



Characterization of large surface area polymer monoliths and their utility for rapid, selective solid phase extraction for improved sample clean up[☆]



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ABSTRACT

While polymer monoliths are widely described for solid phase extraction (SPE), appropriate characterization is rarely provided to unravel the links between physical characteristics and observed advantages and disadvantages. Two known approaches to fabricate large surface area polymer monoliths with a bimodal pore structure were investigated. The first incorporated a high percentage of divinyl benzene (PDVB) and the second explored hypercrosslinking of pre-formed monoliths. Adsorption of probe analytes; anisole, benzoic acid, cinnamic acid, ibuprofen and cortisone were investigated using frontal analysis and the SPE performance was compared with particulate adsorbents. Frontal analysis of anisole described maximum adsorption capacities of 164 mg g⁻¹ and 298 mg g⁻¹ for hypercrosslinked and PDVB adsorbents, respectively. The solvated state specific surface area was calculated to be 341 and 518 m² g⁻¹ respectively. BET revealed a hypercrosslinked surface area of 817 m² g⁻¹, 2.5 times greater than in the solvated state. The PDVB BET surface area was 531 m² g⁻¹, similar to the solvated state. Micropores of 1 nm provided the enhanced surface area for hypercrosslinked adsorbents. PDVB displayed a pore size distribution of 1–6 nm. Frontal analysis demonstrated the micropores present size exclusion for the larger probes. Recovery of anisole was determined by SPE using 0.4 and 1.0 mL min⁻¹. Recovery for PDVB remained constant at 90% ± 0.103 regardless of the extraction flow rate suggesting extraction performance is independent of flow rate. A more efficient sample purification of saccharin in urine was yielded by PDVB due to selective permeation of the small pores.

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1. Introduction

Porous polymer monoliths have been extensively explored as an alternative to particulate materials for sample preparation and chromatography due to the unique features of their structural morphology. First, the macroporous structure is highly permeable, allowing fast fluid flows while maintaining low backpressures. Second, the polymeric globules possess non-porous highly crosslinked cores for improved solute mass transfer kinetics. Unlike particulate adsorbent where the interactable surface area is deep inside

the particle, the interactable surface of a monolith is accessible by a small diffusion distance [1]. Despite these attractive features bed heterogeneity has limited the realization of these materials as genuinely competitive materials for high efficiency chromatographic applications [2]. Unlike chromatographic separations, sample preparation seeks binary analyte interactions (on/off; retained/unretained); thus, is less sensitive to the heterogeneous adsorbent structure. Porous polymer monoliths have the potential to offer genuine benefit in the sample preparation domain.

The first use of polymer monoliths for sample preparation was fabricated in micro columns for the online extraction of polar organic compounds from water [3]. Today, the use of polymer monoliths for sample preparation spans a wide variety of applications and platforms [4–6]. However, the breadth of investigations can be largely ascribed by the ease of fabrication and the wide variety of commercially available functional monomers rather than any

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performance benefits over existing technologies. As such the structure and function of polymer monoliths remains poorly understood and substantial work is necessary to truly determine their applicability for SPE.

Typically, polymer monoliths have a lower extraction capacity than particles; the capacity of an adsorbent bed is strongly related to the surface area available for interaction, thus a greater surface area affords improved assay sensitivity. Whereas surface areas of up to $1000\text{ m}^2\text{ g}^{-1}$ are common for polymer particles, polymer monoliths generally display very small surface areas ($<20\text{ m}^2\text{ g}^{-1}$). While micro (0.3–2 nm) and mesopores (2–50 nm) have been suggested in polymer monolith structures their quantity is substantially lower than for particulate adsorbents. Approaches to prepare a polymer monolith with a bimodal porous structure, meaning that the adsorbent contains both macropores for high flow applications and micro- and mesopores for an associated large surface area are divided into two distinct categories. The first approach is to incorporate a high degree of internal crosslinking in the polymer network. Increased crosslinking at an early stage in the polymerization results in a large number of swollen microspheres and nuclei that aggregate to form the globular structure typical of a polymer monolith [7]. Voids between aggregated microspheres and nuclei deliver micro- and mesoporosity that drive up the surface area of the polymer monolith [7]. Increased crosslinking has been demonstrated using an elevated percentage of crosslinking monomer [3,8–13] which is also achieved by prematurely terminating the polymerization reaction [14–16]. Polymer monoliths which contain a high concentration of the crosslinking monomer divinyl benzene (DVB), possess surface areas as large as $500\text{ m}^2\text{ g}^{-1}$ [8,11,12]. The second approach to generate a large surface area polymer monolith is through extensive post-crosslinking of a pre-formed polymer. The most commonly explored approach is a Davankov reaction where a Friedel-Craft's alkylation introduces structural bridges between neighboring phenyl groups for increased surface porosity [17]. Urban et al. recently applied this technique to polymer monoliths and demonstrated the surface area increase from $29\text{ m}^2\text{ g}^{-1}$ to $663\text{ m}^2\text{ g}^{-1}$ using 4-vinylbenzyl chloride (VBC) as an internal electrophile [18,19]. This was extended by Maya et al. who used an external crosslinker to prepare polymer monoliths with surface areas as great as $900\text{ m}^2\text{ g}^{-1}$ [20]. Given the large surface areas obtained for these polymer monoliths their superiority for SPE is often assumed. However, data that clearly demonstrates the suitability of large surface area polymer monoliths for SPE remains inconclusive, as the structure of these materials is not widely understood. A detailed characterization is necessary to understand these materials and to reveal the cause-effect relationships that may provide benefits or disadvantages for SPE.

