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A hybrid fluorous monolithic capillary column with integrated nanoelectrospray ionization emitter for determination of perfluoroalkyl acids by nano-liquid chromatography–nanoelectrospray ionization-mass spectrometry/mass spectrometry

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ABSTRACT

A hybrid fluorous monolithic column was simply prepared via photo-initiated free radical polymerization of an acylopropyl polyhedral oligomeric silsesquioxane (acryl-POSS) and a perfluorous monomer (2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acrylate) in UV-transparent fused-silica capillaries within 5 min. The physical characterization of hybrid fluorous monolith, including scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, mercury intrusion porosimetry (MIP) and nitrogen adsorption/desorption measurement was performed. Chromatographic performance was also evaluated by capillary liquid chromatography (cLC). Due to the fluorous–fluorous interaction between fluorous monolith and analytes, fluorobenzenes could well be separated, and the column efficiencies reached 86,600–92,500 plates/m at the velocity of 0.87 mm/s for alkylbenzenes and 51,900–76,000 plates/m at the velocity of 1.10 mm/s for fluorobenzenes. Meanwhile, an approach to integrate nanoelectrospray ionization (ESI) emitter with hybrid fluorous monolithic column was developed for quantitative determination of perfluoroalkyl acids by nanoHPLC–ESI-MS/MS. The integration design could minimize extracolumn volume, thus excluding undesirable peak broadening and improving separation performance.

1. Introduction

In the past several decades, high-performance liquid chromatography (HPLC) has become one of the most often-used analysis techniques and covered nearly every chemical application, including quality control of drugs, pharmacokinetic studies, and determination of pollutants or food additives [1,2]. The nanoHPLC has been an attractively alternative for analysis of complex samples because of its speed, ease of automation, and compatibility with mass spectrometry (MS), which requires lower amounts of mobile phases and samples to accomplish detection and achieves lower detection limits and higher mass sensitivities with nanoHPLC/MS [3]. As hearts of nanoHPLC, the columns for nanoHPLC were usually fabricated by packing particulate beads with a controlled range of diameters and pore size. High separation efficiency could be obtained by using particles with smaller diameters. However, the permeability of particulate packed columns is not outstandingly high [4], reaching 2.1×10^{-14} m^2 (column dimension, 75 mm × 2.1 mm, and particle 5 μm), particularly, their preparation is relatively tedious and time-consuming.

Since 1990s, monolithic columns have gained great attention on the separation of small molecules and biomacromolecules. Although organic monolithic columns exhibited several advantages, such as ease of preparation, good biocompatibility and

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varieties of functionality [5–7], the shrinking or swelling in organic solvents could lead to the change of pore structure and lowering the separation efficiency for small molecules [8–10]. Silica monoliths provided good mechanical stability, permeability and high column efficiency for fast separation of small molecules [11]. Unfortunately, the tedious fabrication procedures were the inherent drawbacks for silica monoliths [12,13]. Hybrid monoliths were supposed to combine some merits of organic monoliths and silica monoliths, such as easy preparation, wide pH tolerance, good mechanical and high permeability [14]. Especially, the incorporation of polyhedral oligomeric silsesquioxanes (POSS) into polymeric networks could result in significant improvement of physical and mechanical properties. Many works have adopted several POSS monomers to prepare various hybrid monoliths [14–19], which exhibited good physical properties such as good mechanical stability, good pH stability and high thermos stability, and satisfactory column efficiencies for small molecules in different chromatographic modes.

Monolithic column connecting with a replaceable emitter could directly interface with nanoelectrospray ionization (ESI)-MS [20–22]. Although this method was convenient and flexible, the employment of a zero-dead-volume union to connect a monolithic column with a tapered ESI emitter could still lead to the increase of extracolumn volume and decrease of separation efficiency. Several attempts aimed at decreasing the dead volume. Xie et al. [23] firstly introduced a design for constructing an integrated ESI emitter on silica monolithic column, which could minimize the extracolumn volume without a union and provide high separation column efficiency and peak capacity in proteome analysis. However, this technique was not applied for detecting small molecules by nanoLC–ESI-MS/MS.

Due to their properties such as hepatoxicity, developmental toxicity, immunotoxicity, carcinogenic potency, extremely resistant to degradation, bioaccumulate in food chains, perfluorinated alkylated substances (PFAS) have received much attention to their effects on environment and human health in recent years [24–29]. However, the obvious low levels at which PFAS are found in samples (water in river, sea etc.), and the quantitative determination of PFAS is a vexed question. Fluorous stationary phase as an alternative stationary phase has been applied for separating fluorous compounds due to the specific fluorous–fluorous interaction between stationary phase and analytes [30–32]. The polarizability is a popular opinion at least as part of the explanation fluorous–fluorous interaction. The fluorous stationary exhibited poorly polarizable and interacted with fluorous compounds that are rich in fluorine, which also had low polarizabilities as indicated by low refractive indices. This kind of affinity interaction was just like the "like-dissolves-like" interaction, which caused the desired selectivity [32,33]. Although there are a few reports on the preparation of fluorous monolithic columns, which were successfully used to separate fluorochemicals, the column efficiencies for fluorous compounds were low in cLC [31,32,34,35]. Meanwhile, fluorous monolithic columns connected nanoHPLC–ESI-MS/MS for quantitative determination of PFAS were not reported.

