



# Chromatographic efficiency comparison of polyhedral oligomeric silsesquioxanes-containing hybrid monoliths *via* photo- and thermally-initiated free-radical polymerization in capillary liquid chromatography for small molecules



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## ABSTRACT

Monolithic poly(methacrylate epoxy cyclosiloxane-co-polyhedral oligomeric silsesquioxanes) (epoxy-MA-POSS) capillary columns have been prepared *via* either photo- or thermally-initiated polymerization of the corresponding monomers using a 1-propanol/PEG 400 mixture as porogens. Photochemical polymerization was accomplished by irradiation of the UV-transparent capillary for 10 min at room temperature, while thermal polymerization was performed at 55 °C, 60 °C or 65 °C for 18 h. The evaluation of chromatographic property for two hybrid epoxy-MA-POSS monoliths was carried out. The results indicate that hybrid monoliths fabricated by photochemical initiation exhibit higher column efficiency (97,000–98,400 plates/m) than those synthesized by thermal polymerization (41,100–48,000 plates/m) in cLC. The higher efficiency of photo-initiated hybrid monoliths is closely related to lower eddy dispersion (A-term) and mass transfer resistance (C-term).

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## 1. Introduction

Emerged in the late 1980s and beginnings of the 1990s, monolithic materials have proven to be a good stationary phase in high efficiency separations in high-performance liquid chromatography (HPLC) [1] and capillary electrochromatography (CEC) [2,3]. Numerous monoliths including common polymeric and silica-based monoliths [4] have been developed for the separations of small molecules and high-molecular-weight molecules such as proteins and nucleic acids. As an alternative to organic and silica monoliths, organic-silica hybrid monoliths somewhat blended the merits of organic and silica monoliths such as ease of preparation, less shrinkage, good mechanical stability, wide pH range tolerance and high surface area, and have been applied as the separation matrix of chromatographic columns [5] and immobilized

enzyme reactors (IMERs) [6]. The preparation approaches of hybrid monoliths could be summarized into three categories [5], 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 monomers. Currently, free-radical polymerization is a simple technique for the synthesis of hybrid monoliths, using silane-containing monomer and cross-linker in the presence of pore-forming solvents.

Polyhedral oligomeric silsesquioxanes (POSS) are three-dimensional oligomeric, organosilicon compounds, which consist of cage frameworks covalently surrounded by organic groups on the periphery. The incorporation of POSS nanoparticles into a polymeric matrix can lead to dramatic improvement in its properties such as thermal stability, oxidation resistance, surface hardening and mechanical properties as well as reduction in its flammability, heat evolution, and viscosity during processing [7–11]. As a result, a POSS monomer of POSS-methacryl substituted (POSS-MA) was exploited to copolymerize with several methacrylate monomers

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as the precursors to fabricate a series of hybrid monoliths via thermally-initiated free-radical polymerization by us [12] and other groups [13,14]. As expected, these POSS-containing monoliths exhibited good mechanical stability and good pH stability. They were synthesized via thermal-initiation mode, which could be completed in several hours. Compared to the thermally-initiated polymerization process for the above-mentioned methods, there are only a few studies on the preparation of hybrid monoliths via photo-initiated radical polymerization within 10 min [15].

Herein, a hybrid monolith was prepared by the photo-initiated free-radical polymerization of POSS-MA and methacrylate epoxy cyclosiloxane (epoxy-MA) using 1-propanol and poly(ethylene glycol) (PEG 400, average Mn 380–420) as the binary pore-forming solvents, and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photo-initiator (Fig. 1). The POSS-containing monolith could be formed within several minutes. For comparison, thermally-initiated polymerization was also adopted to prepare a same hybrid monolith using azobisisobutyronitrile (AIBN) as the initiator. Two kinds of POSS-containing hybrid monoliths were assessed and compared in their chromatographic performance for small molecules in capillary liquid chromatography (CLC).

## 2. Experimental

### 2.1. Chemicals and materials

POSS-MA, epoxy-MA, methacryloxypropyl trimethoxysilane ( $\gamma$ -MAPS) ( $\geq 98\%$ ), PEG 400 and polystyrene standards were purchased from Sigma (St Louis, MO, USA). DMPA (99%) was obtained from Thermo Fisher Scientific (New Jersey, USA). AIBN was provided by Shanghai Chemical Plant (Shanghai, China), and purified by recrystallization from methanol. Methanol, 1-propanol, thiourea, benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and other standard analytes used in the experiment were of analytical grade, and obtained from Tianjin Kermel Chemical Plant (Tianjin, China). HPLC-grade acetonitrile (ACN) and tetrahydrofuran (THF) were used for the preparation of mobile phases. Water used in all experiments was obtained by using a Milli-Q water purification system (Milli-pore, MA, USA). Fused-silica capillaries of 375  $\mu\text{m}$  o.d.  $\times$  75  $\mu\text{m}$  i.d. with either polyimide or UV-transparent external coating were purchased from Reafine Chromatography Ltd. (Hebei, China).

