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## Tailoring the morphology of emulsion-based (glycidylmethacrylate-divinylbenzene) monoliths

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## ABSTRACT

Poly(glycidylmethacrylate-divinylbenzene) monoliths [poly(GMA-DVB)] were prepared in the presence of a porogen using a high internal phase emulsion (HIPE) template. Tripolyglycerol monostearate was used as a surfactant to effectively inhibit Ostwald ripening and coalescence, and stable HIPE containing GMA was obtained. Epoxy groups of poly(GMA-DVB) were verified by FT-IR and solid-state <sup>13</sup>C NMR spectroscopy. The effects of surfactant amount, cross-linking degree, water fraction, and porogen amount on the surface area, average void diameter, range of void diameter, average interconnection diameter, and average pore diameter of poly(GMA-DVB) were investigated. The morphology of poly(GMA-DVB) may be tailored by tuning each of the factors described above according to the requirements of specific applications. Finally, poly(GMA-DVB) were further functionalized by diethylamine via the ring-opening reaction of epoxy groups. The results showed that most epoxy groups of poly(GMA-DVB) could react with diethylamine.

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### 1. Introduction

High internal phase emulsion (HIPE,  $\geq 74.5\%$  vol% internal phase) is a versatile method for the preparation of well-defined porous polymer foams known as polyHIPE monoliths [1–7]. These foams are of particular interest in biological tissue scaffolds [8–11], sensor materials [12], supports for solid phase synthesis [13–15], and hydrogen storage [16]. The most widely studied polyHIPE base materials include polystyrene [17–19] and poly(2-ethylhexyl methacrylate) [20], among others.

Many follow-up applications benefit from polyHIPE with reactive groups, such as the epoxy group. The reactivity of the epoxy group has been exploited in enzyme

immobilization [21–26], preparation of stationary phases for chromatographic separation [27–32], and ionic exchange resins for metal recovery [33–35]. Therefore, polyHIPE with epoxy groups presents great advantages in many fields because of the presence of reactive epoxy groups in the material that are suitable for subsequent functionalization [36].

The most readily available polyHIPE for epoxy groups is glycidylmethacrylate (GMA)-based polyHIPE monoliths, which uses GMA as a continuous phase. However, HIPE containing GMA may be destabilized because of the partial solubility of GMA in water, which is attributed to coalescence and Ostwald ripening. Coalescence is an irreversible process in which droplets in contact merge together to form a larger drop [37]. Ostwald ripening, on the other hand, describes the growth of larger droplets at the expense of smaller ones caused by differences in the chemical potential of the materials within the drops. Such

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differences arise from variations in the radius of curvature of the drops [38]. To the best of our knowledge, reports on the preparation of poly(glycidylmethacrylate) polyHIPE monoliths are scarce.

Krajnc et al. prepared poly(GMA-ethyleneglycol dimethacrylate) polyHIPE monoliths for application as stationary phases in the chromatographic separation of proteins [39]. However, in this work, the morphology of poly(GMA-ethyleneglycol dimethacrylate) polyHIPE monoliths presented very large, isolated voids without interconnections, which impair the permeability of the monoliths and therefore decrease the efficiency of separation in chromatographic applications. Yao et al. also prepared GMA-based polyHIPE monoliths using triblock copolymer surfactants and investigated the effect of surfactant concentration on the morphology of the resulting polyHIPE [40]. The morphology was altered dramatically by changing the surfactant concentration in the aqueous phase from 2% to 7% (v/v), such that the monolith became much more homogeneous and interconnected. Barbetta et al. investigated the preparation and hydrolysis of epoxy groups of thermally initiated GMA-based polyHIPE in the presence of a porogen [41]. However, GMA-based polyHIPE obtained by these researchers showed poor uniformity in terms of void diameter [41], and the effects of surfactant amount, cross-linking degree, water fraction, and porogen amount on the surface area, average void diameter ( $D$ ), range of  $D$ , average interconnection diameter ( $d$ ), and average pore diameter ( $D_w$ ) of GMA-based polyHIPE were not discussed.

