



## Fabrication of powdery polymer aerogel as the stationary phase for high-resolution gas chromatographic separation

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### ABSTRACT

Novel powdery polymer aerogel (PPA) prepared via the (micro)emulsion polymerization and the following hyper crosslinking reaction was fabricated as stationary phase of capillary column for the first time. Due to its powdery morphology, unique 3D nano-network structure, high surface area and good thermostability, the PPA-coated capillary column demonstrated high-resolution chromatographic separation towards nonpolar and weakly polar organic compounds, including benzene series, *n*-alkanes, ketone mixtures and trichlorobenzenes. Moreover, the reproducibility, quantitative analysis ability and thermostability of PPA-coated capillary column were also evaluated. The relative standard deviations for three replicate determinations of selected analytes were 0.02–0.11%, 0.12–0.26% and 1.2–3.6% for run-to-run, day-to-day and column-to-column analyses, respectively. The PPA demonstrated good thermostability, and the PPA-coated capillary column was proved to be heat-resistant (270 °C). The results of this study show PPA is an excellent candidate to be employed as stationary phase for gas chromatography capillary.

### 1. Introduction

Gas chromatography (GC) has emerged as a powerful analytical technique coupled with numerous sensitive and selective detection techniques [1–4]. The most obvious advantage for GC is that a mass of analytes can be separated and determined simultaneously with high sensitivity. The high-resolution separation by gas chromatographic column is a decisive stage for the following quantification of analyte, therefore, it is important to select suitable gas chromatographic column [5]. However, the commercial stationary phases appropriate for separation are limited and expensive, leading to great efforts on fabrication of gas chromatographic column with high column efficiency [6].

Porous polymers have been popular stationary phases in gas chromatographic columns due to easy preparation and fabrication, as well as plentiful functional groups [7,8]. With the development of adsorptive materials, carbonaceous materials and metal-organic frameworks (MOFs) have emerged to cooperate with polymers to compensate for their disadvantage of low surface area [9–11]. It was proved that it was an effective way to improve the separation performance of polymer-fabricated column for small molecules by increasing the surface area of the polymer monolith through incorporation of nanoparticles with higher surface area. On the other hand, it is also feasible

for MOFs to be prepared as effective stationary phases in gas chromatographic columns without porous polymers [12–15]. As a kind of microporous materials with unusual properties of high surface area, good thermal stability, uniformly structured nanoscale cavities, and the availability of in-pore functionality and outer-surface modification, MOFs have been regarded as potential stationary phases and attracted great attention in developing new type of chromatographic column [16–19]. However, there still exist limitations to fabricated MOFs-based columns. For example, it is hard for most MOFs to keep stable with solvent or water atmosphere, as well as be produced with uniform morphology under mild condition [20]. The irregular shapes of MOFs may cause the problems of low column efficiency and undesirable peak shapes. Thus it can be seen that it is challenging to obtain a kind of adsorptive material as stationary phase with the advantages of high surface area, uniform morphology, good stability and dispersion.

Polymer aerogels (PAs) are a kind of emerging nanoporous materials with micro- and nano-architectures, which are produced by replacing the liquid component of the gel with gas to leave an intact solid nanostructure without pore collapse [21]. PAs have attracted increasing interest in the community of chemistry because of high porosity, ultralow thermal conductivity, high specific surface area, as well as high stability. In consideration of their charming advantages, great efforts

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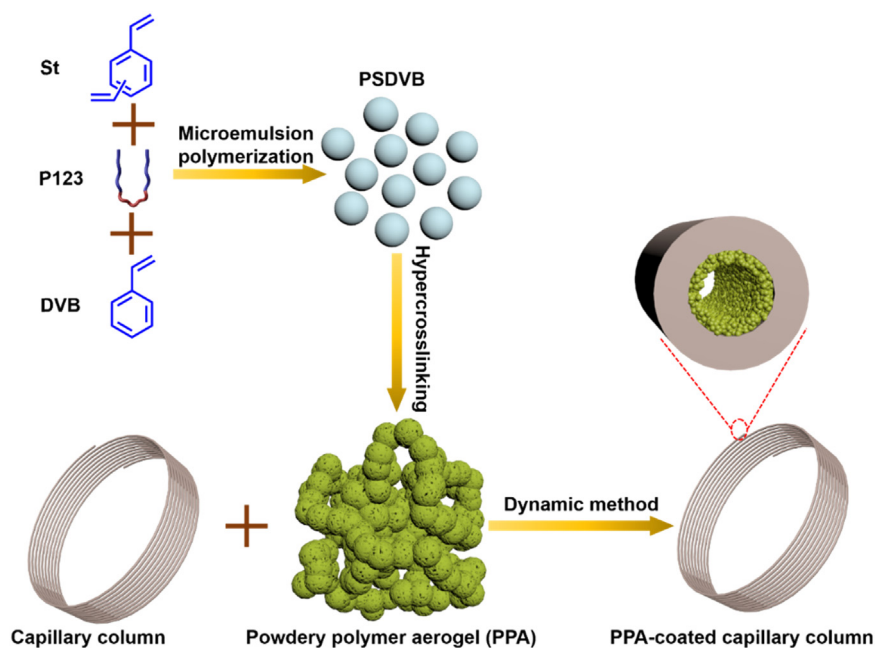


