



Surface-mediated effects on porous polymer monolith formation within capillaries

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ABSTRACT

The formation of a porous polymer monolith (PPM) is influenced by the physico-chemical properties of the wall surface of its container. This influence can have a dramatic effect on the resulting monolith morphology depending on the nature and composition of the wall. Indeed, a dense polymer layer or “sheath”, distinct from the bulk porous material, has been observed at the wall surface of capillaries, and thus a study was undertaken to explore the dependence of this layer on the hydrophobicity of the surface. A range of silanizing reagents were used to modify the surface of the fused silica capillary, including aminopropyl, trimethylsilyl, octadecyl and perfluorooctyl functionalities. Crosslinked butyl acrylate-based PPM was formed in the modified capillaries and extruded. SEM images of the monoliths were used to examine the sheath morphology and thickness, which are discussed with respect to surface hydrophobicity.

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1. Introduction

The development of porous polymer monolith (PPM) technology arose largely from the desire for better separation media that could complement or even substitute packed columns. Having a continuous porous structure characterized by a bimodal pore size distribution, the relatively low flow-induced back pressure for monolithic material makes it ideal for high-throughput flow-through techniques like separations and solid-supported catalysis [1–3].

Traditionally, monoliths were prepared by thermally initiated free radical polymerization in a planar or tubular mould yielding a sheet or cylinder, which would then be cut into disks and packed in a cartridge for chromatography. However, this relatively laborious method has largely been replaced by the versatile single step *in situ* polymerization within the confines of a cartridge, chromatographic column, or capillary [4]. Typically the polymerization mixture consists of a monomer, crosslinker, photo- or thermal initiator and a porogenic solvent. The ease of preparation of these materials in capillaries, especially for micro- and nano-HPLC, which have better resolving power with lower sample and mobile phase consumption compared to their macro analogues, has further led to their appeal in the scientific community. In addition, tailoring the porous properties and functionalities of the monoliths by

optimizing the temperature, composition of the porogenic mixture and amount of crosslinker is well documented, making the technology accessible for many scientists across a variety of disciplines [5–7]. The many different chemistries and monomer systems – the most common being styrenes, methacrylates, acrylates, vinylpyridines, vinylpyrrolidones, polyurethanes, acrylamides and norbornene – available for making monoliths have opened new vistas for the application of these materials in various fields from chromatography and electrochromatography [5–10] to nanoelectrospray ionization mass spectrometry [11–13], solid phase extraction [3,4], photopatterned enzyme immobilization [14,15], molecular imprinting [4], micromixing in microchip devices [16] and heterogeneous catalysis among others [1,17].

Although these materials have generated a great deal of interest, there is a deficiency in the fundamental study of surface chemistry effects in play when these polymers are formed within the confines of a capillary. This study was largely motivated by the observation of spatial variation in the morphology of the monolith when formed in a fused silica capillary that has been pretreated with the heterobifunctional silanizing coupling reagent γ -methacryloxypropyltrimethoxysilane (γ -MAPS), commonly employed to provide a site for covalent attachment of the forming polymer to the capillary wall [9,18–20]. Without these anchoring sites, the polymer cannot withstand high pressure, and often detaches from the capillary wall leaving voids. The monolith formed under such conditions contained a polymer sheath around it, sometimes called a fluid-impervious outer layer [21]. This phenomenon has been observed by others [6], and is, in part, the working concept in the preparation of porous layer open tubular (PLOT) columns for

