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Synthesis of Well-Defined Macroporous Polymer Monoliths by Sol−Gel Polymerization in Supercritical CO_2

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The synthesis of continuous macroporous polymers (i.e., "polymer monoliths") is currently a subject of great interest for a variety of applications. These materials may have certain advantages over more traditional macroporous polymer beads, mainly because of the absence of interstitial voids in the "packed" state. Typically, a mold is filled with a polymerization mixture containing a cross-linking monomer, functional comonomers, initiator, and a porogenic diluent. This mixture is then polymerized to form a continuous porous monolith that conforms to the shape of the mold. One drawback of the method is that large volumes of organic solvents are required (typically ∼1:1 solvent to monomer), and these solvents can be hard to remove from the polymer matrix at the end of the reaction. Also, the pore structure of the polymer can be remarkably sensitive to very small changes in the composition of the porogenic solvent mixture. Recently, we have developed methods for the synthesis of highly cross-linked polymer monoliths using supercritical carbon dioxide as the porogenic solvent (Cooper, A. I.; Holmes, A. B. *Adv. Mater.* **1999**, *11*, 1270). In this paper, we describe how it is possible to achieve fine control over average pore sizes and pore size distributions, both by variations in the density of the supercritical solvent and also via reverse micellar imprinting.

Introduction

Macroporous cross-linked polymers are extremely useful in a wide range of applications.[1] Unlike lightly cross-linked polymers, which become porous when swollen by solvents, macroporous polymers have a permanent porous structure that is formed during their preparation and persists in the dry state. The internal macroporous morphology is characterized by interconnected channels (pores) that permeate the rigid, extensively cross-linked polymer matrix. Macroporous resins are often synthesized in the form of uniform beads by suspension polymerization;[2,3] however, this can lead to performance limitations in certain applications, notably the chromatographic separation of large molecules. A very promising alternative approach has been the synthesis of continuous, macroporous monolithic polymers,[4,5] which have been developed for a variety of applications including HPLC, solid-phase extraction, high-performance membrane chromatography (HPMC), capillary electrochromatography, molecular imprinting, and high-throughput bioreactors. Most systems so far have involved the free-radical polymerization of methacrylate or styrene-based cross-linkers (e.g., ethylene glycol dimethacrylate, divinyl benzene). The porogenic diluent can be either solvating or nonsolvating in nature, and carefully chosen ternary solvent mixtures can be used to allow fine control of the porous properties of the monolithic polymers. In some cases, materials have been optimized to incorporate a distribution of small, diffusive pores (<100 nm), interconnected with larger, flow-through pores with diameters in the range of 700−2000 nm. A key advantage of this methodology is that the macroporous polymers can be prepared directly within a variety of different containment vessels, including both wide-bore chromatography columns and narrow-bore capillaries. Potential difficulties associated with the method include shrinkage during polymerization, heterogeneity throughout the sample (particularly for larger monoliths), and poor mechanical stability. However, these problems can often be overcome by appropriate choice of comonomers.

Carbon dioxide is an attractive solvent for polymer chemistry because it is inexpensive, nontoxic, and nonflammable.[6,7] DeSimone and others have shown that supercritical CO_2 ($scCO_2$) is a versatile medium for both homogeneous and heterogeneous polymerization.[8−11] Supercritical carbon dioxide has also been used for the formation of microcellular polymer foams[12−14] and aerogels.[15] Previously, we demonstrated the synthesis of highly cross-linked polymers by heterogeneous polymerization in $scCO_2$.[16] Dry, free-flowing powders were generated, either as irregular microparticles or, with the addition of CO_2-soluble surfactants, as uniform polymer microspheres (0.4−10 μm).[17] In all cases, the polymers were shown to be completely nonporous. More recently, we described for the first time the synthesis of highly cross-linked macroporous polymer monoliths using $scCO_2$ as the porogenic solvent.[18] This approach eliminates the need for any organic solvent in the polymerization procedure and allows the formation of truly solvent-free products. Herein, we discuss how the average pore sizes and pore size distributions for these materials can be tuned by varying the reaction conditions.

