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Fast preparation of hybrid monolithic columns via photo-initiated thiol-yne polymerization for capillary liquid chromatography

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ABSTRACT

Although several approaches have been developed to fabricate hybrid monoliths, it would still take a few hours to finish the formation of monoliths. Herein, photo-initiated thiol-yne polymerization was first adopted to *in situ* fabricate hybrid monoliths within the confines of UV-transparent fused-silica capillary. A silicon-containing diyne (1,3-diethynyltetramethyl-disiloxane, DYDS) was copolymerized with three multithiols, 1,6-hexanedithiol, trimethylolpropane tris(3-mercaptopropionate) and pentaerythriol tetrakis(3-mercaptopropionate), by using a binary porogenic system of diethylene glycol diethyl ether (DEGDE)/poly(ethylene glycol) (PEG200) within 10 min. Several characterizations of three hybrid monoliths (assigned as I, II and III, respectively) were performed. The results showed that these hybrid monoliths possessed bicontinuous porous structure, which was remarkably different from that via typical free-radical polymerization. The highest column efficiency of 76,000 plates per meter for butylbenzene was obtained on the column I in reversed-phase liquid chromatography (RPLC). It was observed that the efficiencies for strong-retained butylbenzene were almost close to those of weak-retained benzene, indicating a retention-independent efficient performance of small molecules on hybrid column I. The surface area of this hybrid monolith was very small in the dry state (less than 10.0 m^2/g), and the chromatographic behavior of hybrid monolithic columns would be possibly explained by radical-mediated step-growth process of thiol-yne polymerization. Finally, the column I was applied for separation of BSA tryptic digest by cLC–MS/MS, indicating satisfactory separation ability for complicated samples.

1. Introduction

Monolithic materials have attracted considerable attentions for the separations of small molecules and macromolecules as stationary phases in capillary liquid chromatography (cLC) [1–6]. According to the nature of materials, monolithic columns were mainly categorized into three types: inorganic silica-based, organic polymer-based and organic-silica hybrid monolithic columns, which exhibited different properties and column efficiency [7]. Inorganic silica-based monoliths had a bicontinuous skeleton structure providing a rigid inorganic skeleton and a plethora of mesopores with relatively high surface area, which was likely responsible for their enhanced chromatographic efficiencies of small molecules in the isocratic mode. However, silica-based monoliths generally showed lower stability at pH > 8.5, which might impair their separation abilities for polar compounds, especially for basic ones. Organic monoliths had relatively low surface area, leading to lower efficiencies of small molecules. Particularly, the swelling behavior of organic monoliths in several organic solvents would be detrimental to their pore structure and mechanical stability [8–10]. To balance these limitations, organic-inorganic hybrid monolithic materials emerged, which somewhat inherited the merits of both silica materials and organic materials including low shrinkage, satisfactory mechanical stability, controlling porous structure easily and so on [11,12]. As a result, hybrid monoliths were also applied for chromatographic analysis [13,14] and sample pretreament [15,16].

Several approaches have been developed to fabricate hybrid monoliths. Sol-gel chemistry was a common route by using commercial alkyltrialkoxysilanes, limiting the category and selectivity

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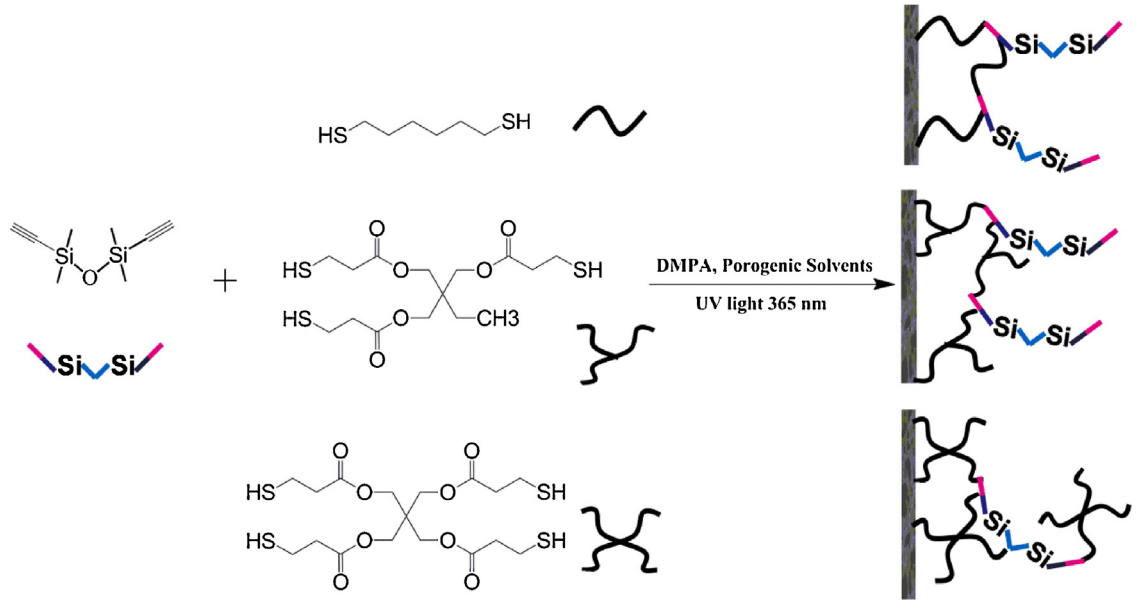