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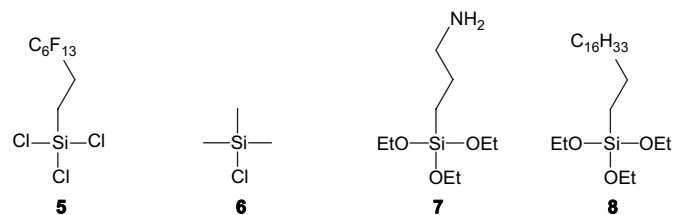
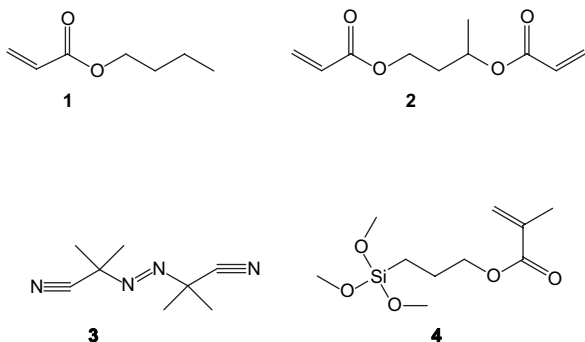
chromatography, especially using the thermally stable poly-(divinylbenzene) [21–24]. This impervious layer has also been reported as advantageous in CE and CEC because it imparts stability to the columns by masking the silanol groups on the wall of the fused silica capillary, thus attenuating undesirable silanophilic interactions [21]. Although the presence of a sheath in chromatographic materials could be an advantage in CE, the difference in the radial morphology of the PPM could result in varied mass transfer in LC leading to band broadening. It is therefore critical to understand the chemistry behind this sheath formation, which hitherto has only been alluded to in the literature and has not been explored in any satisfying detail. It has been suggested in the literature that the sheath formation may be due to the precipitation of the polymer on the capillary walls during polymerization [9], to a different morphology of the copolymerized PPM and γ -MAPS on the wall [25], or to a faster consumption of monomers at the vinyl-coated walls of γ -MAPS-functionalized capillaries resulting in monomer diffusion toward the surface [18]. In Horvath's work describing the formation of a polymer "inner tube" within a capillary, the observation of a 1–2 μm -thick annulus of polystyrene is discussed but not explored further [21]. Recent work in our group on the formation of polymer layers on octadecylsilane-derivatized silica particles, however, has shed some light on the chemistry behind the sheath formation on capillary walls [26].

Herein we report a study of this sheath formation and its dependence on the effects of surface functionality on the confining wall of the capillary. It shall be demonstrated that by changing the surface hydrophobicity of the fused silica capillary wall, the thickness and morphology of the sheath surrounding the porous polymer monolith can be tailored.

2. Experimental

2.1. Materials

All aqueous solutions were prepared using >18 M Ω Milli-Q water (Millipore, Bedford, MA, USA). Butyl acrylate (**1**, monomer), 1,3-butanediol diacrylate (BDDA, **2**, crosslinker) and 2,2'-azobis(2-methylpropionitrile) (AIBN, **3**, initiator) were obtained from Aldrich and used as-received. The siloxanes for wall treatment, γ -methacryloxypropyltrimethoxysilane (γ -MAPS, **4**), trichloro(1H,1H,2H,2H-perfluorooctyl)silane (PFOS, **5**) and chlorotrimethylsilane (TMS, **6**) were obtained from Aldrich while (3-aminopropyl)triethoxysilane (APTES, **7**) was from Sigma and *n*-octadecyltriethoxysilane (ODS, **8**) was from United Chemical Technologies, Inc. (Bristol, PA, USA). Glacial acetic acid and HPLC grade acetonitrile were obtained from Fisher Scientific. Ethanol (95%) was purchased from Commercial Alcohols Inc. (Brampton, ON, Canada). Fused silica capillary, 363 μm outer diameter with polyimide coating, was purchased from Polymicro Technologies (Phoenix, AZ, USA).



2.2. Treatment of capillary walls

Fused silica capillaries with 30 μm , 75 μm , 200 μm and 250 μm inner diameter were flushed with 1 M sodium hydroxide (unless stated otherwise; 30 min reaction time) to enhance hydrolysis of the siloxane groups for subsequent reaction with the silanizing reagents. The residual alkali solution in the capillary was neutralized by flushing with 0.1 M hydrochloric acid for 30 min. The capillaries were then dried with a stream of helium. Five silanizing reagents were chosen for the functionalization of the capillary walls: **4–8**. For all cases, the pretreated capillary was filled with a 20% (v/v) solution of the silanizing reagent in toluene and left overnight at room temperature, after which they were flushed with acetonitrile and dried with helium.

2.3. Contact angle measurements

The hydrophobicity of a surface can be estimated by the contact angle of a droplet of water. For the fused silica capillaries in this work, the contact angle was determined by measuring the rise of water within the capillary. The value can be calculated using the following equation [5,18,21]:

$$\cos \theta = \frac{1}{4} \frac{h_r d (\rho - \rho_v) g}{\gamma} \quad (1)$$

where θ is the contact angle, h_r is the height of the rise (difference between bulk water level and meniscus of water within the capillary) in cm, d is the inner diameter of the capillary in cm, ρ is the density of water (0.997 g/mL), ρ_v is the density of the surrounding air saturated with water vapour (1.1845×10^{-3} g/mL), g is acceleration due to gravity (980.665 cm/s²) and γ is the surface tension of water (71.97 dynes/cm). For these measurements, the capillaries were taped against a white background and immersed in deionized water contained in a 100 mL graduated cylinder. After an equilibration time of 2 h, the meniscus of the water in the cylinder and in the capillary was recorded on the white background and the distance between the markings was measured. This process was repeated at least three times for each capillary, with drying by He gas between measurements. The capillaries used for these measurements had an inner diameter of 200 μm and an overall length of about 20 cm.

