



Chromatographic assessment of two hybrid monoliths prepared *via* epoxy-amine ring-opening polymerization and methacrylate-based free radical polymerization using methacrylate epoxy cyclosiloxane as functional monomer[☆]



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ABSTRACT

Two kinds of hybrid monolithic columns were prepared by using methacrylate epoxy cyclosiloxane (epoxy-MA) as functional monomer, containing three epoxy moieties and one methacrylate group. One column was *in situ* fabricated by ring-opening polymerization of epoxy-MA and 1,10-diaminodecane (DAD) using a porogenic system consisting of isopropanol (IPA), H₂O and ethanol at 65 °C for 12 h. The other was prepared by free radical polymerization of epoxy-MA and ethylene dimethacrylate (EDMA) using 1-propanol and 1,4-butanediol as the porogenic solvents at 60 °C for 12 h. Two hybrid monoliths were investigated on the morphology and chromatographic assessment. Although two kinds of monolithic columns were prepared with epoxy-MA, their morphologies looked rather different. It could be found that the epoxy-MA-DAD monolith possessed higher column efficiencies (25,000–34,000 plates/m) for the separation of alkylbenzenes than the epoxy-MA-EDMA monolith (12,000–13,000 plates/m) in reversed-phase nano-liquid chromatography (nano-LC). Depending on the remaining epoxy or methacrylate groups on the surface of two pristine monoliths, the epoxy-MA-EDMA monolith could be easily modified with 1-octadecylamine (ODA) *via* ring-opening reaction, while the epoxy-MA-DAD monolith could be modified with stearyl methacrylate (SMA) *via* free radical reaction. The chromatographic performance for the separation of alkylbenzenes on SMA-modified epoxy-MA-DAD monolith was remarkably improved (42,000–54,000 plates/m) when compared with that on pristine epoxy-MA-DAD monolith, while it was not obviously enhanced on ODA-modified epoxy-MA-EDMA monolith when compared with that on pristine epoxy-MA-EDMA monolith. The enhancement of the column efficiency of epoxy-MA-DAD monolith after modification might be ascribed to the decreased mass-transfer resistance. The two kinds of hybrid monoliths were also applied for separations of six phenols and seven basic compounds in nano-LC.

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1. Introduction

Monoliths, generally *in situ* formed within a capillary column, are considered as the fourth-generation chromatographic material after the earlier synthesized polysaccharide-based, cross-linked

and coated and monodisperse stationary phases [1–3]. Current monoliths can be mainly divided into three types based on the nature of the matrix chemistry, namely, organic polymer monoliths, silica monoliths and organic-silica hybrid monoliths. Organic polymer monoliths and silica monoliths have been widely used in separation field during the past decades [4] and successfully applied to the analysis of small molecules [5,6] and large biomolecules [7,8]. The organic polymer monoliths, mainly composed of polyacrylamides, polymethacrylates and polystyrenes [9,10], possessed excellent pH stability and could be easily fabricated by single-step polymerization reaction. Unfortunately, this type of monoliths

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was apt to swell in some organic solvents such as tetrahydrofuran [11,12], which led to the change of pore structure and the decrease of mechanical stability and further resulted in a short lifetime [13–15]. In contrast, silica-based monoliths showed good solvent resistance and high mechanical stability, while tedious fabrication procedures were time-consuming and difficult to control, which greatly encumbered the researchers and limited the further application [13,16,17].

Organic-silica hybrid monoliths, somewhat combining advantages of the other two types of monoliths, including ease of preparation, less shrinkage, good mechanical stability, good pH stability and high surface area [14], have gained great popularity in solid-phase extractions (SPEs) [18,19], enzyme microreactors [20], high performance liquid chromatography (HPLC) [21] and capillary electrochromatography (CEC) [22] in recent years. The preparation of hybrid monoliths could be exemplified into three approaches [23], that is, (i) general sol-gel process using trialkoxysilanes and tetraalkoxysilanes as coprecursors. (ii) “One-pot” process of alkoxy silanes and organic monomers concomitantly proceeding sol-gel chemistry and free radical polymerization. (iii) Other polymerization approaches of silane-containing organic monomers. In general sol-gel process, the functional group from trialkoxysilanes was directly introduced to the surface of hybrid monolith and could be employed for further post-column modification. Compared to the traditional sol-gel method in the preparation of hybrid monoliths, the “one-pot” reaction manner would introduce the desirable functional groups into the monoliths. In addition, the hybrid monoliths prepared by other polymerization approaches could also be easily synthesized by ring-opening polymerization [24], free radical polymerization [25–27] or some other polymerizations by using a variety of monomers and crosslinkers.

In this study, methacrylate epoxy cyclosiloxane (epoxy-MA) (Fig. S1, Supporting information) was first adopted to prepare two kinds of hybrid monoliths *via* ring-opening polymerization and free radical polymerization. Ring-opening polymerization was carried out by the reaction between epoxy-MA and 1,10-diaminodecane (DAD) to prepare hybrid epoxy-MA–DAD monolith, while free radical polymerization was performed by the reaction between epoxy-MA and ethylene dimethacrylate (EDMA) to prepare hybrid epoxy-MA–EDMA monolith. Both hybrid monoliths were further modified and evaluated in nano-liquid chromatography (nano-LC).

