



Vinylbenzyl quaternary ammonium-based polymeric monolith with hydrophilic interaction/strong anion exchange mixed-mode for pressurized capillary electrochromatography



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ABSTRACT

A novel polymeric monolith with hydrophilic interaction and strong anion-exchange mixed-mode has been fabricated for pressurized capillary electrochromatography by an in situ copolymerization of vinylbenzyl trimethylammonium chloride (VBTA) and bisphenol A glycerolate dimethacrylate (BisGMA). The optimization of the polymerization mixture composition has been investigated, and column characteristics in terms of mechanical stability, permeability and reproducibility have been studied in detail. Linear responses between back pressure and flow rate have been achieved in different solvents. The absolute value of swelling propensity (SP) factor for poly(VBTA-co-BisGMA) monolith is 0.41, and the degree of permeability drop from pure ACN to water is about 45%. An acceptable mechanical stability of the column is obtained. The suitable reproducibility is also measured with the RSD for day-to-day ($n=3$) of retention time and column efficiency less than 3.3%, and the RSD for batch-to-batch ($n=3$) less than 5.3%, respectively. Under the optimum conditions, the mixed-mode of hydrophilic interaction and strong anion-exchange has been carried out, and efficient electrochromatography profiling of various polar compounds including neutral phenols, negatively charged benzoic acids and positively charged nucleic acid bases and nucleosides are achieved, respectively.

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1. Introduction

Pressurized capillary electrochromatography (pCEC) with hydrophilic interaction (HI) has emerged as an increasingly popular method attributing to its favorable separation capacity to polar compounds with organic-aqueous mobile phases [1–3]. Numerous polymeric monolithic columns have been fabricated for the efficient separations of polar analytes in HI-pCEC [4–6]. Among these columns, polymeric monoliths which possess a mixed mode of hydrophilic interaction/strong anion-exchange (HI-SAX) have been studied and offer an effective approach for the analysis of charged analytes [7–11]. By using HI-SAX monoliths, efficient separations of negatively charged species have been obtained, and the electrostatic adsorption of positively charged compounds on the stationary phase has been effectively restrained [7–11]. Further studies on the functional monoliths with HI-SAX mode for HI-pCEC have attracted increasing attention [7–9].

Cationic polymeric monoliths with the SAX mechanism have been reported by a post-column modification of the pristine monolithic matrix with active groups for functional surface chemistries

[12–14]. The quaternization of tertiary amine on the pristine polymer surface to fabricate a positively charged chromatographic surface has been established in post-polymerization modification [15]. The process needs multiple steps, and the precise quantities of functionalities on the pristine monolith surface might be difficult to be controlled [3,7,8]. With the polymerization of functional monomers with ammonium groups, the direct incorporation of charged ammonium moieties into polymer matrix for the preparation of HI-SAX column is relatively convenient [7,8,16]. By this way, some cationic polymer monoliths for hydrophilic interaction have been reported [7,8,10,16,17]. Lämmerhofer et al. [17] prepared a hydrophilic chiral anion-exchange monolith fabricated with the quinidine-based ligand in one step, which possessed of the chiral recognition ability and generated the anionic EOF. Wang et al. provided a sulfoalkylbetaine-based cationic monolith with HI-SAX mode by a copolymerization of zwitterionic *N,N*-dimethyl-methacryloxyethyl-*N*-(3-sulfopropyl) ammonium betaine (DMMSA), pentaerythritol triacrylate (PETA) and vinylsulfonic acid (VS) [7]. Lin et al. reported a hydrophilic monolith with the SAX mechanism which was prepared by the copolymerization of 2-(methacryloyloxy)ethyltrimethyl ammonium methyl sulfate (META) and pentaerythritol triacrylate (PETA) [8,10]. Satisfying characteristics and chromatographic performances of these stationary phases have been well controlled.

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The mixed-mode of anion exchange/hydrophilic interaction has been applied to negatively charged acids, and electrostatic repulsion/hydrophilic interaction has been also involved for positively charged basic compounds [7,8]. It shed light on the research of HI-SAX monoliths for efficient separation of polar and charged compounds. However, due to the potential intense swelling of polymer monolith in the polar mobile phase, less hydrophilic polymer monoliths with cationic chromatographic surface have been reported [8,9] when compared with those hydrophobic and positively charged polymer monoliths. Further efforts to develop a stable HI-SAX monolith for the efficient profiling of polar analytes in HI-pCEC are desired.

Vinylbenzyl trimethylammonium chloride (VBTA), a versatile functional monomer which possesses quaternary ammonium and vinylbenzyl groups, has been studied attributing to its multiple interactions including electrostatic interaction, π - π conjugation and chromatographic retention [18–20]. In VBTA monomer, ammonium group affording strong electrostatic interaction, and vinylbenzyl group with rigid phenyl framework could be employed to fabricate a stable polymeric structure similar to polystyrene-based monoliths [21] for high mechanical stability, which is favorable to reduce the swelling of polymeric stationary phases in highly polar solutions. With the copolymerization of VBTA, styrene and divinylbenzene monomers, highly hydrophobic polystyrene-based cationic monoliths have been fabricated for a strong anion exchange in reversed-phase mode [20,21]. The negative swelling problem of the monolith could be well avoided, and the strong ion-exchange function was well carried out. Thus, attributing to the versatile functionalities of VBTA, the studies to fabricate a stable quaternary ammonium-functionalized monolith with VBTA monomer to implement strong ion exchange and hydrophilic interaction for polar analytes might be interesting. To date, the studies on quaternary ammonium-functionalized polymeric monoliths prepared with a one-step polymerization for HI-pCEC are still few. Developing a novel VBTA-based monolith with HI-SAX mixed-mode for HI-pCEC would be meaningful.

