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Emulsion-cryogelation technique for fabricating a versatile toolbox of hierarchical polymeric monolith and its application in chromatography

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ABSTRACT

A novel poly (glycidyl methacrylate-co-ethylene dimethacrylate) monolith has been fabricated *via* the environmental friendly cryogelation-emulsion technique. The polymerization process is assisted by self-assembly of typical tri-block copolymer Pluronic F127 at sub-zero temperature using ice crystal as template, which can avoid consumption of organic porogenic solvents and thermal unstability of emulsion system. The developed monolith possesses hierarchical networks, which is confirmed by nitrogen adsorption measurement, mercury intrusion porosimetry, scanning electron microscopy and permeability testing. Further, the effect of the amounts of Pluronic F127 on the microstructure has been investigated. Moreover, the prepared polymer monolith undergoes acidic hydrolysis of epoxy groups into hydroxyl groups on the surface and its liquid chromatographic performance is explored by separating model analytes. The results indicate that the unique porous polymer monolith with hierarchical networks could be prepared *via* an organic porogen-free approach and used for analysis of polar and nonpolar molecules, extending the application of cryogelation-emulsion technique and methacrylate-based monolith.

1. Introduction

Porous monolith has been regarded as a single-piece bulk material and utilized in the fields of separation, solid phase extraction, catalysis and sensor alternative to packed bed, which is featured with key characteristics of excellent permeability and efficient mass transfer [1–3]. Based on the nature of materials, they are divided into two families: silica monolith and polymer monolith. The later is superior in pH stability and various surface chemistries over silica monolith and can be up-valued by purpose-design of its microstructure. In general, the microscopic morphology of polymer monolith is realized by phase separation, which consists of thermally induced phase separation (TIPS), non-solvent induced phase separation (NIPS) and polymerization induced phase separation (PIPS) [4,5]. The significant drawback among these methods is that deleterious organic solvents are often used as either solvent or porogen and removing them also needs extra analogical solvents [6–8]. Moreover, suitable solvents might be found via solvent screen relied on intuition, which leads to time consumption and environment pollution.

The water-in-oil emulsion polymerization is believed to be rather environmentally benign that immiscible water is dispersed into continuous phase of polymerization mixtures in the form of droplets as the emulsion template and porous monolith is fabricated by polymerizing the continuous phase and removing the template. The monolithic materials synthesized by emulsion polymerization are featured by open cell structure with numerous pores [9,10]. When controlling emulsion system, researchers are always faced with the stability problem, which precludes the flexibly modulating monolith morphology. Cryogelation, dated to 40 years ago, has been applied in synthesizing porous polymer monolith and its process is carried out as follow [11,12]. The starting aqueous solution is firstly frozen by cryogenic liquid, then stored at sub-zero temperature for a period of time and finally defrosted to form porous materials by simple thawing or freeze drying [13,14]. The porous microstructure is produced as a replica of the ice crystal network and the resultant porous material is defined as cryogel, which possesses interconnected hierarchical micro-/meso-/macroporous networks [15]. Combination of emulsion polymerization and cryogelation has presented several exciting advantages. In this case, emulsion can be locked by the rapid

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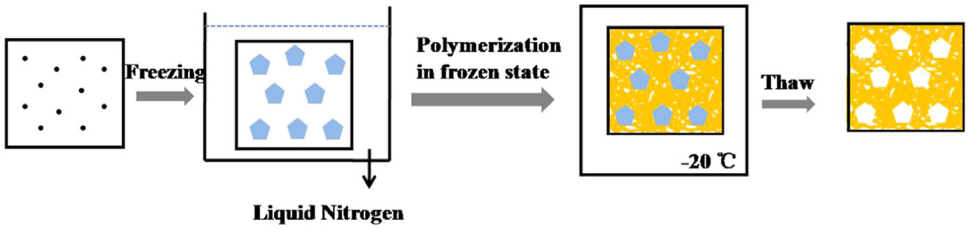

Fig. 1. The scheme of emulsion-cryogelation process for fabricating poly(GMA-co-EDMA) monolith.

