



Facile construction of macroporous hybrid monoliths via thiol-methacrylate Michael addition click reaction for capillary liquid chromatography



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ABSTRACT

A facile approach based on thiol-methacrylate Michael addition click reaction was developed for construction of porous hybrid monolithic materials. Three hybrid monoliths were prepared via thiol-methacrylate click polymerization by using methacrylate-polyhedral oligomeric silsesquioxane (POSS) (cage mixture, $n=8, 10, 12$, POSS-MA) and three multi-thiol crosslinkers, 1,6-hexanedithiol (HDT), trimethylolpropane tris(3-mercaptopropionate) (TPTM) and pentaerythritol tetrakis(3-mercaptopropionate) (PTM), respectively, in the presence of porogenic solvents (*n*-propanol and PEG 200) and a catalyst (dimethylphenylphosphine, DMPP). The obtained monoliths possessed high thermal and chemical stabilities. Besides, they all exhibited high column efficiencies and excellent separation abilities in capillary liquid chromatography (cLC). The highest column efficiency could reach ca. 195,000 N/m for butylbenzene on the monolith prepared with POSS-MA and TPTM (monolith POSS-TPTM) in reversed-phase (RP) mode at 0.64 mm/s. Good chromatographic performance were all achieved in the separations of polycyclic aromatic hydrocarbons (PAHs), phenols, anilines, EPA 610 as well as bovine serum albumin (BSA) digest. The high column efficiencies in the range of 51,400–117,000 N/m (achieved on the monolith POSS-PTM in RP mode) convincingly demonstrated the high separation abilities of these thiol-methacrylate based hybrid monoliths. All the results demonstrated the feasibility of the phosphines catalyzed thiol-methacrylate Michael addition click reaction in fabrication of monolithic columns with high efficiency for cLC applications.

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1. Introduction

Monolithic columns have been widely applied in microscale and nanoscale chromatographic separation as well as sample pretreatment arena [1–7]. As a typical and novel state-of-the-art format, the organic-silica hybrid monoliths, somewhat combining merits of both organic and silica monoliths, such as high permeability, pH tolerance and mechanical strength, have proved to overcome some of the inherent drawbacks of other two types of monoliths, such as the solvent instability of the organic polymeric monoliths and the pH sensitivity of the inorganic silica-based monoliths [8,9]. So far, the organic-silica hybrid monoliths have held an impressively strong position in all chromatographic methods, not

only for separation fields such as capillary liquid chromatography (cLC) and capillary electrochromatography (CEC) *etc.* [4,10,11], but also as the basis for enzyme immobilization [12], or for sample preparation such as solid-phase extraction (SPE) or solid-phase micro-extraction (SPME) [13], *etc.* However, the preparation approaches of hybrid monoliths currently are mainly based on the tedious and condition-sensitive sol-gel process, which greatly encumber their development and applications. Thus, it is still a matter of great concern to develop more facile and easier methods for the fabrication of hybrid monoliths.

The polyhedral oligomeric silsesquioxane (POSS) reagents have been successfully used to replace traditional alkoxy silanes for the preparation of hybrid monoliths via free radical polymerization, in which the preparation procedures were simplified as easy as those of common polymeric monoliths [14–16]. However, the relatively low column efficiencies of those hybrid monoliths (the highest one still below 50,000 N/m in capillary liquid chromatography (cLC)) [14–16] made it still a great challenge to achieve high performance

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chromatographic separation. In order to address the challenge, ring-opening polymerization has been adopted to facilitate fabricate hybrid monoliths by using octaglycidyl dimethylsilyl POSS (POSS-epoxy) and diamines [17,18]. Such POSS-epoxy-diamine hybrid monoliths possessed well-defined 3D skeleton, and exhibited high column efficiency (highest *ca.* 140,000 N/m) in cLC. The success of epoxy-amine ring-opening polymerization in the preparation of hybrid monoliths greatly inspired us that introducing new chemistry to replace the traditional free radical polymerization may possibly translate the various methacrylate monomers into monoliths with high column efficiency.

Due to the high yields and simple reaction conditions, “click” chemistry, such as Cu(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition reaction (CuAAC) and thiol-click reaction, has been highlighted and widely applied in new compounds synthesis, polymer preparation, surface modification, hydrogel formation and so on [19–25]. Particularly, click chemistry has become a very useful and popular tool to modify both particle beads and monolithic matrix for the preparation of novel LC stationary phases [26–33]. However, so far, there are very few reports on the direct construction of macroporous monoliths *via* click chemistry. More recently, Nischang and coworkers have synthesized several hybrid monolithic materials from vinyl-containing POSS and five multi-thiols *via* radical-mediated thiol-ene click chemistry [34]. However, such a radical-mediated thiol-vinyl reaction could not be applied for preparation of monoliths using methacrylate-containing reagents, as the methacrylate groups exhibit low reactivity with thiols in radical-mediated system, in which a serious self-polymerization of methacrylate is preferred [35].

