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Chromatographic selectivity of poly(alkyl methacrylate-*co*-divinylbenzene) monolithic columns for polar aromatic compounds by pressure-driven capillary liquid chromatography

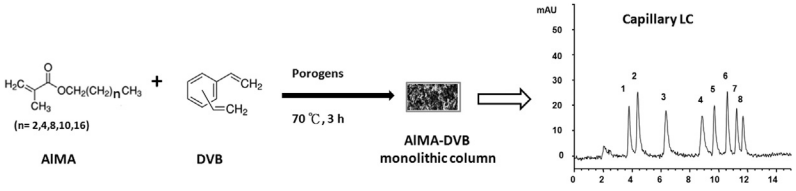
Shu-Ling Lin, Chih-Chieh Wang, Ming-Ren Fuh*

Department of Chemistry, Soochow University, 70 Linhsi Road, Shihlin, 11102, Taipei, Taiwan

HIGHLIGHTS

- First investigation on chromatographic selectivity of AlMA-DVB monolithic columns.
- Good run-to-run/column-to-column repeatability (<3%) on AlMA-DVB monolithic columns.
- Efficient separation of phenylurea herbicides and sulfonamides on AlMA-DVB columns.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, divinylbenzene (DVB) was used as the cross-linker to prepare alkyl methacrylate (AlMA) monoliths for incorporating π-π interactions between the aromatic analytes and AlMA-DVB monolithic stationary phases in capillary LC analysis. Various AlMA/DVB ratios were investigated to prepare a series of 30% AlMA-DVB monolithic stationary phases in fused-silica capillaries (250-μm i.d.). The physical properties (such as porosity, permeability, and column efficiency) of the synthesized AlMA-DVB monolithic columns were investigated for characterization. Isocratic elution of phenol derivatives was first employed to evaluate the suitability of the prepared AlMA-DVB columns for small molecule separation. The run-to-run (0.16–1.20%, RSD; n = 3) and column-to-column (0.26–2.95%, RSD; n = 3) repeatabilities on retention times were also examined using the selected AlMA-DVB monolithic columns. The π-π interactions between the aromatic ring and the DVB-based stationary phase offered better recognition on polar analytes with aromatic moieties, which resulted in better separation resolution of aromatic analytes on the AlMA-DVB monolithic columns. In order to demonstrate the capability of potential environmental and/or food safety applications, eight phenylurea herbicides with single benzene ring and seven sulfonamide antibiotics with polyaromatic moieties were analyzed using the selected AlMA-DVB monolithic columns.

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1. Introduction

Numerous polymer-based monolithic stationary phases have been developed and applied in different types of chromatographic separations including reversed-phase capillary liquid chromatography (LC) [1–6], hydrophilic interaction chromatography (HILIC) [7,8], capillary electrochromatography (CEC) [9–11], and ion-exchange chromatography [12–14]. In previous studies, various polymer-based monolithic stationary phases have been developed for separation of large biomolecules [3,4,15–17] and/or small molecules [18–22]. Moreover, the polymer-based monoliths have also served as extraction sorbents for sample pre-treatment in

* Corresponding author.
E-mail address: msfuh@scu.edu.tw (M.-R. Fuh).

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various environmental and bioanalytical applications [23–27].

For monolith polymerization, functional monomer(s) and cross-linker(s) were two important parameters to control the surface chemistry of monolith for desired separation mechanism as well as the separation selectivity. A number of investigations have been conducted by different research groups to alter the properties of polymeric monoliths [1,14,17,22,28–30]. Aydoğan [14] reported a mixed-mode (anion-exchange/hydrophobic) monolithic stationary phase for separating organic small molecules and inorganic anions by nano LC. The author utilized 3-chloro-2-hydroxypropylmethacrylate (HPMA-Cl) as the functional monomer and ethylene dimethacrylate (EDMA) as the cross-linker for monolith polymerization. HPMA-Cl contains a reactive Cl group for chemical modification after polymerization. The resulting HPMA-Cl-*co*-EDMA monolith was then treated with *N*,*N*-methyl-*N*-dodecylamine to form a mixed-mode stationary phase for separating inorganic anions and neutral organic compounds by ion-exchange and hydrophobic interactions, respectively. Lin et al. [22] incorporated methacrylic acid (MAA) with alkyl methacrylates (AlMA) and EDMA for increasing the hydrophilicity of the synthesized EDMA-based monoliths to separate polar small molecules by capillary LC analysis. The selected poly(lauryl methacrylate-*co*-MAA-*co*-EDMA) monolithic column was able to separate five aflatoxins and three amphenicol antibiotics for potential food safety applications by capillary LC. Huang's group [30,31] synthesized a series of AlMA (C_4–C_{18})-divinylbenzene (DVB) monoliths at a fixed AlMA/DVB ratio to provide additional π–π interactions for analyzing aromatic compounds such as benzophenones and sulfonamide antibiotics by CEC. In the reported investigations, the retention and resolution of aromatic analytes were reduced by increasing the chain length of AlMA. This phenomenon could be attributed to the decreased π–π interactions between the analytes and DVB-based monolithic stationary phases.