Following our recent success with the preparation of POSS-based hybrid monolith via "one-pot" approach [14,16,17], herein, a hybrid fluorous monolith was prepared via photo-initiated free radical polymerization with acrylopropyl-POSS (acryl-POSS) as crosslinker and 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acrylate (DFHA) as fluorous functional monomer. Systematic physical characterization and chromatographic evaluation of hybrid fluorous monolith were performed. Finally, the fluorous column integrated a nano-ESI emitter was applied for the quantitative determination of perfluoroalkyl acids by nanoLC–ESI-MS/MS.

2. Experimental

2.1. Chemicals and materials

The monomer of acryl-POSS cage mixture (molecular weight: 1321.75, and cage content ≥90%) is hybrid molecule with an inorganic silsequioxane at the core and organic acrylopropyl groups attached at the corners (the number of corners is 8, 10 or 12) of the cage, which was obtained from Hybrid Plastics, Inc. (Hattiesburg, MS, USA). Fluorous functional monomer (DFHA, ≥95%), lauryl methacrylate (LMA, contains 500 ppm MEHQ as inhibitor, technical grade), 3-(trimethoxysilyl) propyl methacrylate (γ-MAPS, ≥98%), fluorobenzene, 1,2-difluorobenzene, 1,2,4-trifluorobenzene, 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, hexafluorobenzene, perfloononanoic acid (PFNA), perfluorodecanoic acid (PFDA), tricosafluorododecanoic acid (PFDoA) and perfluorotetradecanoic acid (PFTeDA) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Undecafluorohexanoic acid (PFHxA) and pentadecafluorotanoic acid (PFOA) were obtained from Aladdin (Shanghai, China). 2,2-Dimethoxy-2-phenylacetopheone (DMPA, 99%) was obtained from Acros Organics (New Jersey, USA), and dissolved in 1-butanol (10%, w/w) prior to use. Thiourea, benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, 1-butanol, ethylene glycol and ammonium acetate were of analytical grade, and obtained from Tianjin Kermel Chemical Plant (Tianjin, China). Deionized water was prepared with a Milli-Q system (Milli-pore, MA, USA). Tetrahydrofuran (THF), methanol and acetonitrile (ACN) were HPLC-grade and acquired from Yuwang Group (Shandong, China). Both polyimide coating of fused-silica capillary with 50 μm i.d. and UV-transparent fused-silica capillary with 75 μm i.d. and 365 μm o.d. were the products of Polymicro Technologies (Phoenix, AZ, USA). The samples from Malan river in Dalian were filtered through a 0.45 μm filter prior to use.

2.2. Preparation of hybrid fluorous monolith

Prior to preparation of hybrid fluorous monolithic column, the inner wall of UV-transparent fused-silica capillary was immobilized a layer of methacrylate groups. Briefly, the capillary was rinsed with 0.1 mol/L NaOH for 1 h, H_2O for 0.5 h, 0.1 mol/L HCl for 4 h, H_2O for 0.5 h and methanol for 0.5 h in sequence. The capillary was then filled with γ-MAPS/methanol (50%, v/v) with a syringe, and then sealed with rubber septa at both ends and submerged in the water bath at 50 °C overnight. Finally, the capillary was rinsed with methanol to flush out the residual reagent and dried under nitrogen flow.

Hybrid fluorous monolith was prepared in the pretreated capillary by in situ polymerization. A polymerization solution consisting of crosslinker (acryl-POSS, 30 mg, 0.022 mol), fluorous functional monomer (DFHA, 26.3 mg, 0.066 mol), initiator (DMPA), and a binary porogenic solvents was thoroughly mixed and degassed by a 5-min ultrasonication. This polymerization solution was immediately introduced into the pretreated capillary, and both ends of the capillary were sealed with silicon septa. After a comparison between the hybrid monolith polymerized for 5 min and 10 min. The experimental results illustrated that retention factors for alkylbenzenes, permeabilities and column efficiency of two hybrid monoliths are familiar. Therefore, the capillary was irradiated by UV radiation (λ = 365 nm, 120 mJ/cm^2) with a short time for 5 min. The obtained hybrid fluorous monolithic column was then flushed with methanol to remove residuals. For the bulk material, the rest of prepolymerization mixture (acryl-POSS, 30 mg and DFHA, 26.3 mg) was placed in the UV-transparent centrifuge tubes and also cured under UV radiation for 5 min. After polymerization, the bulk material was rinsed with ethanol three times, cut into small pieces,