In this study, a facile approach for direct construction of a series of macroporous hybrid monoliths was firstly developed by using the multi-methacrylate POSS and multi-thiols as precursor *via* phosphines catalyzed thiol-methacrylate Michael addition click reaction. Three hybrid monoliths were conveniently synthesized by slightly adjusting the feed recipes. Systematical characterization of the monoliths, such as SEM and FT-IR, *etc.* were performed. Comprehensively chromatographic assessments and applications of these monoliths were also carried out by cLC separation of polycyclic aromatic hydrocarbons (PAHs), phenols, anilines, EPA 610 and bovine serum albumin (BSA) digest.

2. Materials and methods

2.1. Chemicals and reagents

Methacrylate-polyhedral oligomeric silsesquioxane (POSS) (cage mixture, $n=8, 10, 12$, POSS-MA), trimethylolpropane tris(3-mercaptopropionate) (TPTM), pentaerythritol tetrakis(3-mercaptopropionate) (PTM), stearyl methacrylate (SMA), 3-methacryloxypropyltrimethoxysilane (γ -MAPS) and poly(ethylene glycol) (PEG, $M_n=200$) were purchased from Aldrich (Milwaukee, WI, USA). 1,6-Hexanedithiol (HDT), dimethylphenylphosphine (DMPP) and potassium hydroxide (KOH) were obtained from J&K Scientific (Beijing, China). 1,2-Epoxyoctadecane (C18-epoxy) was supplied by Alfa Aesar (Ward Hill, MA, USA). Trypsin was purchased from Promega (Madison, WI, USA). Bovine serum albumin (BSA), EPA 610, thiourea, alkylbenzenes and other standard compounds were supplied by Sigma (St. Louis, MO, USA). Dithiothreitol (DTT) and iodoacetamide (IAA) were products of Sino-American Biotechnology Corporation (Beijing, China). The fused-silica capillaries with dimensions of 50, 75 and 200 μm i.d. and 365 μm o.d. were obtained from Refine Chromatography Ltd. (Yongnian, Hebei, China). C18-particles (5 μm , 120 Å pore) were purchased from DAISO (Osaka, Japan). HPLC-grade acetonitrile (ACN) was used for preparation of mobile phases. The water used in all

experiments was doubly distilled and purified by a Milli-Q system (Millipore Inc., Milford, MA, USA). Methanol, *n*-propanol, NaOH, HCl and other chemical reagents were all of analytical grade.

2.2. Pretreatment of fused-silica capillary

Before the preparation of monolithic columns, the inner wall of fused-silica capillary was activated. First, the capillary was rinsed by 1.0 mol/L NaOH for 4 h, water for 30 min, 1.0 mol/L HCl for 14 h, and water for another 30 min, successively, and then dried by a nitrogen stream at room temperature. After that, to modify the capillary inner wall with double bonds, the capillary was filled with a mixture of γ -MAPS/methanol (50%, v/v), sealed with rubbers at both ends and submerged in water bath at 50 °C for 12 h. Finally, the capillary was rinsed with methanol and flush out the residual reagents, and dried again with a stream of nitrogen gas.

2.3. Preparation of hybrid monoliths *via* thiol-methacrylate click chemistry

The prepolymerization solutions were prepared by mixing POSS-MA, a multi-thiol (HDT or TPTM or PTM), porogenic solvents (*n*-propanol and PEG 200) and catalyst (DMPP) with appropriate feed recipes, as listed in Table 1 and Table S1 (SI). After 5 min of sonication at 0 °C for mixing and degassing, the prepolymerization mixtures were injected into the modified capillaries with a syringe. The filled capillaries were then sealed with rubber stoppers and reacted in water baths at appropriate temperature for 2 h. After that, the capillaries were flushed with methanol to remove the unreacted residual. For the preparation of bulk monolithic materials, the polymerization reaction was taken place in centrifuge tubes. The centrifuge tubes filled with the prepolymerization mixtures were placed in water baths under appropriate temperature for 2 h. After polymerization, the bulk monoliths were cut into smaller pieces, extracted with ethanol overnight in a Soxhlet apparatus and dried in a vacuum.

2.4. Post-modification of hybrid monolithic column

To modify the hybrid monolithic column, a *n*-propanol solution containing 0.1 mol/L C18-epoxy and 0.01 mol/L KOH was pumped through the column at room temperature overnight. Then the modified column was washed with ethanol to remove the unreacted residual.

2.5. Capillary liquid chromatography

The chromatographic evaluation of monolithic columns was performed on a LC system equipped with an Agilent 1100 (Hewlett-Packard) micropump, a UV detector (K-2501, Knauer, Germany) and a 7725i injector with a 20 μL sample loop. In order to avoid the sample overloading, the partial injection was adopted in this study. Data was collected at 214 nm or 254 nm, and processed by a chromatography workstation (Beijing Cailu Scientific Instrument Ltd., Beijing, China). A T-union connector served as a splitter with one end connected to the capillary monolithic column and the other end to a blank capillary (95-cm long, 50 μm i.d. and 365 μm o.d.). The outlet of the monolithic columns was connected with a Teflon tube to an empty fused-silica capillary (75 μm i.d. and 365 μm o.d.). A detection window was made by removing a 2 mm length of the polyimide coating in a position of 5.5 cm from the separation monolithic column outlet.

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