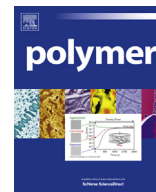




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Facile fabrication of poly(methyl methacrylate) monolith *via* thermally induced phase separation by utilizing unique cosolvency

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ABSTRACT

Poly(methyl methacrylate) (PMMA) monoliths with a three-dimensional continuous interconnected porous structure in a single piece were fabricated *via* thermally induced phase separation (TIPS) by utilizing unique cosolvency toward PMMA. We found that PMMA was soluble in a mixture of non-solvents (ethanol and water) at 60 °C. Cooling the solution resulted in formation of a monolith having interconnected pores. Cross-sectional analysis using scanning electron microscopy (SEM) showed a continuous porous network with submicron-sized skeleton. The pore size of the monolith was readily controlled by varying the fabrication parameters such as the polymer concentration and molecular weight, the cooling temperature and the solvent composition. The cross-section of the monolith showed high water repellency. The PMMA monolith was also obtained in a mixture of isopropanol and water with an appropriate solvent ratio.

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1. Introduction

In general, “monolith” means “one piece”. In the field of materials science and engineering, a monolith is often regarded as a single-piece bulk material having three-dimensionally developed continuous pores [1,2]. Such a monolithic structure is featured by several key aspects such as large surface area, high stability, efficient mass transfer, and high mechanical strength [3–5]. These aspects are attractive for its practical use in chromatography, ion-exchange and catalysis and other applications [6–11]. In addition, they can be further upvalued by purpose-designing of the porosity and/or various chemical modifications [12–14].

Currently, there are two main classes of monolithic materials: silica-based and polymer-based monoliths. Silica-based monoliths have serious defects in their industrial applications such as limited pH stability, complicated and sensitive operating protocols, whereas polymer-based monoliths have attracted great interests because of their good biocompatibility, high mechanical stability and excellent pH stability [15]. Moreover, the polymer monoliths are useful in a wide range of applications since their surface property and functionality can be controlled by the proper selection of polymers and their modification [16].

There are many methods to fabricate porous polymer monoliths from the corresponding monomers including polymerization-induced phase separation, polymerization within high internal phase emulsion templates and cryogelation [17–24]. In most of the reported methods, however, complicated, time-consuming procedures and additives such as porogens are required for the precise morphology control; it is often difficult to obtain the homogeneous porous structure because polymerization and phase separation have to be controlled simultaneously and accurately.

Recently, we have developed an easy and straightforward approach to prepare a polymer-based monolith by using a thermally induced phase separation (TIPS) technique [25,26] which is a template-free method. Polymers are first dissolved in an appropriate solvent by heating, followed by cooling the solution. During the cooling step, the phase separation of the polymer solution takes place to form the monolith with uniform porosity and high surface area without any templates. The shape of the monoliths can be modified by altering the shape of the vessel. Furthermore, polymer monoliths have been also fabricated by non-solvent induced phase separation (NIPS) [27,28]. The addition of a non-solvent to a polymer solution induces the phase separation to form a polymer monolith with controlled porous structure. So far, monoliths of polycarbonate [27,28], polyacrylonitrile [25,26], poly(vinyl alcohol) [29–31], and poly(γ -glutamic acid) [32–34] were successfully fabricated.

In this study, fabrication of a poly(methyl methacrylate) (PMMA) monolith by TIPS is demonstrated. Ethanol and water are

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well known as non-solvent of PMMA. In our previous reports on fabrication of monoliths by TIPS or NIPS, a mixture of solvent and non-solvent is used for the phase separation, meaning that the solubility of the polymer should be precisely tuned by the mixed ratio of solvent and non-solvent. Interestingly, we found that PMMA was solubilized at 60 °C in a mixture of water and ethanol, both of which are non-solvents for PMMA, and the monolith was formed upon cooling.

2. Experimental section

2.1. Materials

PMMA with different molecular weights were used in this study: PMMA-1 ($M_n = 6.0 \times 10^5$, $M_w/M_n = 2.6$); PMMA-2 ($M_n = 3.9 \times 10^5$, $M_w/M_n = 2.7$); PMMA-3 ($M_n = 5.7 \times 10^4$, $M_w/M_n = 2.7$); PMMA-4 ($M_n = 1.2 \times 10^4$, $M_w/M_n = 1.9$). These polymers were obtained from Sigma–Aldrich and Nacalai Tesque. The molecular weight values were obtained by size exclusion chromatographic (SEC) analysis. Other reagents were of analytical grade and used without further purification. A film of PMMA was prepared by solvent casting method from a chloroform solution of PMMA-1 with the concentration of 5% (w/v).

