



Monolithic column modified with bifunctional ionic liquid and styrene stationary phases for capillary electrochromatography



Zhenkun Mao^{a,b}, Zilin Chen^{a,b,*}

^a Key Laboratory of Combinatorial Biosynthesis and Drug Discovery, Ministry of Education, and Wuhan University School of Pharmaceutical Sciences, Wuhan 430071, China

^b State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Beijing 10080, China

ARTICLE INFO

Article history:

Received 19 September 2016

Received in revised form

12 December 2016

Accepted 12 December 2016

Available online 14 December 2016

Keywords:

Ionic liquid

Styrene

Bifunctional stationary phase

Monolithic column

Capillary electrochromatography

ABSTRACT

A novel monolithic column with ionic liquid and styrene-modified bifunctional group was prepared for capillary electrochromatography (CEC) by in situ copolymerization in a ternary porogenic solvent. Ionic liquid (1-allyl-methylimidazolium chloride, $\text{AlMelm}^+\text{Cl}^-$) and styrene served as the bifunctional monomer, while ethylene dimethacrylate (EDMA) was used as the cross-linker. The monomer of $\text{AlMelm}^+\text{Cl}^-$ was introduced as anion-exchange group, while styrene as hydrophobic and aromatic group; the similar conjugated structure in $\text{AlMelm}^+\text{Cl}^-$ and styrene was beneficial for offering obvious synergistic effect. The bifunctional stationary phase possessed powerful selectivity for the separation of neutral compounds, acidic analytes and phenols. The highest column efficiency was 2.70×10^5 plates m^{-1} (theoretical plates, N) for toluene. A relatively strong electroosmotic flow (EOF) was obtained in a wide range of pH values from 2.0 to 12.0, which could successfully achieve the rapid separation of the analytes within 10 min. The proposed monolithic column was characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR). The results indicated that the resultant monolithic column had good permeability and excellent mechanical stability. Good reproducibility was obtained with relative standard deviations (RSDs) of the retention time in the range of 0.24–0.47% and 0.81–2.17% for run-to-run ($n = 5$) and day-to-day ($n = 5$), while 1.09–2.70% and 0.98–1.70% for column-to-column ($n = 3$) and batch-to-batch ($n = 3$), respectively. The combination of $\text{AlMelm}^+\text{Cl}^-$ and styrene was a promising option in the fabrication of the organic polymer monolithic column.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Capillary electrochromatography (CEC) is micro-scaled separation technology with high efficiency and high selectivity which is the combination of capillary electrophoresis (CE) and high performance liquid chromatography (HPLC) [1]. In the last decades, packed column, open-tubular column and monolithic column have been widely used in CEC. Compared with packed column and open tubular column, monolithic column has advantages of high column efficiency and fritless design [2–4]. Swelling in organic solvents was still a problem [5], however monolithic column has been widely developed because of its superior performance. The stationary phase of monolithic columns was mainly prepared through two approaches, which were post modification and direct copolymerization [6–10]. Post modification not only allowed independent

optimization of porous properties of monolithic columns [11], but also increased the diversity of monomers modified on the surface of monoliths. However, the preparation process was complex and time-consuming. For the direct copolymerization, it was very simple and could reduce the potential influence of subsequent modifications on the properties of monoliths. In CEC, the direct copolymerization has always been well developed.

Ionic liquids (ILs), organic salts with relatively low melting points, consist of large asymmetric organic cations and inorganic or organic anions [12,13]. In the past decades, ILs have been popular and promising materials with unique properties, such as thermal stability, chemical tenability, good solubility and high charged nature [14–16]. Therefore, ILs have been widely applied in separation science acting as the stationary phase of GC [17,18], HPLC [19–21] and CEC [13,22–25]. Especially in CEC, ILs served as functional monomers in monolithic columns has been a prevailing trend. Lin's group [14] prepared an ionic liquid-functional monolithic column by in situ urea-formaldehyde polycondensation for pressurized capillary electrochromatography (pCEC). Wang et al. [26] synthesized a novel IL-monolithic column by thermal free rad-

* Corresponding author at: Key Laboratory of Combinatorial Biosynthesis and Drug Discovery, Ministry of Education, and Wuhan University School of Pharmaceutical Sciences, Wuhan 430071, China.

E-mail address: chenzl@whu.edu.cn (Z. Chen).

ical copolymerization, which successfully achieved the separation of alkylbenzenes in 18 min with the column efficiency of 1.47×10^5 plates m^{-1} . The separation time was a little long and the column efficiency was not too high. However, the mechanical stability of the monolithic column was excellent, making up for the inherent drawback of organic polymer-based monolithic columns.

Over the past decades, many types of reverse or polar monolithic columns were developed [19,27–29]. Recently, mixed-mode monolithic columns, which could combine multiple interactions together, such as cation-exchange interaction, hydrophobicity and hydrophilicity, have been investigated. Huang et al. [11] prepared a boronate-functionalized monolithic column by in situ copolymerization of 4-vinylphenylboronic acid (VPBA) and pentaerythritol triacrylate (PETA) for capillary liquid chromatography (cLC). The proposed monolithic column had powerful selectivity by flexible adjustment of hydrophobic, hydrophilic and cation-exchange interaction. Ionic liquids with different cation alkyl chain lengths had different polarity, and the polar character of ionic liquids increased with the decrease of the cation alkyl chain length [30–32] which demonstrated that ionic liquids had anion-exchange interaction in some extent [22]. Nevertheless, only a few attempts have been made on the preparation of the organic polymer monolithic columns with anion-exchange interaction in CEC. Especially there is a little attention on the study of multi-functional organic polymer monolithic columns using IIs as monomers with anion-exchange interaction.