2.4. Porous polymer monolith formation

The formulation for the porous polymer monolith is similar to that described in our previous papers [11,26–28]. The polymerization mixture is composed of 67% porogenic solvent (60% acetonitrile, 20% ethanol (95%) and 20% potassium phosphate buffer (5 mM, pH = 6.7)), 23% butyl acrylate, 10% 1,3-butanediol diacrylate, and 6.8–6.9 mg AIBN. This mixture was introduced into the capillary at 20 $\mu\text{L}/\text{min}$ for 2 min using a syringe pump. Polymerization was initiated by placing the capillaries in an oven at 67 $^\circ\text{C}$. After 1 h the capillaries were removed from the oven and the ends were cut to leave only capillary containing polymer. The capillaries were flushed with 95% CH₃CN/H₂O using a Waters model 590 HPLC

pump. The polymer monoliths were extruded from the capillaries by hydrodynamic pressure using the HPLC pump and collected for SEM imaging. In some cases, such as for the 30 μm i.d. capillaries, the pressures required to extrude the PPM were too high, and so these monoliths were imaged without extrusion.

2.5. Scanning electron microscopy

The polymer monoliths, whether extruded or inside the capillary, were mounted normal to the aluminum stub using tape to facilitate imaging of the cross-section. SEM images were obtained using either a Jeol JSM-840 (Tokyo, Japan) or a Leo 1530 field emission (Oberkochen, Germany) scanning microscope.

3. Results and discussion

3.1. Contact angle measurements

Surface hydrophobicity of the capillary wall has an effect on the morphology of the PPM formed near the surface, thus necessitating the determination of the contact angle inside the capillary. The measurement of the rise of water within a capillary can be used to calculate the contact angle according to Eq. (1) (*vide supra*). Hydrophobicity decreases with contact angle, and the hydrophilic nature of silica (low contact angle) is due to the presence of silanol groups at the surface, which at neutral pH are largely dissociated to Si-O^- . The contact angle for untreated silica capillary (200 μm i.d.) can be found in Table 1. Compared to measurements for fused silica capillaries in the literature (50° [18], 24° [5], 24° [21]), the 54° contact angle obtained in our work was higher. This could be attributed to the buildup of organic matter on the surface over time contributing to the higher wetting angle, or to the batch-related properties of the fused silica itself from the manufacturer [18].

Achieving the lowest possible contact angle, therefore, is important for further surface modification since it indicates the presence of more free reactive silanol groups. Treatment of the capillary wall with NaOH has been found to remove much of the residual organic matter and simultaneously hydrolyze siloxane bridges to free silanols. The action of NaOH on the surface has also been documented to partially etch the surface to provide a rough relief structure, useful for increasing surface area, especially for the improved adhesion of polymer formed within the capillary [18].

The contact angle of the wall surface of the capillaries pretreated with NaOH was compared with that measured for untreated capillaries (Table 1). The contact angle for the 200 μm i.d. fused silica capillary dropped to 50°, similar to the 1 mm i.d. treated capillaries in Ref. [18].

More importantly, the availability of reactive silanol groups was demonstrated by the improvement of their subsequent silanization reaction with typical silica modification reagents. Table 1 delineates the differences in wetting angle between unfunctionalized silica

capillaries and those derivatized with the chlorosilanes **5** and **6** and siloxanes **7** and **8** before and after pretreatment with NaOH. For all the reagents, which feature groups that are hydrophobic to varying degrees, the contact angle determined for silanized pretreated capillaries was higher than for silanized untreated capillaries. Since the contact angle is a measure of the extent of surface coverage by the reagent, the higher angle indicates that a greater amount of surface groups have been functionalized. For bulky groups like perfluorooctyl (**5**) and octadecyl (**8**), whose silanization reaction with the surface is more limited by the steric hindrance of reactive groups rather than the actual number of silanols, the improvement in reaction efficiency is less pronounced. For the smaller trimethylsilyl group (**6**), however, the contact angle rose by nearly 30°. The difference in reaction efficiency for the silanization of silica with these two groups is long known, explaining the higher hydrophobicity for capillaries coated with **6** over **8** despite the longer alkyl chain of the latter. As such, the functionalization of chromatographic silica particles with ODS (**8**) requires the end-capping of residual silanol groups that have not completed the silanization reaction with ODS but still affect the analyte adsorption properties of the column. Indeed, even for the end-capping of a stationary phase with a silane such as **6**, harsh conditions involving high temperatures are employed to ensure that a sufficient number of hindered silanol sites are capped by the condensation reaction [29].