### 2.2. Preparation of photo- and thermally-polymerized hybrid epoxy-MA-POSS monoliths

Prior to the preparation of hybrid monoliths, surface modification of the inner wall of fused-silica capillaries with either polyimide or UV-transparent external coating was performed with  $\gamma$ -MAPS to enable covalent attachment of the monolith to the wall. Briefly, the capillary was rinsed sequentially with 0.1 mol L<sup>-1</sup> NaOH (3 h), H<sub>2</sub>O (1 h), 0.1 mol L<sup>-1</sup> HCl (5 h), H<sub>2</sub>O (1 h) and methanol (2 h). Then, a 50% (v/v) solution of  $\gamma$ -MAPS in methanol was pumped through the capillary for 1 h using a syringe pump. The capillary was sealed with a rubber septum at both ends and placed in the water bath at 60 °C for 24 h. Then, the capillary was rinsed with methanol, and finally dried in a stream of nitrogen flowing through the capillary at 2 MPa pressure for 3 h, and then sealed until used.

The pretreated capillaries were filled with polymerization mixtures consisting of epoxy-MA, POSS-MA, a binary porogenic system (1-propanol/PEG 400) and the initiator. DMPA (0.3 wt% with respect to the monomers) and AIBN (1 wt% with respect to the monomers) were selected as the initiators of photo- and thermally-polymerized hybrid monoliths, respectively. After both ends of the capillaries were sealed with rubber septa,

the monoliths were prepared using photochemical or thermal initiation modes. Photo-polymerization was accomplished by irradiation of the UV-transparent capillary in a UV cross-linker (XL-1500A,  $\lambda = 365$  nm, Spectronics Corporation, New York, USA) for 10 min at room temperature, while thermal polymerization was performed by submerging the polyimide-coated capillary into a water bath at 55 °C, 60 °C or 65 °C for 18 h. The resulting monoliths were finally rinsed with methanol and used for HPLC.

### 2.3. Characterization

#### 2.3.1. Scanning electron microscope (SEM)

After thoroughly flushing out residuals, the monoliths were laid aside for several days at room temperature to allow the methanol evaporate from the pore structure. Then they were cut into 3–4 mm length pieces, and sputtered with gold with an accelerating voltage of 20 kV for 4 min. SEM images were obtained using the secondary electron imaging mode of a JEOL JSM-5600 scanning electron microscope (JEOL, Tokyo, Japan).

#### 2.3.2. Mercury intrusion porosimetry (MIP)

Bulk material (1.0 g) was also polymerized under the same conditions as the preparation of the monolithic capillary columns. To remove the residuals, the synthesized matrix was dipped into ethanol, and ultrasonicated for 5 h. The cleaning step was repeated for 4 times. Ultimately, the matrix was dried under vacuum at 60 °C for 24 h. MIP measurements were accomplished on Pore Master GT-60 (America Quantachrome Instrument Corporation, USA). Prior to the intrusion experiments, the samples were dried at 383 K for 8 h. Pore diameter was calculated according to the Washburn equation [16]:

$$pd = -4\gamma \cos \theta$$

where  $p$  is the applied pressure,  $d$  is the radius of a pore opening,  $\gamma$  is the surface tension of mercury (0.4842 N/m at 25 °C) and  $\theta$  is the contact angle between mercury and the sample. The contact angle ranges from 135° to 142°.

#### 2.3.3. Size-exclusion chromatography (SEC)

SEC on hybrid monoliths was carried out by using LC10AT pump (Shimadzu, Kyoto, Japan), a 7725i injector and a K-2501 UV detector from Knauer (Berlin, Germany). All experiments were performed with THF as the mobile phase. THF was degassed by ultrasonication before use. Polystyrene standards with a molecular weight ranging from 800 to 900,000 Da were dissolved in THF at concentration of 1 mg/mL. Benzene was adopted for the evaluation of the total accessible porosity of the columns. The flow rate of experiments was set at 0.1 mL/min, and the actual flow rate of mobile phase was measured using a stop-watch and a blank capillary (20 cm  $\times$  75  $\mu\text{m}$  i.d.), which was connected to the monolithic column. Thus, the real flow rate was calculated according to the equation,  $\mu = \pi r^2 L/t$ , where  $r$  and  $L$  (m) are blank capillary length and inner diameter of the capillary, respectively,  $t$  is the time that the mobile phase flows through the blank capillary. The UV detection was set at 214 nm. All experiments were repeated three times, and the mean values from three independent runs were adopted for column characterization.

#### 2.3.4. Nitrogen adsorption/desorption measurements

The specific surface area of the dry bulk monoliths was calculated from nitrogen adsorption/desorption measurements on a Quadrasorb SI surface area analyzer (Quantachrome, Boynton Beach, USA). Prior to the analysis, the samples were dried at 393 K for 8 h. The total surface area was calculated using the

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