



# Amphiphilic block copolymer modified magnetic nanoparticles for microwave-assisted extraction of polycyclic aromatic hydrocarbons in environmental water



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## ABSTRACT

In this work, amphiphilic block copolymer poly(*tert*-butyl methacrylate)-block-poly(glycidyl methacrylate) (PtBMA-*b*-PGMA) modified Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub> MNPs) were synthesized, and served as an adsorbent for microwave-assisted extraction of polycyclic aromatic hydrocarbons (PAHs). The PtBMA-*b*-PGMA block copolymers with different block ratios were prepared by two-step atom transfer radical polymerization (ATRP) and the extraction abilities of their corresponding Fe<sub>3</sub>O<sub>4</sub>@PtBMA-*b*-PGMA were investigated. The key factors affecting the extraction efficiency of the adsorbent, including microwave conditions, amount of adsorbent, type and volume of desorption solvent, were studied in detail. In comparison with vortex, which is a conventional method used for assisting extraction, the proposed microwave-assisted method allowed better extraction efficiency and required a shorter extraction time. The calibration curves of PAHs were obtained in the range of 0.05–120 μg/L ( $r > 0.9985$ ) and the limits of detection ( $S/N = 3$ ) were in the range of 2.4–6.3 ng/L. The recoveries of PAHs spiked in environmental water samples were between 62.5% and 104% with relative standard deviations (RSDs) ranging from 0.84% to 9.02%. The proposed technique combining microwave-assisted extraction and magnetic separation was demonstrated to be a fast, convenient and sensitive pretreating method for PAHs.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a class of ubiquitous environmental contaminant, are produced from incomplete combustion of organic materials including coal, gas, garbage, meats, oil and so on [1,2]. They have brought great harm to human beings due to their toxicity, mutagenicity and carcinogenicity [3]. Environmental water, that human beings are susceptible to be exposed to, is one of the most important sources of PAHs. Therefore, the research on analysis of PAHs in environmental water has been a hot topic in analytical chemistry field. However, due to the low PAHs level in environmental water, it is highly necessary to preconcentrate the samples before the instrumental analysis.

Solid-phase extraction (SPE) is a routine method for extracting and concentrating toxic organic compounds from liquid samples due to its low solvent-cost and easy automation. Traditional SPE method involves passing samples completely through cartridges filled with solvents, which leads to time consuming and labor intensive processes [4–6]. Therefore, novel SPE modes are highly

desirable to overcome these drawbacks. In the past decades, magnetic solid phase extraction (MSPE) which is based on Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub> MNPs) has emerged as a new mode of SPE [7–11]. In MSPE, Fe<sub>3</sub>O<sub>4</sub> MNPs can offer high surface area and can be easily and quickly separated from matrix solutions by applying an external magnetic field because of their magnetism. Different surface modifications have been applied to provide suitable properties for Fe<sub>3</sub>O<sub>4</sub> MNPs to serve as adsorbents for preconcentrating various analytes. Among these surface modifications, hydrophobic modified Fe<sub>3</sub>O<sub>4</sub> MNPs with such as metal-organic frameworks [12], ionic liquids [13] and *n*-octadecylphosphonic acid [14] have been used for extraction of PAHs. However, the materials used for surface modification are limited. Thus, developing a new modification strategy to give a hydrophobic surface, which is suitable for fast and efficient extraction of PAHs in water samples, is highly significant.

It has been reported that amphiphilic block copolymers can be prepared by living polymerizations such as atom transfer radical polymerization (ATRP) [15–19]. These polymers composed of segments with different solubility properties toward aqueous solvent have attracted much attention, and their wide applications in biosensors, membranes and drug delivery systems have been found in recent years [20–22]. Considering the properties of amphiphilic block copolymers, modification of Fe<sub>3</sub>O<sub>4</sub> MNPs with amphiphilic

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block copolymer should be interesting and promising for preconcentration application. However, so far to our knowledge, no such research has been performed. Meanwhile, it is well known that the magnetic nanoparticles are good absorbers of microwave radiation and could be used for microwave-assisted extraction [23,24]. Nevertheless, extraction of PAHs in real samples using this method has not been explored till now.

In this study, amphiphilic block copolymer poly(*tert*-butyl methacrylate)-block-poly(glycidyl methacrylate) (PtBMA-*b*-PGMA), in which the PtBMA segment endows the block copolymer with high hydrophobic property for adsorbing PAHs and the PGMA segment provides functional groups for immobilization onto the Fe<sub>3</sub>O<sub>4</sub> MNPs, has been designed, prepared and used to modify Fe<sub>3</sub>O<sub>4</sub> MNPs. The synthesized Fe<sub>3</sub>O<sub>4</sub>@PtBMA-*b*-PGMA was served as an adsorbent for microwave-assisted extraction of PAHs. The influence of block ratio of the well-defined PtBMA-*b*-PGMA on the extraction efficiency has been investigated. Other key factors that affected the extraction efficiency, such as the microwave conditions, the amount of adsorbent, the type of desorption solvent and the volume of desorption solvent, have also been studied. Furthermore, using this novel preconcentration technique, we analyzed four environmental water samples.

