Journal of Chromatography A, 1412 (2015) 112–125

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Radical-mediated step-growth: Preparation of hybrid polymer monolithic columns with fine control of nanostructural and chromatographic characteristics

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ARTICLE INFO

Article history:
Received 24 June 2015
Received in revised form 5 August 2015
Accepted 10 August 2015
Available online 13 August 2015

Keywords:
Adsorption
Click chemistry
Mass transfer
Network Ideality
Step-growth
Partition

ABSTRACT

The currently most successful type of porous polymer monoliths utilized in chromatography is prepared by free-radical cross-linking (co)polymerization in porogenic solvents and a single-step molding process. Though such types of materials are well-recognized in the scientific community, they suffer from their multi-scale heterogeneity originating from the nanoscale through to their microscale and ultimately limited performance on their macroscale. This is in particular true when estimating their performance under equilibrium (i.e. isocratic) elution conditions for retained compounds.

In this contribution, we study a new concept in the preparation of porous monolithic hybrid materials based on polyhedral oligomeric vinylsilsesquioxanes which undergo radical mediated step-growth cross-linking with thiol-linkers. Fundamental characterization of this new entry of materials is performed via a variety of characterization approaches including infrared and Raman spectroscopies, thermogravimetric analysis, gel fraction, dry-state surface area analysis, and visualization of the capillary-scale porous structure by scanning electron microscopy. This characterization identifies that a rational choice of experimental conditions in monolith preparation leads to destined and desirable materials' properties, in particular with experimentally accessible near-ideal nanoscale network structures. With the obtained structural informations at hand, we finally evidence the monoliths' tailored chromatographic performance by isocratic elution experiments of structurally similar small molecules under reversed-phase type of chromatographic conditions. This validates the fundamental origin for an improved performance of these types of monolithic materials under solvated conditions that has its foundation established in the creation of near-ideal nanoscale networks of material. This identified ideality is manifested in an enhanced and almost retention-insensitive performance in liquid chromatographic separations of small molecules across wide ranges of retention factors over at least two orders of magnitude and wide ranges of mobile phase compositions. Such experimental observation is explained by a more homogeneous energetic distribution of partition and adsorption sites. A reference analysis of normalized plate height data at varied retention was performed and set in context with data of state-of-the-art silica- and polymer-based monoliths. This analysis clearly identifies the present materials to display performance behavior clearly located in the domain of derivatized silica-based monoliths.

1. Introduction

High performance chromatographic separations are typically performed using packed beds of (porous) adsorbent particles with reversed-phase liquid chromatography being the major workhorse in related industries and academic studies. Despite its success, other modes of chromatography are gaining in importance as well, the most prominent of which is hydrophilic interaction liquid chromatography [1,2].

Overarching, chromatography desires separation of complex mixtures of compounds. Fundamentally, in terms of mass transport in both reversed phase and hydrophilic interaction chromatographic modes, the mechanisms of retention can be described by both partition as well as adsorption, respectively their interplay [3–5].

While the majority of stationary phases utilized in chromatography are based on packed beds, the paradigm in stationary phase design was altered at the end of the last century with two major

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http://dx.doi.org/10.1016/j.chroma.2015.08.019

breeds of monolithic columns entering the chromatographic arena. These were polymer monoliths derived from free-radical cross-linking (co)polymerization processes [6–9] as well as monoliths based on (derivatized) silica-based materials [10,11].

Though some apparent conceptual similarities in both types of monoliths (polymer- and silica-based) can be found, the mechanism of interaction, in particular that of small sized solutes, differs profoundly [12,13]. While partition processes associated to the bonded layer positioned at the pore surface (or inside smaller-sized pores) in silica-based materials are increasingly understood in detail [14–16], associated processes are far more dominant and more difficult to comprehend in polymer-based adsorbents [12,17–19]. Associated to permanently porous structures of heterogeneously cross-linked polymer in the dry state, the polymer constituting the backbone of polymer monoliths shows certain dynamics when operated in liquid chromatographic applications. In contact with the mobile phases utilized, the heterogeneously cross-linked polymer suffers from (solvent-selective) nanoscale solvation and swelling [20,21]. The resultant solvent-associated free volume of polymer allows permeation of appropriately-sized solutes to a varying degree through (macro)pore fluid–gel interfaces. This process is primarily driven by partition, adsorption, and associated diffusion [22]. Nanoscale solvation and swelling becomes affected by the nanoscale backbone polymer structure, nanoscale distribution of cross-link density, and distribution of chemistry within structural elements of the monoliths. Therefore typical also, is the variation of the performance of polymer monoliths with mobile phase composition both for styrene–divinylbenzene and methacrylate-based chemistries in reversed-phase liquid chromatographic applications [20,23,24], as well as in hydrophilic interaction liquid chromatography [25].