PolyHIPE monoliths may be used in many applications, particularly as scaffolds for cell culture and tissue engineering, because of their highly porous and interconnected structure and tunable morphology; this morphology may be tailored by varying the physical properties of HIPE prior to curing [19]. Several parameters may be adjusted to alter the  $D$  and  $d$  of polyHIPE, including the emulsifier content [42], crosslinker concentration [43,44], water fraction [44,45], additives in the aqueous phase [19,44,46], and classification of porogenic solvents [17,18,41].

In this work, poly(GMA-DVB) are successfully prepared using an HIPE template. Tripolyglycerol monostearate (TGPS) is used as a surfactant to effectively inhibit Ostwald ripening and coalescence and stabilize the HIPE containing GMA. The effects of surfactant content, degree of cross-linking, volume percentage of the aqueous phase, and amount of the porogenic solvent on the morphology of the resultant poly(GMA-DVB) are investigated with the aim of tailoring the morphology of poly(GMA-DVB). Finally, poly(GMA-DVB) was further functionalized by diethylamine via the ring-opening reaction of epoxy groups.

## 2. Experimental

### 2.1. Materials

Glycidylmethacrylate (GMA, 99%, Sigma–Aldrich) and divinylbenzene (DVB, 55%, the remainder being *m*- and *p*-ethylstyrene, Sigma–Aldrich) were purified by passing

through a basic alumina column to eliminate inhibitors. Potassium persulfate (KPS, 98%, Shanghai Lingfeng Chemical Reagent Ltd., Co.) was purified via recrystallization. TPGS and Span 80 were obtained from Zhengzhou Honest Food Co., Ltd. and used without further purification. All other materials, including toluene, anhydrous calcium chloride, diethylamine (DEA) and ethanol, were of analytical grade and obtained from Shanghai Lingfeng Chemical Reagent Ltd., Co.

### 2.2. Preparation of poly(GMA-DVB)

In a typical poly(GMA-DVB) synthesis, 1 g of TPGS was first dissolved in an organic solution consisting of 2 mL of GMA, 3 mL of DVB, and 5 mL of toluene at room temperature. Then, 56.5 mL of a water solution containing 0.5 g of  $\text{CaCl}_2$  and 0.15 g of potassium persulfate was added dropwise to this organic phase under stirring at 500 rpm. Once all of the aqueous phase had been added, the speed of stirring was increased to 700 rpm. The prepared HIPE was transferred into glass tubes, sealed, and polymerized at 60 °C for 24 h. The crude products obtained were purified by Soxhlet extraction with ethanol for 24 h and then dried under vacuum at 40 °C for 24 h. The characteristics of the poly(GMA-DVB) samples are listed in Table 1.

### 2.3. Functionalization of poly(GMA-DVB)

Sample 2 (20 mg) was first crushed into particles of 40–80 mesh. Then, they were immersed in 50 ml of DEA at 60 °C for 24 h. The polymer was filtered, washed with ethanol and water, and then dried under vacuum at 50 °C for 12 h.

### 2.4. Characterization

Fourier transform infrared (FTIR) spectra were carried out on a Bruker Vector-22 FTIR spectrometer using the KBr method. Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were acquired on a Bruker AV 400 WB NMR spectrometer operating at 100 MHz using the CP/MAS technique. Nitrogen adsorption/desorption measurements were performed at 77 K on a Micromeritics TriStar 3020 model. The amounts of carbon, hydrogen and nitrogen of amine-functionalized poly(GMA-DVB) were determined by FLASH EA 1112 elemental analyzer. Field-emission scanning electron microscopy (FESEM) images were obtained on a JEOL JSM-6700 field-emission scanning electron microanalyzer. The average  $d$  and their distributions were recorded by a Micromeritics Autopore IV 9500 porosimeter. The  $D$  of poly(GMA-DVB) was determined from the SEM images and then corrected to take the statistical nature of the cross section into account using the following equation [17,19].

$$R = 2r/\sqrt{3}$$

where  $R$  is the equatorial value of the void size and  $r$  is the diameter value measured from the micrographs.

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