In this study large surface area polymer monoliths were explored and a detailed investigation of their physical properties in the dry state and solvated in aqueous environments was performed to accurately determine suitability for SPE. The two categories of large surface area polymer monoliths were compared. Frontal analysis was employed with probe analytes of increasing molecular weight to explore *adsorption behavior, capacity and surface area*. In addition, *porous properties* were characterized by scanning electron microscopy (SEM) and argon adsorption/desorption to unravel any links between physical characteristics and extraction performance. This information promotes a better understanding of polymer monolith morphologies and could be of assistance in further tailoring their physical properties as SPE adsorbents. Finally, we have benchmarked the SPE performance of polymer monolith against commercially available polymer particulate adsorbents for *SPE sample purification* of complex matrices.

2. Experimental

2.1. Chemicals and materials

DVB (containing 80% 1,3-DVB+1,4-DVB and 20% 1-ethyl-3-vinylbenzene + 1-ethyl-4-vinylbenzene), (97%), styrene (S) (99%), VBC (99%), 1-dodecanol, toluene, 1,2 dichloroethane (DCE) (anhydrous 99.8%), ferric chloride, anisole, benzoic acid, cinnamic acid, ibuprofen, cortisone, formic acid, hydrochloric acid and phosphoric acid were all purchased from Sigma Aldrich (Castle Hill, Australia). Inhibitors were removed by passage through a packed bed of basic alumina. The initiator 2,2'-azo-bis-isobutyronitrile (AIBN) was obtained from MP Biomedicals (Santa Ana, CA) and recrystallized with methanol. HPLC grade methanol and acetonitrile were purchased from Sigma Aldrich and water was purified with a Milli-Q system (Millipore, Bedford, MA).

Polyethylene (PE) tubing (1.57 mm i.d.) was obtained from SDR Scientific (Chatswood, Australia). The MEPS cartridge assembly included frits, shank and needle hub components. The particulate MEPS cartridge contained a 2.5 mm PE inner lining and was packed with $85\text{ }\mu\text{m}$ poly(S-co-DVB) (P(S-DVB)); both were provided by SGE Analytical Science (Ringwood, Australia). The polypropylene (PP) insulin syringes (1 mL and 4.3 mm i.d.) were obtained from Medshop Australia (Preston, Australia).

2.2. Instrumentation

The frontal analysis of the adsorbents in the MEPS format was assessed using an ICS3000 system (Thermo Scientific, Scoresby, Australia) consisting of two quaternary solvent pumps and an ultraviolet (UV) detector. The MEPS cartridge was inserted between the pump and the detector by connecting the MEPS directly to the 6-port injection valve using a fill port (VICI, Houston, TX). To analyze recovery for offline SPE the MEPS assemblies comprised a cartridge coupled to $100\text{ }\mu\text{L}$ controlled directional flow (CDF)-MEPS syringe driven by a hand held semi automated analytical syringe (SGE Analytical Science). A ProteCol C18 (4.6 mm i.d. \times 250 mm) HPLC column was employed (SGE Analytical Science) and chromatograms were achieved isocratically using 80:20 methanol:water (v/v) at a flow rate of 1 mL min^{-1} . To analyze real samples a Prominence LC system (Shimadzu, Seacliff, Australia) was employed consisting of a solvent delivery system, an auto sampler and a UV detector operated at 220 nm. Chromatograms were achieved isocratically using 80:20 0.5% phosphoric acid:acetonitrile (v/v) at a flow rate of 1 mL min^{-1} .

The macroporous properties of the adsorbent materials were measured using an Autopore IV mercury intrusion porosimeter. The Brunauer-Emmett-Teller (BET) surface area and microporosity were assessed using a Tristar II analyzer for the argon adsorption/desorption at 77 K (Particle and Surface Science, Gosford, Australia). Microporous surface area was determined using t-plots and the pore size was assessed using the non-localized density functional theory (NLDFT), as no model is available for polymer monoliths the model was selected based on the goodness of fit of the data.

The surface morphologies of the adsorbents were analyzed using a Hitachi SU-70 field emission scanning electron microscope (SEM) in the Central Science Laboratory, University of Tasmania. The polymer monoliths were sputter-coated with platinum.

2.3. Preparation of the monolithic SPE adsorbents

The compositions of poly(VBC-co-S-co-DVB) (P(VBC-S-DVB)) were adapted from Urban and coworkers [19]; monoliths prepared from poly(DVB) (PDVB) were based on an approach described by Sýkora et al [8]. Briefly, the P(VBC-S-DVB) was prepared from 18%

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