In the past, fundamental aspects of heterogeneities found in porous polymer monoliths were discussed of having their origin in a compositional drift of the polymerization precursor mixtures and limited control of free-radical cross-linking (co)polymerization in material formation [23,24]. It results in a distribution of cross-link density as well as associated chemistry within the monoliths' internal backbone structure on a submicrometer-scale [21]. We believe that addressing the early events of nanoscale materials' formation need to be addressed as a major key element for the creation of chromatographically efficient stationary phases [22]. Undoubtedly, retention processes and resulting selectivity for separations have their origin in a partition-controlled process and the materials' complex nanoscale physicochemical structure.

In the search for alternate approaches to create monolithic materials offered by the suite of techniques of polymer chemistry, while retaining the technological simplicity of polymer monolith preparation, the radical-mediated reactions of thiols with vinyl containing monomers seems readily straightforward. Such reaction may belong to the family of "click" reactions, but only if they follow a step-growth pathway [26], an implementation most often not realized in more applied studies [27–29].

Not long ago we utilized polyhedral oligomeric vinylsilsesquioxanes (vinylPOSS) (Fig. 1a) and a diverse choice of thiol linkers, two of which selected in the present study (Fig. 1b) [30]. In situ monitoring of the reaction confirmed an exclusive radical-mediated step-growth reaction of such precursors. Such prerequisite is highly desired for the creation of materials of a near ideal cross-linked nanostructure that as well may open new avenues for tailoring the microscale physical structure of porous adsorbents. Proper choice of porogenic diluents in the single-step molding process allowed for a variation of microstructural pore constitution and capability for operation in liquid chromatography. With the demonstration of the creation of rigid and also soft materials via such thiol-ene "click" pathway at hand [30,31], other processes related to the preparation of hybrid monolithic columns have been reported [32–36].

The hypothesis at the foundation of the present report is in experimentally exploring rational design criteria for the creation of hybrid monolithic columns with near-ideal nanoscale networks based on a radical process (Fig. 1c). This comes along with suiting a straightforward technological accessibility of macroporous monolithic columns applicable in liquid chromatography. The foundation of this experimental study can therefore be related to our recent progress in related materials' design approaches [30,31,37]. In the present study, we demonstrate a radical-mediated step-growth network creation which is fundamentally different from that of typically utilized free-radical chain-growth and cross-linking processes and marks the fundamental difference to materials created by such processes. In addition to variable linker identities interconnecting POSS network knot construction elements (Fig. 1b), we systematically varied the materials derivation parameters such as phase ratio (controlled by monomer content of the polymerization mixture), variation in porogenic solvent composition (determining polymerization-induced phase separation and microscale modulation of pore structure) and stoichiometry of reactants (determining cross-link density and nanoscale network ideality) of resultant monolithic entities. The resultant impact of all these parameters on the hybrid monoliths' chromatographic performance is then detailed for the first time. Fundamentally, this comes along with limits and rationales for further opportunities in the area of separation science.

2. Experimental

2.1. Chemicals and materials

Polyhedral oligomeric vinylsilsesquioxane (vinylPOSS) cage mixture ($(CH_2CHSiO_{3/2})_n$ ($n = 8$, 10, 12) with a nominal molecular weight of 633–950 g/mol, was purchased from Hybrid Plastics, Inc. (Hattiesburg, USA). Azobisisobutyronitrile (AIBN) was purchased from Acros Organics (Geel, Belgium). Concentrated acetic acid (99–100%), 1 M sodium hydroxide, and 1 M hydrochloric acid were acquired from J.T. Baker (Deventer, Holland). Tetrahydrofuran, ethanol, and acetone were purchased from VWR (Fontenay-Sous-Rois, France). All other chemicals were acquired from Sigma Aldrich (Vienna, Austria) and used as received.

Water was purified on a Milli-Q Reference water purification system from Millipore (Vienna, Austria).

Teflon coated fused-silica capillaries of 100 μm I.D. were purchased from Optronis (Kehl, Germany) and were used as a mold for in situ, thermally initiated monolith preparation.

2.2. Preparation of hybrid monolithic materials in fused-silica capillaries and bulk

A priori, the inner wall of the 100 μm I.D. fused silica capillaries was provided with pendant methacrylate functionality used to anchor the in situ prepared monolith to the confine by an adapted procedure described previously [38]. In detail, the inner surface of the capillaries was activated by successively rinsing it with acetone, water, 0.2 M sodium hydroxide for 1 h, water, 0.2 M hydrochloric acid for 1 h, water, and ethanol by means of a syringe pump. Then, a solution of 50% of 3-(trimethoxysilyl)propyl methacrylate in ethanol (v/v) (adjusted to an apparent pH of 5 with acetic acid) was pumped through the capillary for 2 h. Subsequently, the capillary was flushed with ethanol and acetone followed by drying under a stream of nitrogen.

For hybrid column preparation, the capillaries were filled with the polymerization mixtures, sealed with rubber stoppers, and