Fig. 1. Synthetic route diagram of porous hybrid monoliths via thiol-yne polymerization.

of hybrid monoliths to satisfy the requirement of several chromatographic modes [17]. As an alternative to sol-gel chemistry, a "one-pot" approach emerged in 2009, in which the monoliths were also formed via a sol-gel process, and various organic monomers could be simultaneously grafted onto the surface of monoliths via free radical polymerization [18–20]. It would take a longer time to optimize the preparation conditions once the organic monomer was changed. In 2008, Bonn's group [21] pioneered the preparation of an organic-silica based monolithic column via thermally initiated free radical polymerization, in which silicon was incorporated into polymeric monolith. Zou's group also adopted polyhedral oligomeric silsesquioxanes (POSS) monomers to prepare hybrid monolithic columns via free radical polymerization [19,22,23] and ring-opening polymerization [24]. Although the fabrication process of these hybrid monoliths was as easy as organic monoliths, it would take a few hours to finish these polymerization reactions.

As a kind of click chemistry, thiol-ene reaction has been adopted for preparation or modification of monolithic materials [23,25–27]. For the first time Nischang and co-workers have prepared monolithic materials [28] and hybrid monolithic columns [29] via thiol-ene polymerization reaction using vinylPOSS and multifunctional thiols. Recently, thiol-yne polymerization was adopted to fast prepare organic monolithic columns in the UV-transparent fused-silica capillary by using 1,7-octadiyne and a dithiol/tetrathiol monomer [30], exhibiting the minimum plate heights of 9.5–11.0 μm for alkylbenzenes in reversed-phase liquid chromatography (RPLC). All of these opened an avenue to prepare novel hybrid monolithic columns via thiol-yne polymerization.

Herein, 1,3-diethynyltetramethyl-disiloxane (DYDS) was first selected as the precursor to react with three types of multithiol monomers (1,6-hexanedithiol, 2SH; trimethylolpropane tris (3-mercaptopropionate), 3SH and pentaerythriol tetrakis (3-mercaptopropionate), 4SH) via photo-initiated thiol-yne polymerization reaction for fabrication of hybrid monolithic columns (Fig. 1). All reactions could be completed within 10 min. The resulting three kinds of hybrid monolithic materials were characterized and further applied for separations of small molecules and tryptic digest of bovine serum albumin (BSA) in RPLC.

2. Experimental

2.1. Chemicals and materials

DYDS was purchased from Meryer Co. Ltd. (Shanghai, China). Vinyltrimethoxysilane (VTMS) and 1,6-hexanedithiol (2SH) were from J&K Scientific Ltd. (Beijing, China). Diethylene glycol diethyl

Table 1
Typital composition of prepolymerization solution and permeability of monolithic columns.

Column	DYDS(g/mL)	Thiol (g/mL)	DEGDE/PEG200 (v/v)	Monomer/porogen (v/v)	Permeability ($\times 10^{-14}$ m^2)
I-1	0.0872	2SH(0.1439)	79/21	1/4	14.6
I-2	0.0872	2SH(0.1439)	81/19	1/4	1.09
I-3	0.0872	2SH(0.1439)	84/16	1/4	–
I-4	0.0774	2SH(0.1277)	81/19	1/4.5	1.73
II-5	0.0996	2SH(0.1644)	81/19	1/3.5	–
II-1	0.0588	3SH(0.1743)	54/46	1/4	6.97
II-2	0.0588	3SH(0.1743)	53/47	1/4	9.30
II-3	0.0588	3SH(0.1743)	51/49	1/4	21.5
II-4	0.0528	3SH(0.1566)	53/47	1/4.5	12.3
II-5	0.0678	3SH(0.2011)	53/47	1/3.5	4.57
III-1	0.0630	4SH(0.1717)	51/49	1/4	–
III-2	0.0630	4SH(0.1717)	49/51	1/4	0.91
III-3	0.0630	4SH(0.1717)	39/61	1/4	3.04
III-4	0.0602	4SH(0.1641)	49/51	1/4.5	1.72
III-5	0.0517	4SH(0.1410)	49/51	1/4.9	3.22

All prepolymerization solutions contained 1.0% DMPA with respect to DYDS (mol%).

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