3.2. Sheath formation and surface hydrophobicity

The formation of PPM within capillaries has been studied extensively. Most of the volume within the capillary contains bulk PPM, and it is this structure that is the focus of discussion in the literature. However, a certain fraction of the volume falls within the range of influence of the surface of the capillary wall. It is known that the surface can have a strong effect on the formation of the polymer in contact with it, often causing differences in morphology from the bulk polymer up to a few microns into the bulk volume, an effect that becomes more important as the environment becomes more confined. For example, assuming that the influence of a surface extends 1 μm into the bulk, for a 250 μm i.d. capillary the volume occupied by this layer of influence is only 0.8% of the total volume of the capillary, but as the capillary gets smaller and the surface-to-volume ratio increases, the surface effects become much more important. For a 30 μm i.d. capillary, the volume occupied by a 1 μm layer amounts to 6.6% of the total volume. Aside from structural changes, this phenomenon has been observed for other properties such as crystallization behaviour [30], glass transition temperature [31], chain association [32] and physical aging [33,34]. In many studies, the formation of a more ordered and dense polymer layer near the capillary wall is observed, yet it is not often discussed or explained, at least in terms of surface interactions. Typically, the layer, or “sheath”, is found when hydrophobic polymers are formed within a capillary silanized with the common silica wall anchor γ -methacryloxypropyltrimethoxysilane (**4**). The exposed methacrylate group on the inner wall of the capillary renders the surface somewhat hydrophobic. Consequently, we propose that the primary reason for the dense layer of polymer forming at the surface stems from the hydrophobic van der Waals interactions involving the capillary wall and the forming polymer.

Using a variety of functional silanizing reagents on the capillary walls, the interactions between the wall and poly(butyl acrylate-co-1,3-butanediol diacrylate) were explored through the morphology of the sheath formed at the interface. As judged by the contact angles (Table 1), the hydrophobicity of the fused silica capillary wall increases with the functional group in the order: untreated < aminopropyl < octadecyl < trimethylsilyl < perfluorooctyl. The absolute values for these contact angles appear high compared to similar examples in the literature (e.g. 82.8° for an

Table 1

Contact angles for the surfaces of capillary walls functionalized with the various reagents as determined by the rise of water within a 200 μm i.d. capillary. The number of measurements is in parentheses

Surface functionalizing reagent	Contact angle, θ (°)	
	Without NaOH pretreatment	With NaOH pretreatment
Unfunctionalized	54.3 \pm 6.1 (4)	49.7 \pm 2.3 (3)
γ -MAPS, 4	88.7 \pm 3.1 (3)	96.0 \pm 3.9 (4)
PFOS, 5	131.3 \pm 1.2 (3)	134.7 \pm 3.5 (3)
TMS, 6	100.0 \pm 0.0 (3)	127.3 \pm 2.1 (4)
APTES, 7	86.3 \pm 0.6 (3)	107.3 \pm 2.6 (4)
ODS, 8	98.7 \pm 0.6 (3)	108.0 \pm 5.7 (4)

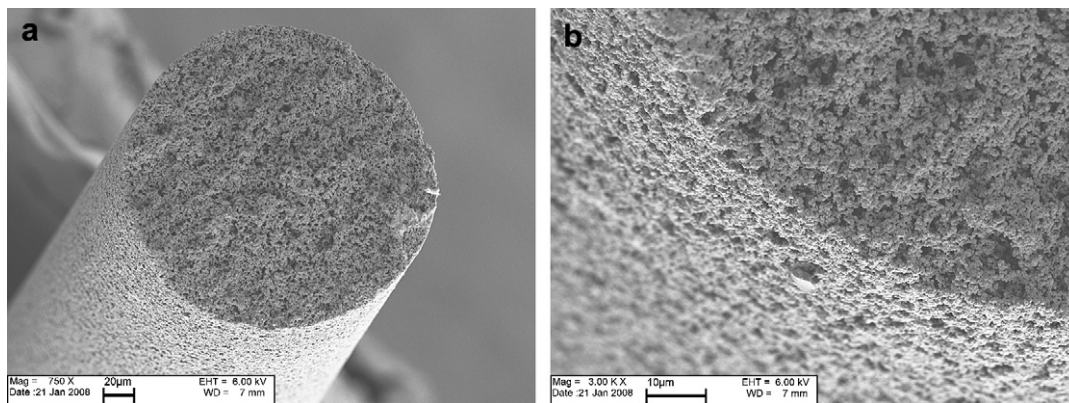


Fig. 1. SEM image of PPM extruded from a capillary with an unfunctionalized wall surface. (a) Cross-section, 750 \times magnification (scale bar 20 μ m); (b) further magnified section focusing on the outside of the sheath, 3000 \times magnification (scale bar 10 μ m).

aminopropyl-functionalized fused silica plate [35]), but these values are greatly dependent on the initial surface and the method of modification, ultimately making the given values (at least relative to each other) most appropriate for interpretation of the data in this work.

