



Knitting aromatic polymers for efficient solid-phase microextraction of trace organic pollutants



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ABSTRACT

A series of knitting aromatic polymers (KAPs) were successfully synthesized using a simple one-step Friedel-Crafts alkylation of aromatic monomers and were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). Then, as-synthesized KAPs with large surface areas, unique pore structures and high thermal stability were prepared as solid-phase microextraction (SPME) coatings that exhibited good extraction abilities for a series of benzene compounds (i.e., benzene, toluene, ethylbenzene and *m*-xylene, which are referred to as BTEX) and polycyclic aromatic hydrocarbons (PAHs). Under the optimized conditions, the methodologies established for the determination of BTEX and PAHs using the KAPs-triPB and KAPs-B coatings, respectively, possessed wide linear ranges, low limits of detection (LODs, 0.10–1.13 ng L⁻¹ for BTEX and 0.05–0.49 ng L⁻¹ for PAHs) and good reproducibility. Finally, the proposed methods were successfully applied to the determination of BTEX and PAHs in environmental water samples, and satisfactory recoveries (93.6–124.2% for BTEX and 77.2–113.3% for PAHs) were achieved. This study provides a benchmark for exploiting novel microporous organic polymers (MOPs) for SPME applications.

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1. Introduction

Substantial advances have been made in the analysis of trace environmental pollutants during the past few decades [1–3]. However, the effective and sensitive detection of organic pollutants in water continues to attract considerable attention [4,5] because water remediation remains a global challenge. In pollutant analysis, the tedious sample preparation procedures must be minimized or eliminated [6–8] because this step is always the slowest part of the entire analytical procedure and determines the final speed. Therefore, solid-phase microextraction (SPME), which requires only a small volume of adsorbent as the extraction phase and integrates sampling, isolation and enrichment into one step, has become a popular sample pretreatment technique [7,9]. Moreover, the flexibility in the design, geometry and calibration strategies of SPME

makes it a suitable choice for applications in environmental and life sciences [9–11].

The development of novel and effective coating materials could substantially promote SPME development because the method sensitivity and mass transfer rate rely primarily on the adsorbents [12,13]. Various materials with superb adsorption abilities have been exploited as SPME adsorbents in diverse applications [14–19]. Among these materials, porous materials, especially carbon materials [14] and metal organic frameworks (MOFs), are the most popular due to their high surface areas and unique pore structures [15,16]. However, the limited scope of synthetic diversification and narrow pore window apertures of carbon materials [18,20] inhibit their application for preparation of SPME coatings. In addition, the instability of MOFs in solvent and the moisture resulting from their unsubstantial coordination bonds [18,21] limit their extensive utilization as SPME adsorbents.

In contrast, microporous organic polymers (MOPs) constructed using numerous organic reactions and building blocks can provide flexibility in material design to achieve desirable properties and avoid the instability observed in MOFs [22,23]. In general, MOPs can be divided into several types based on the adsorption of

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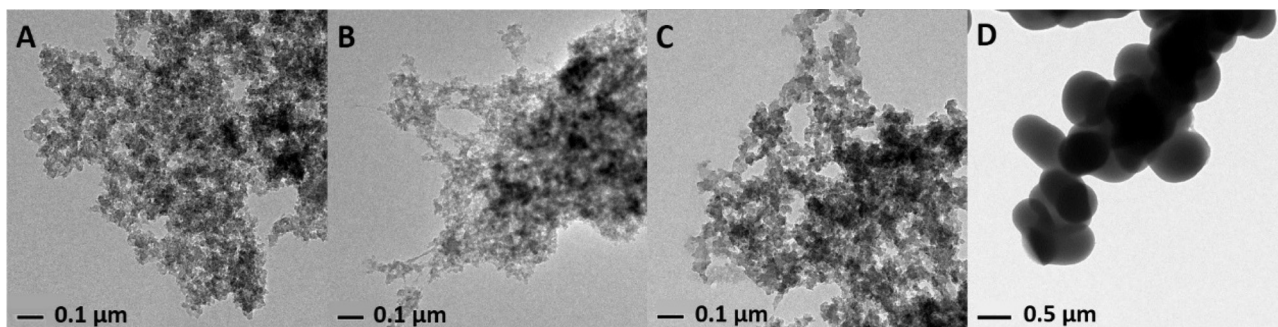


Fig. 1. TEM images of KAPs-B (A), KAPs-triPB (B), KAPs-CB (C) and KAPs-P (D).