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Experimental Section

The polymerization reactions were carried out in stainless steel reactors (either 10 or 40 cm^3 in volume) equipped with sapphire view windows, as described previously.[18] The reactor was cooled to approximately 35 °C after polymerization before the CO_2 was vented. The polymers were removed from the reactor as dry, white, continuous monoliths. (**Safety Note:** These reactions form porous materials that fill almost the entire volume of the reaction vessel. To minimize any risk that residual CO_2 could be trapped within the polymer matrix, the system was typically allowed to stand overnight after venting *before* the reactor was opened.) For porosity/surface area analysis, the monoliths were crushed and sieved to a particle size of greater than 2 mm, to eliminate any contribution from fine powder. Porosity and surface area were measured by a combination of mercury intrusion porosimetry and nitrogen adsorption/desorption (BET method).[18]

Results and Discussion.

Figure 1 shows a series of electron micrographs for a fractured polymer monolith, synthesized using $scCO_2$ as the porogen. The material was formed by the free-radical polymerization of trimethylolpropane trimethacrylate (TRIM) (see caption for reaction conditions). The polymer is highly porous, as can be seen in the lower micrograph. Initially, a clear, homogeneous solution of CO_2, TRIM, and initiator (AIBN) was formed at room temperature. The mixture was then heated to 50 °C, whereupon polymerization was initiated. After approximately 20−30 min, the solution became translucent (i.e., gelation of the CO_2/monomer mixture occurred). After 2 h, the mixture appeared white and opaque, indicating phase separation. The CO_2 was vented, and the polymer was removed as a dry, white, cylindrical monolith that conformed precisely to the shape of the reactor (Figure 2). The pressure could be vented quite rapidly (over a period of a few minutes), and no cracking of the materials was observed during depressurization. However, the mechanical stability of the monoliths was generally quite low, and brittle materials were formed that were easily fractured. One method for addressing this problem would be to incorporate a monofunctional monomer (e.g., MMA), which would be expected to improve the mechanical stability. Alternatively, in real applications (e.g., polymerization within a silica capillary), one might vinylize the capillary walls, thus providing an anchoring point that would minimize polymer shrinkage and also increase mechanical stability.[19]

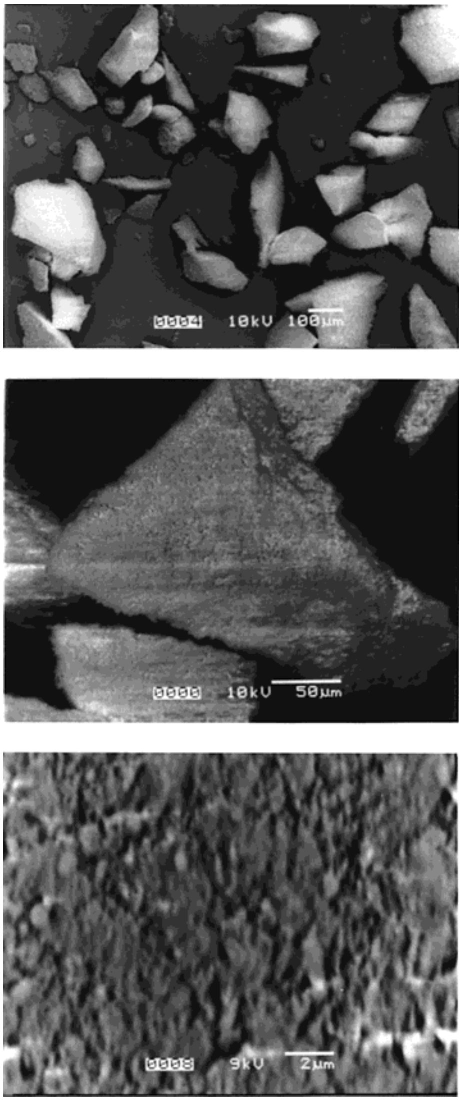

Figure 1. SEM images showing a fractured porous monolith at increasing magnification. Surface area = 328 m^2/g. Median pore diameter = 20 nm. (Samples were sputter-coated with 2 nm of gold before analysis.) Scale bar = 100 μm (top), 50 μm (middle), and 2 μm (bottom). Reaction conditions: TRIM (60% v/v), CO_2 (40% v/v, 310 bar), AIBN (2% w/v based on TRIM), 50 °C, 12 h.