Porous polymer monolith formed within 250 μ m i.d. capillaries pretreated with NaOH and silanized with the various functional groups was extruded by pressure and imaged by SEM. Shown in Fig. 1 is a monolith formed in a capillary with an unfunctionalized wall (*i.e.* bare silica) and extruded. From the image, it can be seen that the polymer formed near the wall surface is not dense. No fully formed distinct layer is observed, and the bulk PPM morphology continues right up to the wall surface. In this case, the interactions between the forming hydrophobic polymer and the silica wall are minimal, and so the polymer formed there is no different from anywhere else in the capillary. In contrast, for a capillary functionalized with a hydrophobic group such as ODS, as shown in Fig. 2, there is a distinct dense layer near the wall-polymer interface of considerable thickness (up to 1 μ m) that looks like a “sheath” around the monolith. The thickness and density of the sheath increases with the relative hydrophobicity of the surface coating. A comparison of the formation of this layer is provided in Fig. 3 as representative SEM images for PPM extruded from capillaries with the various capillary wall surface functionalities.

The sheath thickness was generally difficult to quantitatively define, partly because it tended to fluctuate around the circumference of the monolith, but primarily because the bulk PPM nodules formed strong connections with the sheath often making it difficult to separate the dense layer from the bulk polymer. The sheath thickness for extruded monoliths from the various

functionalized capillaries is given in Table 2. The thickness was measured at representative points around the monolith circumference and the data is given as the mean and standard deviation of these measurements.

In addition to the sheath itself, the structure of the monolithic porous polymer formed near this layer is somewhat disrupted as well, being less dense than in the bulk PPM and the connections made to the sheath *via* the coalescence of nodules are generally fewer. This phenomenon is observed to become stronger as the contact angle of the capillary surface rises. Similar disruption was observed in the formation of a siloxane-based monolith in confined spaces, where the polymer density near the surface polymer layer is significantly less than in the bulk [36]. In fact, in many of our cases, especially for the ODS- and TMS-derivatized capillaries, the extrusion of the monolith from the capillary resulted in the stripping of the sheath from the bulk material, *e.g.* the PPM in Fig. 4 extruded from a capillary silanized with ODS. In this figure, the underside of the sheath is clearly visible showing some nodules from the PPM bulk still connected to the surface. The number and strength of these connections between the PPM and its sheath are diminished to the point that they are overcome by the friction arising between the sheath and the capillary wall when hydrodynamic pressure is applied.

All these observations support the idea that the hydrophobic interactions between the functionalized capillary wall and the forming polymer in the capillary are the cause of the dense layer that forms at the interface. Where this layer was previously observed in capillaries treated with γ -MAPS (4), a coupling reagent designed to form permanent covalent bonds between the PPM and

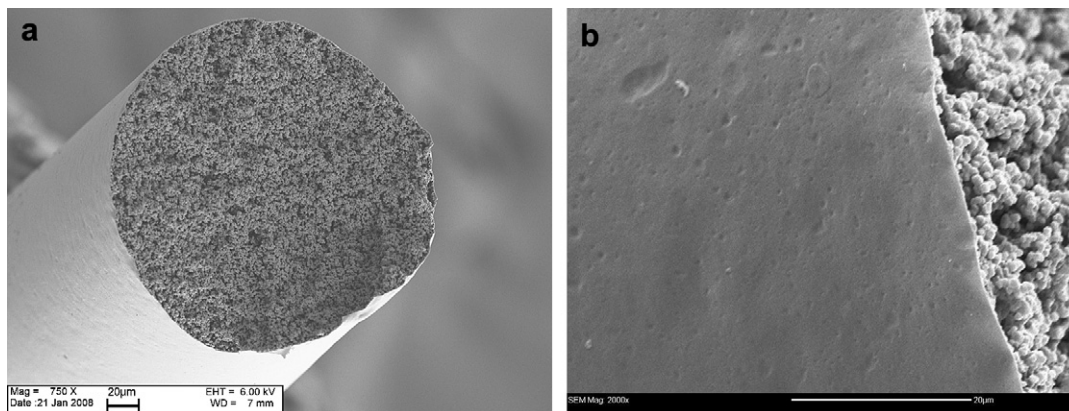


Fig. 2. SEM image of PPM extruded from a capillary functionalized with octadecylsilane. (a) Cross-section, 750 \times magnification (scale bar 20 μ m); (b) further magnified section focusing on the outside of the sheath, 2000 \times magnification (scale bar 20 μ m).

