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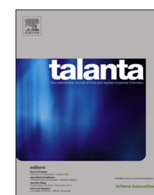

Octadecylamine-modified poly (glycidylmethacrylate-divinylbenzene) stationary phase for HPLC determination of *N*-nitrosamines

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ABSTRACT

Poly (glycidylmethacrylate-divinylbenzene) (Poly (GMA-DVB)) microspheres were prepared by the two-staged swelling and polymerization method, and modified with octadecylamine (ODA) to obtain ODA-poly (GMA-DVB) stationary phase for HPLC. The new material was characterized by scanning electron microscope, nitrogen adsorption-desorption measurement, Fourier transform infrared spectrum, elemental analysis and thermogravimetric analysis. The results showed that poly (GMA-DVB) microspheres had good monodispersity, porosity and ball shapes. The diameters and specific surface area of the microspheres were about 6 μm and 396 $m^2\,g^{-1}$, respectively. ODA-poly (GMA-DVB) stationary phase had good thermal stability. Furthermore, the chromatographic performance of the stationary phase was illustrated by separating n-alkylbenzenes, mono-substituted benzenes and *N*-nitrosamines. Auxiliary quantum chemistry calculation was also carried out to evaluate the interaction mechanism. According to the evaluation, ODA-poly (GMA-DVB) stationary phase exhibited good hydrophobicity and hydrophobic selectivity, strong stereo-selectivity, polar interaction and π-π interaction. The multi-interaction mechanisms could very likely guarantee its excellent chromatographic performance for the analysis of complex samples. Finally, the column was successfully applied in the determination of *N*-nitrosamines in pickles sample.

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1. Introduction

Organic polymer microsphere is an important kind of supporting material for high-performance liquid chromatographic stationary phase, which mainly includes poly (styrene-divinylbenzene) (PS-DVB), poly (acrylates) and poly (methacrylates). PS-DVB microspheres have been successfully applied in high-performance liquid chromatographic stationary phase, while the derivatization of PS-DVB is complex and difficult which greatly restrains its further applications. In contrast to PS-DVB resins, poly (acrylates)- and poly (methacrylates)-based supports offer a straightforward access to prepare the stationary phases by simple reaction procedures [1–5]. In recent years, glycidylmethacrylate (GMA) has caused researchers' attention as it owns epoxy group which can be readily modified via various chemical reactions to introduce different functional groups under mild reaction conditions, such as amines, anhydrides and polyamides. Poly (glycidylmethacrylate-ethylenedimethacrylate) (Poly (GMA-EDMA)) beads have been applied to the preparation of stationary phase as supports; the epoxy groups act as the reaction sites to introduce the functional groups [6–9]. GMA can also be copolymerized with divinylbenzene (DVB) to produce poly (GMA-DVB) microspheres for different purposes by diverse methods. Zhou et al. [10] synthesized poly (GMA-DVB) particles of about 50 μm by the surfactant reverse micelles swelling method and investigated the formation mechanism of the microspheres. Zhang et al. [11] prepared mono-dispersed poly (GMA-DVB) microspheres with a mean particle diameter of 3 μm by one-step disperse polymerization process, which were applied in the capillary electrochromatography. Jin et al. [12] prepared the core/shell poly (GMA-DVB) microspheres of 1.5–2.5 μm in the precipitation polymerization and investigated the formation mechanism of the beads. To the best of our knowledge, poly (GMA-DVB)

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microspheres of about 6 μm prepared by the two-staged swelling and polymerization method and their applications in HPLC have not been published.

N-nitrosamines can be formed when appropriate amines and nitrile precursors are present, which have been found existing in ground water, cosmetic products, tobacco smoke and curing meat [13,14]. There are about 300 *N*-nitrosamines at present and most of them are classified as carcinogens for animals [15,16]. *N*-nitrosodibutylamine (NDBA), *N*-nitrosopyrrolidine (NPYR) and *N*-nitrosopiperidine (NPIP) have been listed as possibly carcinogenic substances by International Agency for Research on Cancer (IARC). *N*-nitrosodimethylamine (NDMA) and *N*-nitrosodiethylamine (NDEA) are listed as the most-likely carcinogenic substances [17]. In general, *N*-nitrosamines are defined as either volatile ones or non-volatile ones. Gas chromatography tandem mass spectrometry (GC/MS) has been usually applied to analysis of volatile *N*-nitrosamines in the literature. High performance liquid chromatography tandem mass spectrometry (HPLC/MS) could be used for the detection of both volatile and non-volatile *N*-nitrosamines, which has a bigger scope of application than GC-based method. The determination of *N*-nitrosamines by HPLC is of great analytical importance and a lot of researches have been performed by HPLC/MS [18–24]. Therefore, finding a column suitable for the separation of *N*-nitrosamines is essential as the chromatographic column plays a vital role in the HPLC-based system.

In this work, poly (GMA-DVB) microspheres with diameters of about 6 μm were prepared by the two-staged swelling and polymerization method. Meanwhile, octadecylamine (ODA) was introduced onto the surface of poly (GMA-DVB) microspheres due to its excellent hydrophobicity of the long alkyl chain and good reactivity of nitrogen atom [25,26]. The ODA-modified poly (GMA-DVB) (ODA-poly (GMA-DVB)) stationary phase was obtained and applied to the HPLC. The structure characteristics of the microspheres and chromatographic properties of the stationary phase were investigated, respectively. Finally, ODA-poly (GMA-DVB) column was applied in the determination of *N*-nitrosamines in pickles sample.

