



# Preparation of poly(trimethyl-2-methacroyloxyethylammonium chloride-co-ethylene glycol dimethacrylate) monolith and its application in solid phase microextraction of brominated flame retardants



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## ABSTRACT

A capillary poly(trimethyl-2-methacroyloxyethylammonium chloride-co-ethylene glycol dimethacrylate) monolith was in situ synthesized by thermally initiated free radical co-polymerization using trimethyl-2-methacroyloxyethylammonium chloride (MATE) and ethylene glycol dimethacrylate (EGDMA) as functional monomer and cross-linker, respectively. N,N-dimethylformamide and polyethylene glycol 6000 were used as solvent and porogen, respectively. The morphology and porous structure of the resulting monoliths were assessed by scanning electron microscope. In order to prepare practically useful poly(MATE-co-EGDMA) monoliths with low flow resistance and good mechanical strength, some parameters such as PEG-6000 to DMF ratio, total monomer to porogen ratio, and crosslinker to monomer ratio were optimized systematically. Moreover, the extraction mechanism was evaluated using two series of compounds, alkylbenzenes and weak acids, as model compounds on poly(MATE-co-EGDMA) monoliths as liquid chromatographic stationary phase. Finally, the monoliths were applied as the solid phase microextraction medium, and a simple off-line method for simultaneous determination of three brominated flame retardants, 2,4,6-tribromophenol (TBP), tetrabromobisphenol A (TBBPA) and 4,4'-dibrominated diphenyl ether (DBDPE), in environmental waters was developed by coupling the polymer monolith microextraction to HPLC with UV detection. The regression equations for these three brominated flame retardants showed good linearity from their limit of quantification to 5000 ng/mL. The limits of detection were 0.20, 0.15 and 0.10 ng/mL for TBP, TBBPA and DBDPE, respectively. The recovery of the proposed method was 78.7–106.1% with intra-day relative standard deviation of 1.3–4.4%.

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## 1. Introduction

Monolithic stationary phases have grown in interest because of their characteristic enhanced mass transfer and simple preparation. Polymeric monoliths, in particular, prepared by optimizing the polymerization conditions including temperature as well as composition of monomers and porogenic solvents offer efficiency approaching the feature of silica-based monoliths. Recently, some other new approaches have been proposed to improve the performance of monolith, such as preparing monoliths under conditions of incomplete conversion, use of single crosslinkers, hypercrosslinking of monoliths, and utilization of nanostructures [1].

There are a number of ways in which ion exchange functionality can be introduced in a polymeric monolithic column, such as functionalization by co-polymerization or post-polymerization modification. Typical examples of post-polymerization modification employed for polymeric monoliths include reaction of different reagents with functional groups on the monolith surface [2], grafting of monomer to or from the surface [3,4], and coating procedures including the use of latex particles [5]. Methacrylic acid, sulfopropyl methacrylate, 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-(diethylamino)ethyl methacrylate, and 2-(acryloyloxy)ethyl trimethylammonium chloride were all reported as the functional monomer which introduced charges to materials [6,7]. Polymeric ion exchange monoliths have been widely used for the separation and preconcentration of various analytes from large molecular compounds to small ionic species [8].

During the last decade, sample preparation technologies have gained widespread attention. Methods such as single-drop

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microextraction, liquid-phase microextraction, stir-bar sorptive extraction and thin film microextraction have been introduced extensively [9]. Among them, in-tube solid-phase microextraction (in-tube SPME) integrates sample extraction, concentration and injection into one step. For this reason, it became a suitable sample preparation technique prior to HPLC and HPLC–MS [10]. For in-tube SPME, increasing the extraction efficiency can be achieved by either increasing the coating thickness [11] or increasing the surface area of the sorption material [12]. However, the former requires long equilibrium time, so the latter method is more ideal. Polymer monolith microextraction (PMME) was first introduced by Feng's group, now has been successfully applied to the preconcentration step when combined with CE [13], ICP–MS [14], HPLC [15], HPLC–MS [16] and GC–MS [17].

Flame retardants are a diverse group of chemicals, mainly based on bromine, chlorine or phosphorus, which are added to a broad range of commercial products to provide fire protection. Some flame retardants may be covalently bound into materials, but most of them are simple additives. Recently, concerns over the persistence, ability to bioaccumulate and potential for toxicity of some of the most widely used brominated flame retardants (BFRs), polybrominated diphenyl ethers (PBDEs), have led to increasing regulation and restriction on their production and use [18].

In this work, a functional monomer containing anion-exchange functionality, trimethyl-2-methacroyloxyethylammonium chloride (MATE), was utilized. By direct co-polymerization of MATE and ethylene glycol dimethacrylate (EGDMA), the anion exchange monolithic material was prepared in a fused silica capillary. The monolith then was used to enrich three BFRs, 2,4,6-tribromophenol (TBP), tetrabromobisphenol A (TBBPA) and 4,4'-dibrominated diphenyl ether (DBDPE), in aqueous samples, followed by HPLC analysis. Although many polymeric monoliths mentioned above have been widely used as extraction medium in analytical field, up to date, no application for separation and preconcentration of BFRs by polymeric monoliths has been reported. To our knowledge, this is the first attempt to extract BFRs in environmental waters using PMME.