Fig. 1. Schematic illustration for the fabrication of PPA-coated capillary column.

have been made in syntheses of PAs and their practicalities have been verified by wide applications, including chemical sensors, thermal insulations, chemical adsorbents, separation, catalysts or catalytic carriers, and space explorations [22–26]. In addition to the above-mentioned advantages, the powdery morphology of powdery polymer aerogel (PPA) makes it promising in promoting the development of analytical chemistry as adsorbent [27–29]. However, it is still challenging for PPA to be synthesized in a microscale powdery form for the convenience of fabrication of high-resolution gas chromatographic column.

Hence, a kind of PPA was prepared by the (micro)emulsion polymerization and the following Friedel-Crafts (F-C) crosslinking reaction, with uniformly powdery morphology, high surface area and a unique three-dimensional (3D) pore structure. For the first time, the PPA was coated on the inner face of capillary column by dynamic method for high-resolution separations towards nonpolar and weakly polar organic compounds (Fig. 1). Due to van der Waals force, hydrophobic and  $\pi$ - $\pi$  interactions, benzene series, *n*-alkanes, ketone mixtures and trichlorobenzene isomer mixtures were separated precisely on the PPA-coated capillary column. In particular, challenging separation of cyclohexanone and 2-heptanone was also realized on the PPA-coated capillary column, benefiting by large amount of carbonyl groups from the F-C crosslinking reaction.

## 2. Experiments

### 2.1. Chemicals and reagents

The reagents employed for the synthesis of PPA were analytically pure. The poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123), styrene (St), divinyl benzene (DVB), 2,2-azobisisobutyronitrile (AIBN), aluminum trichloride ( $\text{AlCl}_3$ ) were bought from Sigma-Aldrich (Shanghai, China). The methanol, tetrachloromethane ( $\text{CCl}_4$ ), acetone and hydrochloric acid (HCl) were from Guangzhou Chemical Reagent Company (Guangzhou, China).

The chemicals used for the preparations of standard samples were of high purity (analytical grade or higher) and used as supplied without further treatment, which were purchased from Sigma-Aldrich (Shanghai, China), Alfa Aesar (Beijing, China) and J&K technology co. LTD (Beijing, China). In addition, the reagents employed for the

pretreatment of capillary column were bought from Guangzhou Chemical Reagent Company (Guangzhou, China), including sodium hydroxide (NaOH), HCl and acetone. The deionized water was produced by the Direct Q3 (Millipore, USA).

The blank quartz capillary columns were purchased from Ruifeng spectrum devices co. LTD (Yongnian, China).

### 2.2. Synthesis of PPA

The PPA was synthesized according to the literature [30]. In detail, deionized water was placed in three-necked flask which was full of nitrogen. The mixtures were slowly added into the three-necked flask. The reaction solution was prepared by mixing 18.3 g P123 dissolved in 160 mL deionized water, St (4 g) and DVB (0.32 g). Then, the reaction was initiated by 0.04 g AIBN and refluxed for 3 h. Finally, the PSDVBs were obtained after centrifugation, and the powdery products were cleaned with methanol and dried at 50 °C for 24 h.

PSDVB (1.0 g) was swelled completely in 120 mL  $\text{CCl}_4$ . Subsequently, the cross-linking reaction was started by adding 1.4 g  $\text{AlCl}_3$ , and the reaction was kept for 24 h with stirring at 75 °C. The reaction was stopped and washed for three times by the mixed solutions of acetone/hydrochloric acid/water. After centrifugation, the products were cleaned with methanol and dried at 120 °C for 24 h to obtain PPA.

### 2.3. Preparation of PPA-coated capillary column

The capillary column was pretreated with NaOH solution ( $1 \text{ mol L}^{-1}$ ) for 2 h, deionized water for 0.5 h, acetone for 0.5 h, HCl solution ( $0.1 \text{ mol L}^{-1}$ ) for 2 h and deionized water for 2 h in turn. Then, the washed capillary column was dried with nitrogen at 150 °C.

The PPAs were coated on the inner surface of pretreated capillary column by the dynamic coating method. A 1.5-mL acetone suspension of PPA (20 mg) was sealed in a sample vial, which was first filled into the capillary column (20 m long  $\times$  0.25 mm i.d.) under gas pressure with stable velocity of  $30 \text{ cm min}^{-1}$ . After the mixture was blown out, the PPA-coated capillary column was kept with nitrogen-blow overnight. Subsequently, the PPA-coated capillary column was treated at 250 °C for 1 h with heating rate of  $1 \text{ }^\circ\text{C min}^{-1}$ , and the treatment procedure was repeated for three times. Finally, the investigations of separation properties could be carried out after the treatment procedure.

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