2. Experimental

2.1. Reagents and materials

Epoxy-MA, EDMA (98%), DAD ($\geq 98\%$), stearyl methacrylate (SMA) (contains 90–150 ppm monomethyl ether hydroquinone as inhibitor, technical grade), methacryloxypropyl trimethoxysilane (γ -MAPS) ($\geq 98\%$) and (3-aminopropyl) trimethoxysilane (APTMS) ($\geq 98\%$) were purchased from Sigma (St Louis, MO, USA), and used directly without further purification. Azobisisobutyronitrile (AIBN) was gotten from Shanghai Chemical Plant (Shanghai, China), and recrystallized in ethanol prior to use. Octadecylamine (ODA) was gotten from Alfa Aesar (Ward Hill, MA, USA). 1,4-Butanediol, 1-propanol, 2-propanol (IPA), ethanol, thiourea, benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, hydroquinone, pyrocatechol, phenol, *p*-cresol, 2,6-xyleneol, 4-*tert*-butyl-phenol, 1,4-phenylenediamine, 2,4-diaminotoluene, carbamazepine, barbitone, benzidine, 2,4-dinitroaniline, 4-aminobiphenyl and other standard analytes were of analytical grade, and obtained from Tianjin Kermel Chemical Plant (Tianjin, China). Methanol and acetonitrile (ACN) were HPLC-grade and acquired from Merck (Darmstadt, Germany). Deionized water was prepared with a Milli-Q system (Milli-pore, MA, USA).

The fused-silica capillaries with 50 and 75 μm i.d. were the products of Reafine Chromatography Ltd. (Hebei, China).

2.2. Preparation and modification of two kinds of hybrid monoliths

2.2.1. Preparation of hybrid epoxy-MA–DAD monolith (Route I in Fig. 1)

Prior to preparation of hybrid epoxy-MA–DAD monolith, the capillary was pretreated with APTMS to immobilize a layer of amino groups into its inner wall, using the procedure developed previously [28]. In brief, the capillary was rinsed sequentially with 0.1 mol L⁻¹ NaOH (3 h), H₂O (1 h), 0.1 mol L⁻¹ HCl (5 h), H₂O (1 h) and methanol (2 h). The washed capillary was brimmed with APTMS/methanol (50%, v/v) for 0.5 h, and then sealed with rubber septa at both ends and placed in the water bath kept at $60 \pm 0.2^\circ\text{C}$ for 24 h. Using an HPLC pump, the obtained capillary was purged with methanol at a flow rate of 20 $\mu\text{L}/\text{min}$ for 1 h. Then, it was dried using a stream of nitrogen at 2 MPa pressure for 3 h, and sealed until used.

The procedures for preparation of hybrid epoxy-MA–DAD monolith were as follows. Briefly, epoxy-MA, DAD, IPA, H₂O and ethanol were mixed together in a centrifuge tube. Then the mixture was ultrasonicated for 15 min at ice bath to be degassed and form a homogeneous solution. After the resultant transparent solution was introduced into the APTMS-pretreated capillary to an appropriate length, both ends were sealed with a rubber septum, followed by immersion into a water bath at $65 \pm 0.2^\circ\text{C}$ for 12 h. The capillary was washed with methanol at a flow rate of 20 $\mu\text{L}/\text{min}$ for 3 h to remove the residuals. Finally, the ends of the capillary were dipped in water until further use.

2.2.2. Preparation of hybrid epoxy-MA–EDMA monolith (Route II in Fig. 1)

Prior to fill the capillary with prepolymerization solution, the fused-silica capillary was also pretreated, as similar to the above-mentioned procedures except that APTMS was replaced by γ -MAPS.

The preparation of hybrid epoxy-MA–EDMA monolith was carried out in the light of following procedures. First, epoxy-MA, EDMA, 1-propanol, 1,4-butanediol and AIBN were mixed together in a centrifuge tube. The mixture was ultrasonicated for 30 min in order to be degassed. After the resultant solution was introduced into the γ -MAPS-pretreated capillary to an appropriate length, both ends were sealed with a silicon rubber, followed by immersion into a water bath at $60 \pm 0.2^\circ\text{C}$ for 12 h. The capillary was washed with methanol at a flow rate of 20 $\mu\text{L}/\text{min}$ for 3 h to remove the residuals, and the ends of the capillary were dipped in water until further use.

2.2.3. Modification of two kinds of hybrid monoliths

To modify the hybrid epoxy-MA–DAD hybrid monolith, an ethanol solution containing 10.0% (v/v) SMA and 0.5% (w/v) AIBN was pushed through the hybrid monolith and reacted in a water bath at $50 \pm 0.2^\circ\text{C}$ for 12 h, while a solution consisting of 16.2 mg ODA and 300 μL ethanol was pushed through the hybrid epoxy-MA–EDMA monolith for post-column derivatization reaction, which was also carried out in a water bath at $50 \pm 0.2^\circ\text{C}$ for 12 h. Finally, they were washed with methanol at a flow rate of 20 $\mu\text{L}/\text{min}$ for 1 h to remove the residuals.

2.3. IR and SEM

The excess of the polymerization mixture remaining in the centrifuge tube was also polymerized under the same conditions as the preparation of the monolithic capillary columns. To remove the

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