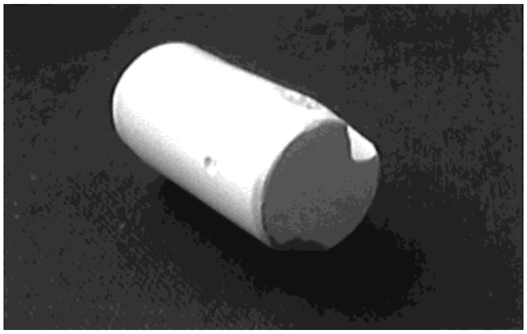

Figure 2. Photograph showing cross-linked polymer monolith prepared in $scCO_2$ (60% v/v). Approximate dimensions: diameter = 19 mm, length = 40 mm.

Our process differs from the method described by Beckman[12,13] in that the TRIM-based polymer is much more rigid and highly cross-linked. As a consequence, pore growth via gas expansion was not a viable mechanism, and the pore structure of these materials was not microcellular, but rather consisted of a series of interconnected channels between fused particles. In this sense, our method is more similar to the sol−gel route described by Shea, although our materials have very different pore sizes and chemical structures.[15] It was found that monomer concentration had a very strong influence on the porous properties of monoliths formed via this route.[18] For example, the monolith shown in Figure 1 was prepared from a 60:40 v/v TRIM/CO_2 mixture and had a median pore diameter of 20 nm and a surface area of 328 m^2/g. By contrast, a similar monolith prepared from a 40:60 v/v TRIM/CO_2 mixture was found to have a median pore diameter of 7880 nm and a surface area of just 5.2 m^2/g. In general, higher monomer concentrations led to smaller average pore sizes and larger surface areas. Below a threshold monomer concentration of between 30 and 35% v/v,

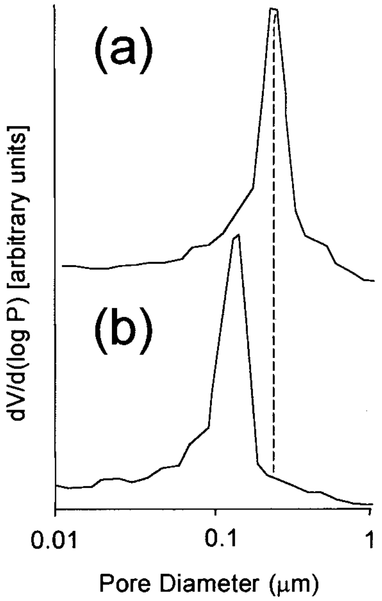

Figure 3. Pore size distributions (as measured by Hg intrusion porosimetry) for polymer monoliths synthesized at two different CO_2 pressures. (a) $P(CO_2) = 155$ bar; (b) $P(CO_2) = 310$ bar. Reaction conditions: TRIM (50% v/v), CO_2 (50% v/v), AIBN (2% w/v based on TRIM), 50 °C, 12 h.