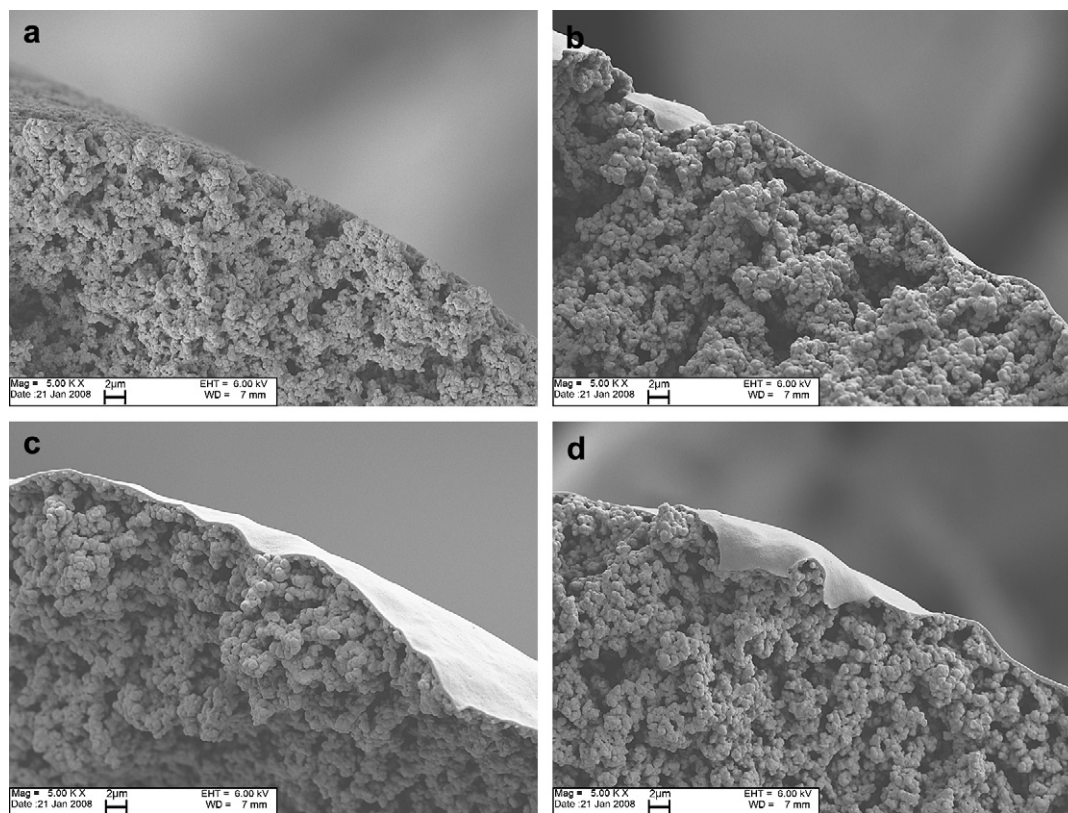


Fig. 3. SEM images of PPMs extruded from capillaries functionalized with (a) no reagent; (b) APTES; (c) ODS; (d) TMS. 5000× magnification (scale bar 2 μm).

Table 2

Thickness of the sheath formed at the wall surface of 30 μm i.d. capillaries functionalized with the various reagents. The value is the mean and standard deviation of eight measurements

Surface functionalizing reagent	Sheath thickness (nm)
Unfunctionalized	Indeterminably thin
PFOS, 5	842 ± 56
TMS, 6	537 ± 90
APTES, 7	404 ± 99
ODS, 8	420 ± 9

the capillary wall, the cause of the sheath formation was less likely due to the suggested faster chain formation at these sites [18] but rather the interactions between the forming polymer and the organic coating of the capillary. The wetting angle for 4-functionalized capillary (reported in Table 1) indicated such a surface to be considerably hydrophobic. Many examples of PPM morphology found in the literature support this idea, such as the extruded polystyrene-based monolith formed in a fused silica capillary in Ref. [37]. Images in that work clearly show the absence of a polymer sheath, as expected since the hydrophobic monomers would not be attracted to the hydrophilic wall. Another example is the polystyrene-based PPM shown in Ref. [6], which has a very large, dense sheath when formed in a γ-MAPS-functionalized capillary yet has no sheath at all when the capillary is not functionalized.