2. Experimental

2.1. Apparatus and instruments

All chromatographic tests were carried out by an Ultimate 3000 HPLC system (Thermo Fisher, Agawam, USA) including a pump (LPG-3400), an autosampler (WPS-3000TSL), a thermostat column compartment (TCC-3000), a variable-wavelength UV detector (VWD-3400) and an ODS (Dionex, Aclaim® 120 C_{18}, 4.6 × 250 mm). The eluent flow rate was generally 1.0 mL min^{-1} and the system temperature of all chromatographic tests was set at 30 °C. Data were collected with Chromeleon 6.80 chromatogram workstation (Thermo Fisher, Agawam, USA). The JY92-Π ultrasonic disrupter (Scientz Biotechnology Co. Ltd., Ningbo, China) was employed to emulsify organic compounds. Fourier transform infrared (FT-IR) spectrum was achieved by a Spectrum 100 spectrometer (PerkinElmer, Massachusetts, USA). Elemental analysis (EA) was performed with a Flash EA 1112 elemental analyzer (Thermo Fisher, Agawam, USA). The scanning electron microscopy (SEM) images were obtained using a HITACHI S-4700 field emission SEM (Hitachi, Tokyo, Japan). The surface characteristics were measured on a surface area and porosity analyzer ASAP 2020 HD88 (Micromeritics, Atlanta, Georgia, USA). Thermogravimetric analysis (TGA) was carried out on DSCQ1000 differential scanning calorimetry (TA, New Castle, Delaware, USA). The column was packed by pneumatic-pump K-1900 (Knauer, Berlin, German). A water purification system of Millipore Simplicity (Millipore, Agawam, USA) was used to purify the water for all eluents.

2.2. Reagents

Styrene (ST) (99+%, Lingfeng Chemical Reagent Co., Ltd., Shanghai, China), DVB (55+%, Zhengguang Chemical Plant, Hangzhou, China) and GMA (97+%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) were used after washing with 10% (w/v) sodium hydroxide aqueous solution. Azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Co., Ltd., China) and benzyl peroxide (BPO) (99+%, Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) were recrystallized before use. Polyvinylpyrrolidone (PVP, K-30), dibutyl phthalate (DBP), polyvinyl alcohol (PVA, 1750 ± 50), sodium dodecylsulfonate (SDS) and toluene were purchased from Huipu Chemical Reagent Co., Ltd. (Hangzhou, China). ODA was bought from Aladdin Industrial Co. (Shanghai, China). *N*-nitrosamines were supplied by Sigma-Aldrich (Poole, UK). Pickles sample was purchased from the local market (Hangzhou, China). All reagents employed for the synthesis were of analytical grade.

2.3. Preparation of chromatographic stationary phase

Mono-dispersed and highly cross-linked poly (GMA-DVB) microspheres were prepared by the two-staged swelling and polymerization method. Then, the microspheres were modified with ODA to obtain ODA-poly (GMA-DVB) stationary phase (Fig. 1).

2.3.1. Preparation of polystyrene seeds

Mono-dispersed polystyrene seed microspheres were prepared by dispersion polymerization method [27]. The typical procedure was as follow: the reaction was conducted in a 250 mL four-neck round bottom flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel in a temperature-controlled water bath at 70.0 °C. Firstly, 0.3 g PVP and 100 mL mixture of ethanol and water (95:5, v/v) were added to the flask, and then a blend of 0.7 g AIBN and 20 mL styrene was added dropwise within 30 min under the protection of nitrogen. The mixture was stirred at the rotational speed of 250 rpm for 24 h. The beads were collected by suction filtration and washed with excess water, and then the microspheres were stored in 30 mL 1% SDS (m/v) aqueous solution.

2.3.2. Preparation of poly (GMA-DVB) microspheres

The mono-dispersed and highly cross-linked poly (GMA-DVB) microspheres were prepared by the two-staged swelling and polymerization method. First-step swelling: a blend of 2.0 mL polymer seeds solution and 15 mL SDS aqueous solution (0.2%, w/v) was placed into a 500 mL four neck flask. Then, an emulsified solution containing 4.0 g DBP, 30 mL SDS aqueous solution (0.2%, w/v) was added and stirred at the rotational speed of 120 rpm for 24 h. Second-step swelling: another emulsified mixture comprised 30 g organic compounds and 250 mL PVA aqueous solution (1%, w/v) was prepared by an ultrasonic disrupter and poured into the flask for swelling. The above organic compounds consisted of GMA, DVB, toluene, BPO and SDS. The amount of toluene was equal to the sum of GMA and DVB, while BPO was only 1.5% of the sum (w/w). The amount of SDS was 0.25% of the PVA aqueous solution (w/v). Polymerization: after 24 h of swelling, the temperature of water bath was increased to 70 °C under nitrogen atmosphere and lasted for 24 h. Subsequently, the resulting microspheres were washed successively with hot water and alcohol. The crude products obtained were purified by soxhlet extraction with toluene for 48 h and then washed with water and absolute ethyl alcohol followed by drying under vacuum at 60 °C for 24 h.

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