The retention mechanism study of monolithic materials to target analytes is very important to develop their application potential. Some researchers have reported the characterization of different kinds of ion exchange monoliths. For example, Huang et al. [19] and Abbood et al. [20] used anilines and peptides, respectively, to characterize cation-exchange ability of poly(4-vinylphenylboronic acid-co-pentaerythritol triacrylate) and hexylacrylate-based monoliths, while Zhang et al. [21] used aromatic acids to characterize anion-exchange ability of N-methylimidazolium-functionalized monolithic silica column. In this present work, the hybrid hydrophobic interaction and ion-exchange extraction mechanism of poly(MATE-co-EGDMA) monolith for BFRs was elucidated by using respective model compounds for the first time.

## 2. Experimental

### 2.1. Chemicals

Ethylene glycol dimethacrylate (EGDMA) was purchased from Alfa Aesar (Tianjin, China), trimethyl-2-methacroyloxyethylammonium chloride (MATE) was from Adamas Reagent (Shanghai, China), and  $\gamma$ -methacryloxypropyltrimethoxysilane ( $\gamma$ -MAPS) was from Yaohua (Shanghai, China). 2,2'-Azobis(2-methylpropionitrile) (AIBN), N,N-dimethylformamide (DMF) and polyethylene glycol-6000 (PEG-6000) were purchased from Shanghai Chemical Reagent (Shanghai, China). All of these reagents were of analytical reagent grade.

Toluene, ethylbenzene, propylbenzene, n-butylbenzene, m-toluic acid (mTA), 3,5-dihydroxybenzoic acid (DHBA), 3-hydroxybenzoic acid (HBA) and phenylacetic acid (PAA) were purchased from J&K Chemical (Beijing, China).

2,4,6-Tribromophenol (TBP) was purchased from TCI (Tokyo, Japan), and tetrabromobisphenol A (TBBPA) and 4,4'-dibrominated diphenyl ether (DBDPE) were from Accustandard (New Haven, USA). The analytes were prepared as 1.0 mg/mL stock solution in methanol and stored at 4 °C.

Dipotassium hydrogen phosphate, hydrochloric acid and phosphoric acid were purchased from Nanjing Chemical Reagent (Nanjing, China), and tris(hydroxymethyl)aminomethane (Tris) was from Biosharp (Seoul, Korea).

Methanol (MeOH) was HPLC grade (Merck, Darmstadt, Germany). Double distilled water (DDW) was used for all experiments.

### 2.2. Equipment

The scanning electron microscopy (SEM) images of poly(MATE-co-EGDMA) monolith were obtained using a S-3400N scanning electron microscope (Hitachi, Tokyo, Japan). The pH values of mobile phase were measured with a Seven Multi electrochemical analytical meter (Mettler-Toledo, Schwerzenbach, Switzerland). The electrode system was standardized with ordinary aqueous buffers of pH 2.00, 4.01 and 7.01 at 25 °C (Mettler-Toledo, Shanghai, China).

HPLC measurements were performed on three liquid chromatograph (LC) systems according to different purposes: LC 1 – Agilent 1200 separations module equipped with a quaternary pump, a thermostatted column compartment, a diode array detector (DAD) and a chemstation (Agilent, Santa Clara, USA); LC 2 – Lab Tech 600 liquid chromatograph pump (Lab Tech, Beijing, China); LC 3 – Waters Alliance 2695 separations module equipped with a vacuum degasser, a quaternary pump, an auto-sampler, a 996 UV–vis photodiode-array detector (PDA) and an Empower chromatography manager system (Milford, MA, USA).

### 2.3. Preparation of poly(MATE-co-EGDMA) monolith

Prior to polymerization, the fused silica capillary (530  $\mu$ m i.d., Reafine Chromatography Ltd., Hengshui, China) was pretreated according to the following procedure [22]: first, the capillary column was rinsed with 0.1 M NaOH, water and 0.1 M HCl, respectively, for 1 h, and then dried by passage of nitrogen gas.  $\gamma$ -MAPS solution by its dilution with DMF at a volume ratio of 1:1 was injected into the capillary. The capillary was sealed with rubber stoppers at both ends and put into an oven at 60 °C for 12 h, and finally, rinsed with methanol to flush out residual reagent and once again dried by nitrogen gas.

The monolith was prepared from polymerization reaction of the mixture consisted of monomer MATE and crosslinker EGDMA, porogens DMF and PEG-6000, and initiator AIBN (Fig. 1). At first, the polymerization mixture was sonicated to obtain homogeneous solution, and then the solution was filled into the capillary. After sealed at both ends with rubber stoppers, the capillary was put into an oven at 60 °C for 17 h and then washed with methanol at 0.3 mL/min for 30 min to remove unreacted monomer, crosslinker and porogen before use.

### 2.4. PMME procedure

The PMME device shown in Fig. 1 was referred to the work of Feng and co-workers [13]. The brief description of it is that the indispensable part of the PMME device is an interface capable of connecting the monolithic capillary and a syringe seamlessly. In

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