The analogous situation, where hydrophilic polymers such as silica sol-gel monoliths are formed within fused silica capillaries, should in principle show similar sheath formation. SEM images in Refs. [3,38–40] show the presence of a thin sheath of dense silica at the capillary wall, consistent with the attractive interactions between the sol-gel precursors and the wall surface. In addition, it was apparent from these images that the weakest part of their monolith (*i.e.* fewest bonds) was the region between the bulk silica

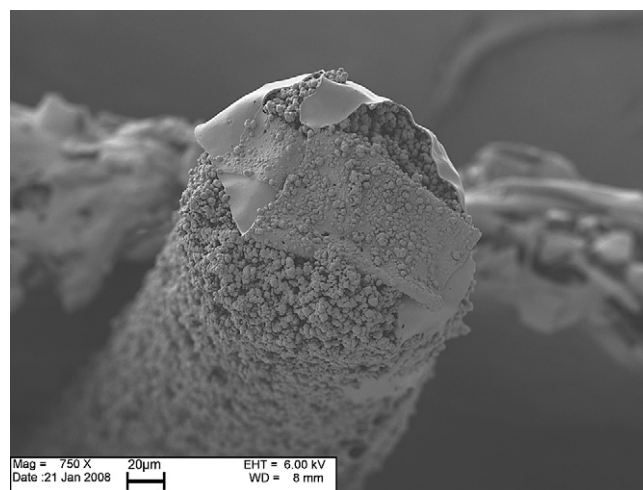


Fig. 4. SEM image of PPM extruded from a capillary functionalized with ODS, showing a partially stripped sheath, 750× magnification (scale bar 20 μm).

and the sheath, analogous to the weak connectivity between the bulk PPM network structure to the sheath discussed above.

Lastly, the fact that a polymer sheath forms without a source of radical formation (*i.e.* absence of vinyl groups) at the surface suggests that the surface vinyl groups are not directly responsible for sheath formation.

3.3. Effect of capillary diameter

The influence of the surface on polymer formation extends into the bulk medium to a certain degree. Based on the appearance of the sheath and nearby PPM even in the most extreme cases in this

report, this distance is only a few microns at most. For smaller capillaries with larger surface-to-volume ratios, however, even these few microns can account for a significant portion of the total bulk volume, although the sheath formation itself should not change.

Capillaries with inner diameters of 30 μm , 75 μm , 200 μm and 250 μm were silanized with each of the reagents discussed above, and PPM was formed and extruded from each for SEM analysis. For the smaller diameters, the PPM had too much surface contact with the walls relative to its total volume and so these could not be extruded from the capillaries, making sheath evaluation more difficult. In any case, it appears that neither the sheath nor the bulk PPM is significantly affected by capillary diameter within the range studied. A comparison is made for PPM formed in and extruded from ODS-functionalized capillary of 30 μm (Fig. 5) and 250 μm (Fig. 2a). In both cases, the sheath morphology and thickness are approximately the same (420 ± 9 nm for 30 μm i.d., 421 ± 66 nm for 250 μm i.d.), regardless of capillary diameter. Since the extent of surface influence is estimated to be only a micron or two, it is not surprising that no changes are evident at these capillary sizes. When the diameter is reduced enough, such that most or all of the volume in the capillary is within the influence of the wall surface, the polymer is said to be “confined” and has been known to show completely different morphology [36]. This is not expected in our case until the inner diameter is less than about 5 μm , however the use of capillaries with such diameters is impractical due to clogging and high back pressures and thus they were not included in this study.

3.4. Perfluorinated surfaces

The wetting of the perfluorooctyl-functionalized surface by water, as determined by capillary rise measurements ($\theta = 134.7^\circ \pm 3.5^\circ$, Table 1), is extremely poor. The high contact angles, even without wall pretreatment, suggest that the PFOS-coated capillaries are the most hydrophobic of all the functionalities used. This effect was manifested in the morphology of the polymer that formed near these surfaces, and indeed the sheath of the PPMs in these capillaries had interesting properties. An SEM image of extruded PPM from a 75 μm i.d. perfluorinated capillary is shown in Fig. 6. For this sample, the sheath seems to have some mobility along the monolith, and has folded over the end, presumably during extrusion. In fact, the sheath has shown longitudinal