2.2. Measurements

Scanning electron microscopic (SEM) images were recorded on a HITACHI S-3000N instrument at an accelerating voltage of 15 kV. A thin gold film was sputtered on the samples before the images were collected. Nitrogen adsorption/desorption isotherms were measured with a NOVA 4200e surface area & pore size analyzer (Quantachrome Instruments) at 25 °C. The specific surface area of the sample was calculated by the Brunauer–Emmett–Teller (BET) method at the linear part ($0.05 < P/P_0 < 0.25$) of the adsorption branch. Before the measurements, all samples were degassed at 25 °C for at least 6 h under vacuum. Contact angle of water on the cross section of monolith was measured with a Drop Master DM 300 (Kyowa Interface Science). SEC analysis was carried out using a TOSOH SC8020 apparatus with an RI detector at 40 °C under the following conditions: TOSOH TSKgel G3000H_{HR} column and chloroform eluent at a flow rate of 1.0 mL/min. The calibration curve was obtained using polystyrene standards.

2.3. Fabrication of PMMA monolith by TIPS

A typical fabrication protocol for a PMMA monolith is as follows (Fig. 1). PMMA powder was completely dissolved in an ethanol-water mixture (80/20 vol) at 60 °C and the solution was cooled to 20 °C. The mixed solvent in the resultant monolith was replaced with water by immersing the monolith in a large excess of ion-exchanged water for at least 6 h under gentle shaking at 25 °C. Water was refreshed three times. Finally, the monolith was dried under vacuum.

3. Results and discussion

3.1. Fabrication of PMMA monolith

Water and ethanol are well known as non-solvent for PMMA. These solvents are more hydrophilic than PMMA. Thus, such a mixed solvent, in general, would not solubilize PMMA. Actually, PMMA (PMMA-1, $M_n = 6.0 \times 10^5$) was not soluble in a mixture of ethanol and water (80/20 vol) at room temperature, but we found that it became soluble in this solvent at 60 °C at the concentration of 40 mg/mL, which may be explained by the unique cosolvency of such a mixed solvent for PMMA [35]; the cosolvency effect is that binary solvent mixtures of which both do not solubilize a polymer, but when they are used together in a homogeneous mixture, they create a powerful polymer dissolving system. Furthermore, the phase separation of the PMMA solution took place upon cooling to form the monolithic material. The distribution of the skeleton and pore sizes was relatively narrow (Fig. S1), suggesting the size uniformity of the pore structure. The cross-sectional image of the isolated monolith showed the homogeneous three-dimensional interconnected porous structure (Fig. 2(a)).

Interesting characteristics were observed for the obtained PMMA monolith. After the phase separation, the obtained columnar product contained the mixed solvent, which showed good flexibility (Fig. S2). Since glass transition temperature of PMMA is about 100 °C, this unique behavior may be because the solvent acts as plasticizer of PMMA. The dried PMMA monolith was very hard and such a flexible behavior was not observed even for the monolith immersed in water.

Moreover, the high water repellency was found on the basis of the unique morphology of the monolith. Contact angle of water on the cross section of the monolith of PMMA-1 and the PMMA film prepared by solvent casting method was measured (Fig. 3). The contact angle for the monolith was 139°, which was much higher than that for the PMMA film (69°). This high water repellency probably is attributed to the uniform structure of the submicron-sized skeleton despite a lack of perfluoroalkyl, silicone, or higher alkyl groups in the present monolith.

3.2. Effects of fabrication parameters

In order to control the morphology inside the PMMA monolith, the fabrication parameters have been examined systematically. The solution of PMMA-1 in the mixed solvent of ethanol and water could be prepared in the concentration range from 1 to 200 mg/mL at 60 °C. After cooling to 20 °C, a columnar material with uniform shape was obtained in the range from 40 to 80 mg/mL. The skeleton size of the monolith obtained at 40 mg/mL was thicker than that at 80 mg/mL (Fig. 2). The effect of polymer concentration on the morphology of monolith might be explained as follows. There are polymer-rich phase and polymer-lean phase when the phase separation takes place; the former one develops into skeleton of the monolith and the latter one mainly consisting of the solvent mixture results in pores. The volume ratio of polymer-lean phase to polymer-rich phase would be higher at a lower polymer

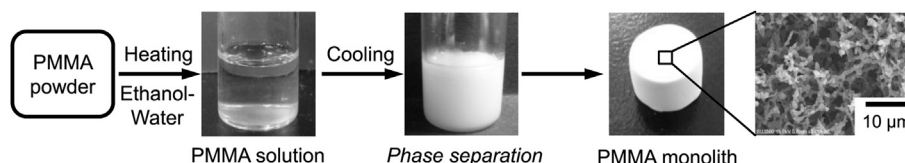


Fig. 1. Procedure for fabrication of PMMA monolith via TIPS.

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