 mm, i.d.) was subjected to a saturated solution of sodium chloride in methanol and kept for 90 min for its inner surface roughening [20]. First, 6 mL of the saturated solution of sodium chloride in methanol was added to 8 mL of chloroform under stirring and then another 8 mL of chloroform and 0.6 mL of methanol were added. Afterwards, the obtained suspension of sodium chloride in the solvent mixture was passed through the capillary column and stayed for 90 min. Then, the solution was removed and the column was conditioned up to 200 °C at 10 °C/min and held at the terminal temperature for 3 h under nitrogen. The P3HT polymer was dissolved in the solution of chloroform and dichloromethane (1:5, *v*/*v*) with the concentration of 1.5 mg/mL (0.15%, *w*/*v*). Then, the pretreated column was statically coated with the P3HT solution at 40 °C by one end of the column sealed and the other end connected to a vacuum pump to remove the solvent. Further conditioning of the coated column was performed with a temperature program: 40 °C for 30 min, then conditioned up to 200 °C at 1 °C/min and held at the final temperature for 4 h under nitrogen. The thickness of the P3HT column was about 0.10 μm obtained by the empirical formula, $d_f = (d_c \times c)/400$, where d_c is the capillary inner diameter (μm), c is the concentration of the stationary phase solution (%, *w*/*v*).

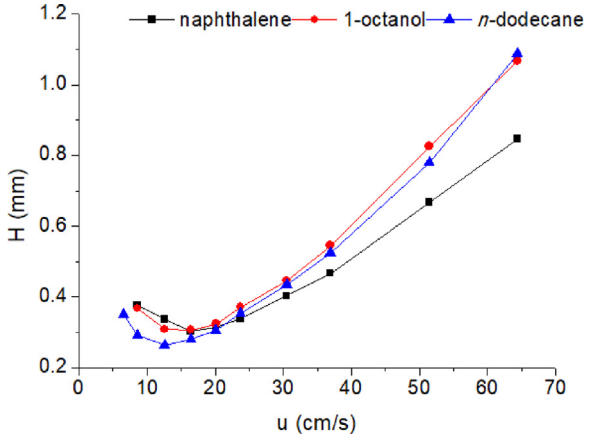

Fig. 2. Golay curves of the P3HT column determined by naphthalene, 1-octanol and *n*-dodecane at 120 °C, respectively.

3. Results and discussion

3.1. Characterization of the P3HT stationary phase and its capillary column

The TGA curve of the P3HT stationary phase is provided in Fig. 1B, showing its thermal stability up to 446 °C with 5% weight loss. This result suggested its feasibility as the GC stationary phase. The P3HT capillary column was evaluated for its column efficiencies by three probing analytes at 120 °C. To this end, their Golay curves were measured by plotting the height equivalent to a theoretical plate

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