Many contaminants in environmental and food samples, such as herbicides and veterinary drugs, are relatively polar and have aromatic ring(s) in their molecular structures. In order to efficiently separate these polar aromatic compounds, we had developed 1,6-hexanediol ethoxylate diacrylate (HEDA)-based and MAA-incorporated alkyl methacrylate monolithic columns for analyzing polar aromatic contaminants by introducing additional dipole-dipole interactions or increasing hydrophilic interactions between the analytes and the stationary phases. The recently developed HEDA-based and MAA-incorporated alkyl methacrylate monolithic columns could efficiently separate polar aromatic small molecules such as phenylurea herbicides (PUHs) and/or amphenicol antibiotics for potential environmental and/or food safety applications [32,33]. However, poorer resolution of other polar aromatic analytes such as sulfonamides, a group of commonly used veterinary drugs, was observed using these columns. In this study, we utilized DVB as the cross-linker to prepare AlMA-DVB monoliths for incorporating additional π–π interactions between the aromatic analytes and AlMA-DVB monolithic stationary phases in capillary LC analysis. The enhanced hydrophobic interactions between the analytes and the stationary phases could be achieved by increasing the alkyl chain length in AlMA. Therefore, various chain lengths of AlMA were utilized to prepare AlMA-DVB monoliths. In addition to varying the alkyl chain length, different AlMA/DVB ratios in the precursor solution were applied to prepare 30% AlMA-DVB monoliths in fused-silica capillaries (250-μm i.d.) to investigate the effect of AlMA/DVB ratios on π–π interactions between the analytes and DVB-based monolithic stationary phases. The important properties including porosity, permeability, and column efficiency of synthesized monolithic columns were examined. A mixture of phenol derivatives, with a single aromatic ring and a polar hydroxyl (–OH) group, was first chosen as model compounds to evaluate the suitability of the prepared AlMA-DVB columns for separating polar aromatic molecules by isocratic elution. In order to demonstrate the capability of potential environmental and/or food safety applications, eight PUHs with single benzene ring and seven sulfonamide antibiotics with polyaromatic moieties were analyzed using the selected AlMA-DVB monolithic columns. For comparison, two previously developed LMA-HEDA (12:18) and LMA-MAA-EDMA (7.5:4.5:18) monolithic columns [22,32] were also applied for separation. To our knowledge, this is the first investigation on chromatographic selectivity of AlMA-DVB monolithic columns for separating polar aromatic small molecules by reversed-phase capillary LC.

2. Experimental

2.1. Materials and reagents

Sodium hydroxide (NaOH), hydrochloric acid (HCl), TPM (3-[trimethoxysilyl]propyl methacrylate), AIBN (2,2-Azobis[2-methylproprionitrile]), butyl methacrylate (BMA), hexyl methacrylate (HMA), lauryl methacrylate (LMA), stearyl methacrylate (SMA), divinylbenzene (DVB; 80%), sulfamonomethoxine (SMM), sulfamethazine (SMZ), sulfapyridine (SPD), sulfadimethoxine (SDM), sulfisoxazole (SIA), sulfaphenazole(SPA), sulfaquinoxaline(SQX), thiamphenicol (TAP), florfenicol (FF), 1,4-butanediol, uracil, and formic acid were obtained from Sigma-Aldrich (Steinhelm, Germany). Octyl methacrylate (OMA) was purchased from Polysciences, Inc. (Warrington, PA, USA). Cyclohexanol was obtained from Nacalai Tesque (Kyoto, Japan). Chloramphenicol (CAP) was purchased from Fluka (Steinheim, Germany). Metoxuron, monuron, isoproturon, monolinuron, metobromuron, buturon, linuron, and chlorbromuron were obtained from Riedel-de Haen (Seelze, Germany). Acetonitrile (ACN), 1-propanol, and tetrahydrofuran (THF) were purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). Analytical standards of phenol, 3,5-dimethylphenol (3,5-DMP), 2,3,5-trimethylphenol (2,3,5-TMP), 3,5-dichlorophenol (3,5-DCP), and 2,3,5-trichlorophenol (2,3,5-TCP) were obtained from Supelco (Bellefonte, PA, USA). Reagents and solvents, except for DVB, used in this study were either HPLC or analytical grade. For monolith polymerization, all reagents were used as purchased without further purification process. A Milli-Q Integral 5 water purification system (Millipore, Bedford, MA, USA) was used to provide deionized water. All stock solutions (1000 μg mL^{-1}) were prepared individually in ACN and then stored at −20 °C. A mixture of uracil (10 μg mL^{-1}) and phenol derivatives (10 μg mL^{-1} each, except 30 μg mL^{-1} for 2,3,5-TCP) was prepared in 50% ACN-water solution. A mixture of 7 sulfonamide standards (20 μg mL^{-1} each) was prepared in 10% ACN-water solution. Fused silica capillaries (250-μm i.d., 360-μm o.d.) for accommodating monolithic stationary phases were purchased from Polymicro Technologies (Phoenix, AZ, USA).

2.2. Preparation of polymeric monoliths for capillary LC

Fused silica capillaries were treated by NaOH, HCl, and TPM for silanization on the inner surface prior to monolith polymerization [22]. Table 1 shows various AlMA/DVB ratios in the precursor solution for preparing a series of 30% AlMA (C_4–C_{18})-DVB monolithic stationary phases. The porogenic solvents included 1-propanol (25%, w/w), 1,4-butanediol (15%, w/w), cyclohexanol (20%, w/w), and THF (10%, w/w) for monolith polymerization, where the w/w was relative to the complete mixture for polymerization. 1% AIBN (w/w, relative to the sum of AlMA and DVB) was added to all precursor solutions for initiating monolith polymerization. The resulting solution was first sonicated for 3 min and then transferred

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