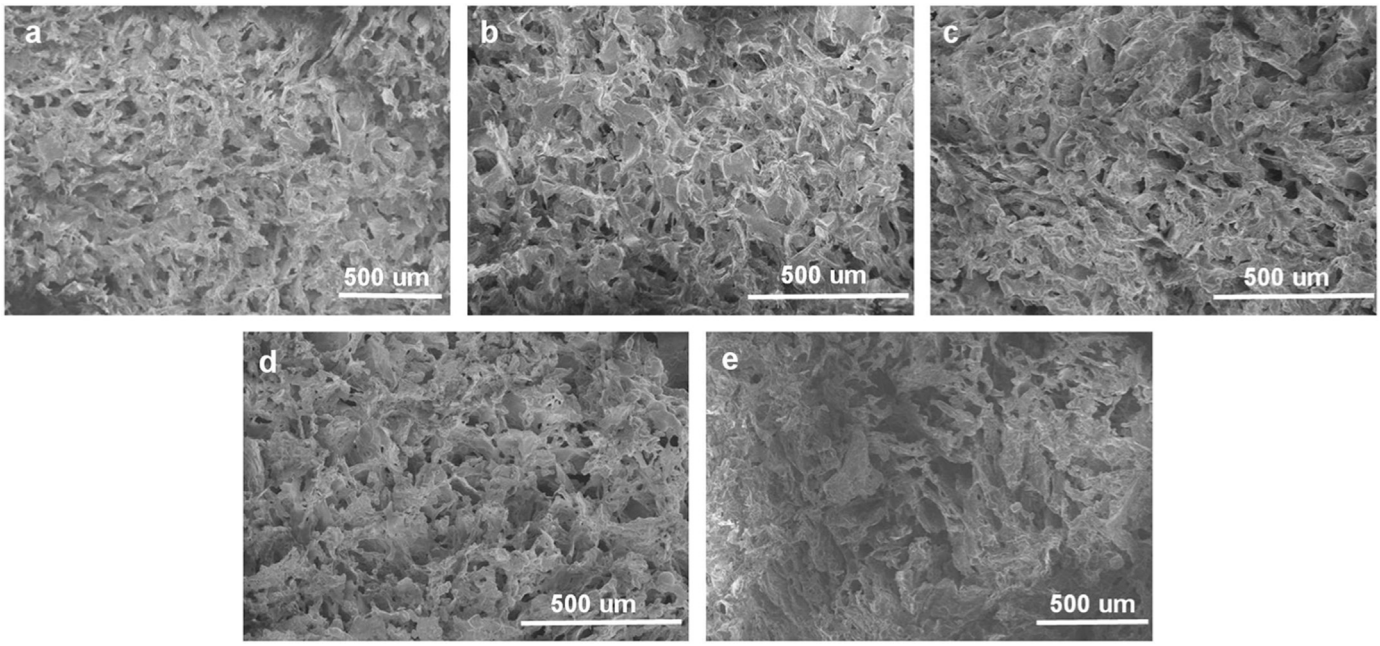

Fig. 2. SEM imaging of poly(GMA-co-EDMA) monolith with different amounts of GMA (v/v). (a) 5%; (b) 8%; (c) 11%; (d) 15%; (e) 18%.

freezing process, which can avoid emulsion instability and improve its tunability, contributing to greatly control on the morphology and porosity of the porous material [16]. Moreover, polymerization proceeds at low temperature, preventing biomolecules in the polymerization mixture from inactivation and benefiting for bio-applications.

Glycidyl methacrylate (GMA) is one of most studied monomers with high reactive side epoxy groups, which could facilitate post modification and provide a versatile platform for chemical transformation for various applications [17–19]. Furthermore, GMA possesses good biocompatibility and might be considered as the ideal monomer for preparing polymer monolith *via* emulsion polymerization. However, so far to our best knowledge, there has not been reported about the fabrication of methacrylate-based monolith for HPLC separation based on emulsion-cryogelation technique.

In this study, methacrylate-based polymer monolith is fabricated by environmental friendly emulsion-cryogelation technique *via* self-assembly of typical tri-block copolymer (Pluronic F127) with ice crystal as the template. The effects of key parameters (the internal phase ratio, the ratio of monomer to crosslinker and the copolymer concentration) on the morphology of polymer monolith are investigated in detail. The developed versatile toolbox of the monolith is illustrated as HPLC supports through a simple epoxy ring-opening reaction and its chromatography performance is evaluated by separating polycyclic aromatic hydrocarbons and basic aromatic amines as the probe molecules.

2. Experimental section

2.1. Materials and chemicals

Glycidyl methacrylate (GMA), Ethylene dimethacrylate (EDMA), 3-(trimethoxysilyl)propyl methacrylate (MPS) and N,N,N',N'-Tetramethylethylenediamine (TEMED) were obtained from Acros (NJ, USA). Pluronic F127 (PF127) was provided by Chuang Qi Company (Beijing, China). Ammonium persulfate (APS), anhydrous calcium chloride and sulfuric acid were from Beijing Chemical Company (Beijing, China). HPLC grade acetonitrile (ACN) and methanol were provided by Fisher Scientific (Springfield, NJ) and Kangkede Technology Co. Ltd (Tianjin,China). Benzoic acid, pyrene, and 9,10-diphenylanthracene were supplied from Aldrich (Milwaukee, WI, USA). *O*-Phenylenediamine, α-naphthylamine and 4,4′-diaminobiphenyl were purchased from Beijing Chemical Factory (Beijing, China). Other reagents were all of analytical reagent grade. Ultrapure water was obtained from Millipore Simplicity system (Millipore, Bedford, MA, USA) and solutions were filtered through a 0.45 μm membrane before use.

2.2. Apparatus

Chromatographic experiments were performed on a Shimadzu LC-20A HPLC system (Shimadzu, Japan) equipped with a binary LC-20AT HPLC pump and an SPD-20A UV–vis detector. Data processing was performed with an HW-2000 chromatography workstation (Nanjing Qianpu Software, China). Fourier transform infrared (FTIR) measurements were performed on TENSOR-27