In this work, we synthesized a novel monolithic column modified with bifunctional stationary phases with monomers $AlMeIm^+Cl^-$, styrene and cross-linker EDMA by a single-step copolymerization in a ternary porogenic solvent consisting of DMF, *n*-propanol and dodecanol. The proposed method is simple and time-saving. Due to the presence of $AlMeIm^+Cl^-$, a strong anodic EOF was obtained and the monolithic column possessed good morphology with high permeability, good homogeneity and excellent mechanical stability. The introduction of styrene greatly improved the column efficiency and separation selectivity. The separation selectivity of the monolithic column was powerful as the presence of hydrophobicity, aromaticity and anion-exchange interactions could successfully result in the separation of neutral, acidic compounds and phenols.

2. Experimental

2.1. Instrumentation

All CEC experiments were carried out on an Agilent 7100 CE system (Waldbronn, Germany) equipped with an auto-sampler, a diode array detector and a temperature controlled column compartment. Data acquisition and handling were controlled by chromatographic workstation (Chemistry Station, USA). A Shimadzu LC-20AD NANO pump (Japan) was used to determine the backpressure of monolithic column. FT-IR spectra were determined on a Thermo Nexus 470 FT-IR system (MA, USA). The morphology micrographs of the monolithic column were obtained on a Carl Zeiss Ultra PlusField Emission scanning electron microscope (FESEM, Carl Zeiss, Germany) at an accelerating voltage of 5.0 kV. A precise mechanical syringe pump (LSP04-1A, Longer Pump Company, Baoding, China) was used to introduce the solution through capillaries.

2.2. Chemicals and materials

Methanol and acetonitrile (ACN) of HPLC grade were purchased from Sigma-Aldrich (Steinheim, Germany). 1-allyl-methylimidazolium chloride ($AlMeIm^+Cl^-$) was obtained from

Shanghai Cheng Jie Chemical Co. LTD. (Shanghai, China). Ethylene glycol dimethacrylate (EDMA) was obtained from Alfa-Aesar (Lancashire, UK). 3-(triethoxysilyl)propyl methacrylate (γ -MAPS), 2,2-Azo-bis(isobutyronitrile) (AIBN) were purchased from Aladdin Reagent Factory (Shanghai, China) and were analytical grade. Styrene, *N,N*-dimethylformamide (DMF), *n*-propanol, dodecanol, sodium phosphate dibasic dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), thiourea, toluene, sodium hydroxide (NaOH), hydrochloric acid (HCl), chlorobenzene, *p*-dichlorobenzene, 1,2,4-trichlorobenzene, phenol, hydroquinone, resorcinol, pyrocatechol, tyrosine, tryptophan, phenylalanine were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water used was purified with a Milli-Q system (MA, USA). Fused silica capillary (100 μm i.d., 365 μm o.d.) was purchased from Ruifeng Chromatographic Devices (Yongnian, Hebei, China). Other reagents used in the experiments were analytical grade and from commercial sources.

2.3. Column pretreatment

Firstly, the fused-silica capillary was preconditioned with 1.0 M NaOH for 2 h, H_2O for 30 min, 1.0 M HCl for 1 h, H_2O for 30 min in sequence. After subsequent flushing with methanol for 20 min, it was dried by nitrogen stream. The preconditioned capillary was then filled with a solution of 50% γ -MAPS in methanol with both ends sealed by a piece of Teflon tubing, kept in a 45 °C water bath overnight to make the inner wall of the capillary vinylized [33]. Finally, the capillary was flushed with methanol to remove the residuals and then dried with a flow of nitrogen for further use.

2.4. Preparation of monolithic capillary column

The polymerization mixture consisting of $AlMeIm^+Cl^-$ (64.3 mg), styrene (30 μL), EDMA (87 μL), AIBN (1.5 wt% with respect to the monomers), and the ternary porogenic solvent of DMF (388 μL), *n*-propanol (123 μL), dodecanol (309 μL), was sonicated for 10 min to degas and form a homogeneous solution. Subsequently, the homogeneous solution was infused into 100 μm i.d. γ -MAPS pretreated capillary of certain length by a manual syringe, and then both ends were sealed with rubbers. The capillary was submerged into a water bath at 60 °C for 3 h. The resultant polymer monolithic capillary column was flushed with methanol for 2 h to remove unreacted monomers and porogenic solvents. A detection window (about 3 mm) was made at the edge of the monolithic continuous bed by burning the outer polyimide coating. Finally, the capillary was cut to a total length of 34 cm with an effective length of 25.5 cm.

2.5. CEC experiment

The mobile phase was prepared by mixing 10 mM $Na_2HPO_4 \cdot 12H_2O$ of different pH values with a certain amount of acetonitrile. The pH values of phosphate buffer (PB) were adjusted to 2.0–12.0 using phosphoric acid solution or sodium hydroxide solution (H_3PO_4 - Na_2HPO_4 for pH 2.0–9.0, Na_2HPO_4 -NaOH for pH 9.0–12.0), and then stored at 4 °C in a refrigerator. Before use, all these solutions were filtered through a 0.22 μm nylon membrane filter (Shanghai Xinya Jinghua Material Factory, Shanghai, China). The monolithic column was first conditioned by mobile phase for 20 min with the mechanical syringe pump, and then equilibrated on the Agilent 7100 CE system at a low voltage –5 kV for 10 min.

Download English Version:

<https://daneshyari.com/en/article/5135852>

Download Persian Version:

<https://daneshyari.com/article/5135852>

[Daneshyari.com](https://daneshyari.com)