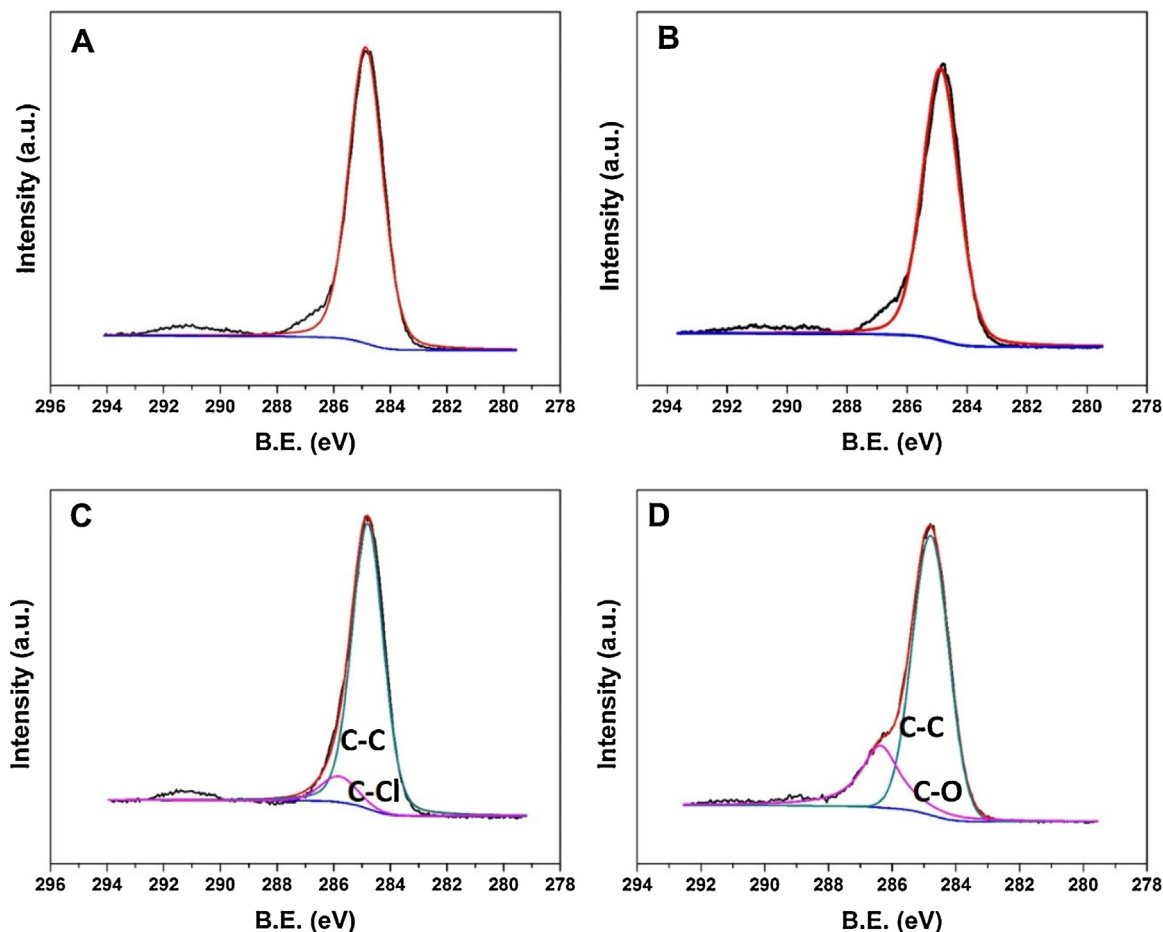


Fig. 2. C1s spectra of XPS experiment for KAPs-B (A), KAPs-triPB (B), KAPs-CB (C) and KAPs-P (D). Blue lines: backgrounds; black lines: initial spectra; red lines: fitting spectra, only C—C bonds were existed in Fig. 2A and B; green lines: C—C bonds; purple lines: C—Cl bonds for Fig. 2C and C—O bonds for Fig. 2D. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

different types of chemical reactions including hyper-cross-linked-polymers (HCPs) [24,25], polymers of intrinsic microporosity (PIM) [26], covalent organic frameworks (COFs) [27], conjugated microporous polymers (CMPs) [28], and porous aromatic frameworks (PAFs) [29]. Unfortunately, in contrast to the numerous advantages of these types of microporous materials, the applications of these promising polymers as SPME adsorbents remain underdeveloped [18,19].

Herein, we report the preparation and characterization of a series of knitting aromatic polymers (KAPs) for use as SPME coatings. As one type of HCP, KAPs were prepared using a cost-effective strategy involving “knitting” rigid aromatic building blocks with an external cross-linker [23,30]. This strategy can not only

eliminate the need for polymerizable monomers but also avoid the use of expensive metal coupling catalysts. Moreover, the extensive cross-linking bonds in KAPs will prevent the polymer chains from collapsing into a dense and nonporous state after the evaporation of the solvents, which will lead to their permanent porosity [23]. This highly cross-linked nature endows this material with high thermal stability and a high surface area.

In this study, four monomers including benzene, 1,3,5-triphenylbenzene, chlorobenzene and phenol were used as the aromatic building blocks, and the obtained polymers of the previously mentioned monomers are referred to as KAPs-B, KAPs-triPB, KAPs-CB and KAPs-P, respectively. Then, the as-synthesized polymers were prepared as SPME coatings, and the extraction

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