Here, by using an in situ copolymerization of cationic VBTA monomer and polar cross-linker bisphenol A glycerolate dimethacrylate (BisGMA), the polymeric monolith with highly positively charged groups has been fabricated for HI-pCEC. VBTA monomer possessing quaternary ammonium and vinylbenzyl groups is favorable to provide the highly SAX interaction and stiff mechanical properties. BisGMA acting as the popular cross-linking dimethacrylate for the polymeric compounds, is superior to other dimethacrylates due to its relatively high molecular weight and stiff partial aromatic molecular structure, providing low polymerization shrinkage, low volatility, and outstanding mechanical properties of the polymer [22]. Furthermore, BisGMA contains multiple polar hydroxyl and ester groups, which can enhance the polarity of the target monolith and offer hydrophilic interaction. With the merits mentioned above, poly(VBTA-co-BisGMA) has been studied for HI-pCEC in this work. The optimization of the polymerization mixture composition was investigated, and column characterization in terms of mechanical stability, permeability and column reproducibility has been tested. The typical hydrophilic property and electrochromatographic performance for polar analytes such as phenols, benzoic acids, nucleic acid bases and nucleosides were also characterized with HI-pCEC, respectively.

2. Experimental

2.1. Reagents and materials

Vinylbenzyl trimethylammonium chloride (VBTA), Bisphenol A glycerolate dimethacrylate (BisGMA), 3-(trimethoxysilyl)propyl

methacrylate (γ -MAPS), cinnamic acid, 2,2'-azobisisobutyronitrile (AIBN), 4-hydroxybenzoic acid (4-HB), 2-hydroxybenzoic acid (2-HB), 3,4-dihydroxybenzoic acid (2,3-DHB), 2,5-dihydroxybenzoic acid (2,5-DHB) are purchased from Aldrich (Milwaukee, WI, USA). Uracil, uridine, guanine, guanosine, cytosine, cytidine, adenine, adenosine are purchased from Sigma (St. Louis, MO, USA). Phenol, resorcinol, catechol, hydroquinone, phloroglucinol, and pyrogallol were purchased from Chemical reagent Plant (Shanghai, China). Other reagents are obtained from Chemical Reagent Corporation (Shanghai, China). Fused-silica capillaries (I.D. 100 μ m, O.D. 365 μ m) are purchased from Yongnian Optic Fiber Plant (Hebei, China). Stock solutions of analytes are prepared as 1 mg/mL solutions in ACN and working standard solutions are diluted to appropriate final concentrations with water. Water used in the experiment is doubly distilled and purified by a Milli-Q system (Millipore, Milford, MA, USA).

2.2. Instrumentation

All pCEC experiments are performed on a Trisep-2010GV pCEC system (Unimicro Technologies, Pleasanton, CA, USA) comprising a solvent gradient delivery module, a high-voltage power supply, a microfluid manipulation module (including a six-port injector), and a data acquisition module (Fig. S1, in supplementary data). A continuous mobile phase is generated by merging two flows in a mixer and enters six-port injection valve. Samples injected are delivered to the injection valve and introduced in the internal 2 μ L sample loop, and then carried to the four-port split valve by the mobile phase flow. After splitting in a four-port valve, the flow enters a capillary column under constant pressure controlled by a back-pressure regulator. The splitting ratio of the pump flow is about 1:200 (v/v) at 3.5 MPa in this work. A high voltage is applied to the outlet of column, and the inlet of column is connected to the split valve and grounded.

Scanning electron micrographs (SEM) of monolithic columns were carried out with XL30E scanning electron microscope (Philips, The Netherlands).

2.3. Preparation of monolithic column

Prior to use, the inner wall of the capillary has been treated with 3-trimethoxysilyl propyl methacrylate (γ -MAPS) according to the procedure reported previously [23]. The polymerization mixture composed of the monomers (VBTA and BisGMA), polymerization initiator (AIBN, 1 wt% with respect to the monomers), and porogenic solvents (methanol and dodecyl alcohol) are mixed ultrasonically for 15 min (low temperature) to yield a homogeneous solution. The monomer and the porogenic solvent are mixed in a certain ratio. After bubbling with nitrogen for 5 min and the sonication for 5 min (low temperature), the homogeneous polymerization mixture is achieved and then injected into the capillary. The capillary is plugged at both ends with rubber stoppers and submerged in a water bath at 60 °C for 10 h. The preparation scheme was shown in Fig. S2 (seen in supplementary data). Finally, the obtained monolithic column is washed by methanol with an HPLC pump to flush out the residual reagents. The monolith is prepared with a length of 30 cm for the effective polymer bed and the total length is 50 cm. By using a tool to cauterize the column, a 1 mm width of detection window is created after the end of monolithic stationary phase. Toluene is used as the t_0 marker in HI mode.

2.4. Calculation method

2.4.1. Permeability

By using Darcy's Law, the permeability (B_0) is calculated by the following formula [24]:

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