## 2. Experimental

### 2.1. Reagents and materials

CuBr was purchased from Chuang Qi Chemical Plant (Beijing, China). 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) was obtained from JK Chemical Ltd. (Tokyo, Japan). Ethyl-2-bromoisobutyrate (EBIB, 98%) was obtained from Shanghai Crystal Pure Reagent Co. Ltd. (Shanghai, China). *Tert*-butyl methacrylate (*t*BMA), glycidyl methacrylate (GMA), ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), ferrous chloride (FeCl<sub>2</sub>·4H<sub>2</sub>O), methanol (HPLC grade), tetrahydrofuran, acetonitrile, acetone, hexane, and cyclohexanone were all purchased from Beijing Chemical Plant. 3-Aminopropyltriethoxysilane (APTES) was purchased from Acros Company (New Jersey, USA). Water prepared from a triple distilled water system was filtered through 0.45 μm membrane before use. Pyrene (PYR), 9,10-diphenylanthracene (DPA) and perylene (PER) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). Standard stock solutions containing these compounds were prepared in acetonitrile and stored at 4 °C. Working solutions were prepared daily by appropriate dilution of the stock with acetonitrile and stored at 4 °C. Tap water, lake water, river water and waste water samples were collected locally. All of the water samples were filtered through 0.45 μm filter head. After sampling, they were stored in clean glass bottles, and analyzed immediately by HPLC.

### 2.2. Instrumentation and analytical conditions

Chromatographic investigation was carried out with a Shimadzu LC-20A HPLC system (Shimadzu, Japan) consisting of a binary LC-20AT HPLC pump and an SPD-20A UV-Vis detector. All separations of PAHs were achieved on an analytical reverse-phase C18 column (5 μm particle diameter, 4.6 mm i.d. × 25 cm length), supplied by Agela Technologies (Beijing, China), with methanol as the mobile phase at a flow rate of 1.0 mL/min under isocratic conditions. Detection wavelength was 254 nm. Data processing was performed with an HW-2000 chromatography workstation (Nanjing Qianpu Software, China). <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) of the block copolymers was performed on Bruker Avance 400 spectrometer (Bruker biospin, Switzerland) (400 MHz). TEM images were obtained on a JEOL JEM-2010 high-resolution TEM

at an accelerating voltage of 200 kV. XRD analysis was carried out using a Rigaku D/max2500 diffractometer with Cu-Kα radiation (λ = 1.54056 Å) over the 2θ range of 10–80°. Magnetization measurements were studied with a vibrating sample magnetometer (VSM, LakeShore 7307 USA). Gel permeation chromatography (GPC) was performed on a Waters 1515 HPLC solvent pump equipped with a set of Waters Styragel columns and a Waters 2414 differential refractometer detector. THF was used as eluent at a flow rate of 1.0 mL/min with polystyrene calibration. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Bruker Tensor-27 spectrophotometer in KBr medium. A Galanz microwave oven emitting 2.45 GHz and 800 W microwave energy (Shun De, China) was used for microwave-assisted extraction.

### 2.3. Preparation of the amphiphilic block copolymer

The amphiphilic block copolymer PtBMA-*b*-PGMA was synthesized with a two-step ATRP procedure [25]. Firstly, a typical procedure to prepare the bromine end-functionalized PtBMA was as follows: EBIP (0.20 mmol, 39.0 mg), PMDETA (0.20 mmol, 42 μL), *t*BMA (40.00 mmol, 5.1 g) and 1.5 mL cyclohexanone were added into a flask. The mixture was degassed by three freeze-pump-thaw cycles and then CuBr (0.20 mmol, 28.8 mg) was added into the flask. The flask was evacuated and backfilled with nitrogen twice. The polymerization was carried out in an oil bath at 60 °C. The resulted crude product was purified by precipitation into a large amount of methanol and water mixture (1:1, volume ratio) three times. Secondly, block copolymerization was followed. PtBMA-Br (0.03 mmol, 0.5 g), PMDETA (0.03 mmol, 6.3 μL), GMA (6 mmol, 0.9 g) and 1.5 mL cyclohexanone were added into a flask. CuBr (0.03 mmol, 3.0 mg) was added after three freeze-pump-thaw cycles. Then, the flask was disposed as above and the mixed solution was reacted at 50 °C in oil bath in the atmosphere of N<sub>2</sub>. The resulted product was isolated by precipitation into a large amount of methanol and water mixture (2:1, volume ratio) three times. The product was obtained by drying under vacuum at 50 °C for 12 h.

### 2.4. Preparation of the amphiphilic block copolymer modified magnetic nanoparticles

The route for preparation of Fe<sub>3</sub>O<sub>4</sub>@PtBMA-*b*-PGMA including three steps is illustrated in Scheme 1. In the first step, Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by the coprecipitation method [26]. Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (5.4 g) and FeCl<sub>2</sub>·4H<sub>2</sub>O (2.0 g) were added into 100 mL water with a magnetic stirrer in a round bottle. Then, ammonia (25 wt%) was added dropwise until pH = 12. The solution was heated at 70 °C for 3 h. Finally, the black precipitate was filtered and washed three times with deionized water and acetone, respectively. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained by drying under vacuum at 50 °C for 12 h. In the second step, APTES-modified Fe<sub>3</sub>O<sub>4</sub> MNPs, namely Fe<sub>3</sub>O<sub>4</sub>-APTES, were achieved by the reaction between APTES and the hydroxyl groups on the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Typically, 500.0 mg of the obtained nanoparticles were dispersed in ethanol (50 mL). APTES was added to the above mixture under mechanical stirring at room temperature for 24 h. The product was filtered and washed with deionized water and acetone three times respectively, and then vacuum dried at 50 °C for 24 h. In the third step, PtBMA-*b*-PGMA was functionalized onto Fe<sub>3</sub>O<sub>4</sub>-APTES through the reaction between the amine groups and epoxy groups. 25.0 mg Fe<sub>3</sub>O<sub>4</sub>-APTES magnetic powder was dispersed in 30 mL of tetrahydrofuran. Subsequently, PtBMA-*b*-PGMA (25.0 mg) was added to the above solution, and the reaction was allowed to proceed for 24 h at room temperature. The product was dried under vacuum at 50 °C overnight.

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