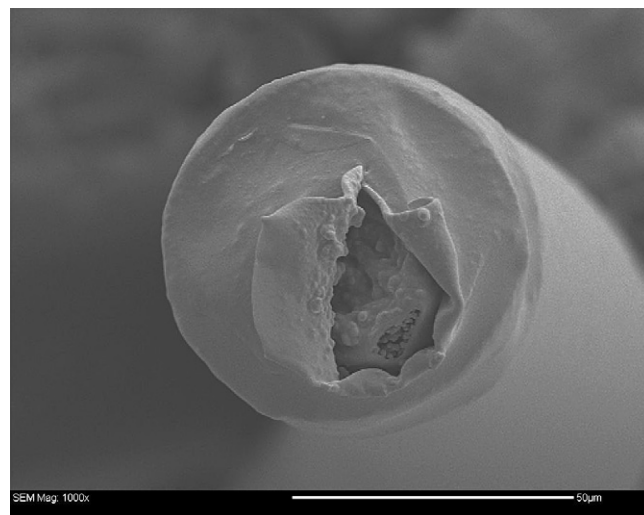


Fig. 6. SEM image of PPM extruded from a capillary functionalized with PFOS, 1000 \times magnification (scale bar 50 μm).

movement or complete removal for all PPMs extruded from capillaries coated with PFOS. Perhaps the fluorinated surface is an extreme case, where the sheath formation is almost completely distinct from the bulk PPM. In all measurable cases, the sheath thickness was significantly larger than that for PPM in TMS-functionalized capillary (846 nm vs. 537 nm, Table 2), and the sheath contains very few connections with the bulk PPM nodules while the bulk polymer near the sheath is less dense than elsewhere. Following the same reasoning as for the hydrocarbon-coated capillaries, the forming acrylate polymer is strongly attracted to the surface, being the most hydrophobic of any tested in this study, resulting in a dense, thick, distinct layer at the surface at the expense of bulk polymer near it.

4. Conclusion

The layer formation phenomenon arising from surface-mediated effects when porous polymer monolith is moulded in a confined environment has been critically studied. The sheath formation has been largely attributed to the affinity behaviour of the monomer system to the surface of the capillary through hydrophobic van der Waals interactions. As such, it has been demonstrated that the sheath thickness can be tailored depending on the functionality anchored to the wall of the capillary. A predictable correlation has been found between the contact angle measurements and the sheath thickness. For example, PPM formed in a capillary derivatized with chlorotrimethylsilane or *n*-octadecyltriethoxysilane formed a consistently thick and pronounced sheath with a butyl acrylate monomer system.

The ability to control the sheath may prove to be very important. This technology could find application, for example, in the fabrication of PLOT columns and PPM columns for CE and CEC where this layer could play an important role in masking the silanol groups, hence avoiding the silanophilic interactions with the analytes that often results in poor chromatography. Controlling sheath morphology could also be of importance when preparing molecular imprinted and PPM fibres for solid phase microextraction in tailoring the extraction efficiency [41]. Lastly, while the resulting fibre may be relatively fragile, the formation of a protective, fluid-impermeable sheath around an extruded PPM allows a fluidic monolith with a very thin wall. This may be very useful for applications such as nanoelectrospray ionization for mass spectrometry, where wetting of the blunt capillary end by fluids exiting the monolith can significantly hamper the ionization performance.

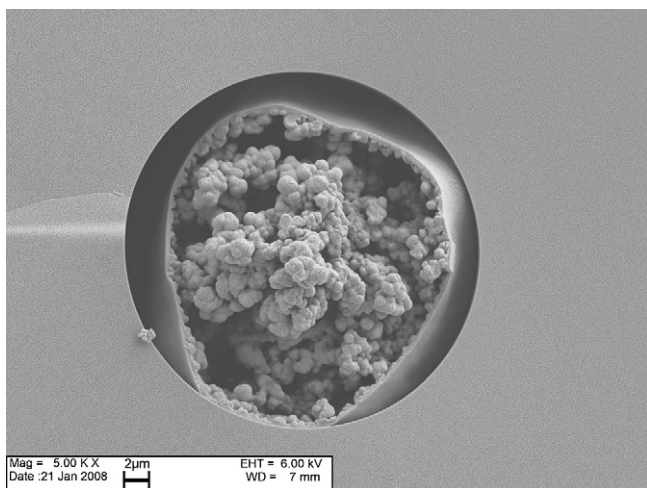


Fig. 5. SEM image of PPM formed in a 30 μm i.d. capillary functionalized with ODS, 5000 \times magnification (scale bar 2 μm). Compare the sheath thickness and morphology to that of Fig. 2a showing a PPM from a similar 250 μm i.d. capillary.

Ultimately, this study has provided an explanation for sheath formation in the fabrication of porous polymer monoliths, and will enable researchers to control sheath morphology and to adapt it to a given application.

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