monolithic products were *not* formed, and polymers were isolated as free-flowing microgel powders.[17] Variations in monomer concentration led to the formation of materials with average pore sizes and surface areas that spanned a very broad range (i.e., 10−8000 nm and 5−350 m^2/g). One of our aims was to identify methods whereby these properties could be "fine-tuned" for particular applications. First, our results indicate that it is possible to influence pore size distributions by varying the CO_2 pressure (and hence the CO_2 density). Figure 3 shows pore size distributions for porous monoliths synthesized at two different pressures [(a) 155 bar, (b) 310 bar]. All other reaction variables were exactly equivalent in the two experiments. It is important to note that the relative *volumes* of CO_2 and monomer are the same in both experiments (because the volume of the high-pressure cell is constant). It is the *density* of the CO_2 phase (and hence the solvent properties) that varies. It is clear that the monolith synthesized at the higher pressure (Figure 3b) has significantly smaller pores (100 vs 185 nm) and a correspondingly larger surface area (269 vs 89 m^2/g). This is analogous to varying pore size by changing the porogenic solvent composition, and our early results are in accordance with previous studies in which an increase in the porogenic solvent strength led to smaller average pore diameters and larger surface areas.[20,21] We are currently evaluating a similar method for control over pore size in the synthesis of macroporous polymer beads via oil-in-water suspension polymerization.[22]

Another method for the control of pore size distributions in cross-linked polymers is "reverse micellar imprinting", as described by Zhu et al.[23,24] We have shown that this can be achieved in $scCO_2$ by polymerizing TRIM in the presence of an aqueous microemulsion, which acts as a template for pore formation. When TRIM was polymerized at 50% v/v in $scCO_2$, the pore size distribution was narrow and unimodal, peaking at around 100 nm (Figure 4a). When the experiment was repeated in the presence of a water-in-CO_2 microemulsion stabilized by sodium bis(2-ethylhexyl) sulfosuccinate (AOT), the pore size distribution was significantly broader and shifted to include a wide range of pores with much smaller diameters (median pore diameter = 25 nm, Figure 4b). Before polymer phase separation, a clear, transparent aqueous microemulsion was observed in the reaction vessel. Previous studies have shown that it is very difficult to form stable aqueous microemulsions in *pure* $scCO_2$ by using conventional surfactants, and highly fluorinated stabilizers have usually been required.[25] The stability of the microemulsions in our experiments was presumably a result of the high concentration (40−60% v/v) of monomer in the CO_2 phase.

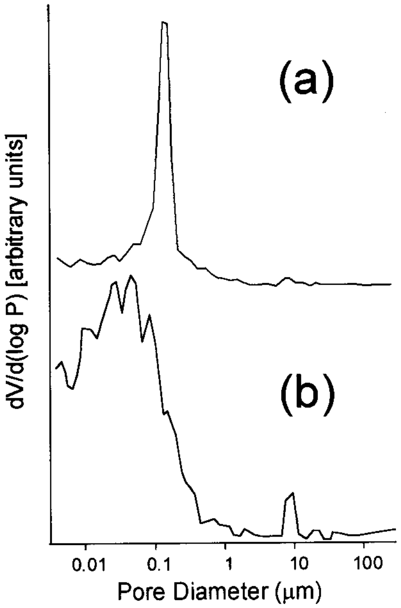

Figure 4. Pore size distributions illustrating the effect of reverse micellar imprinting using $scCO_2$ as the porogenic solvent. Reaction conditions: (a) TRIM (50% v/v), CO_2 (50% v/v); (b) TRIM (50% v/v), CO_2 (37.5% v/v), H_2O (12.5% v/v), AOT (4% w/v based on H_2O); (a) and (b) AIBN (2% w/v based on TRIM), 50 °C, 12 h.

Conclusions

We conclude that it is possible to synthesize well-defined, highly porous cross-linked monoliths using $scCO_2$ as a nonsolvating porogenic diluent. We have demonstrated the synthesis of polymers with narrow, unimodal pore size distributions, without the use of complex ternary solvent mixtures. The separation of solvent from polymer is very simple, and no solvent residues are left in the polymer after depressurization. This may be useful, for example, in the formation of molded macroporous polymers within narrow-bore capillaries, where the removal of the porogenic solvent can be difficult. Preliminary results show that it is possible to fine-tune the pore size distribution with pressure or by reverse micellar imprinting. We believe that our methods can be applied to the synthesis of a wide range of porous materials, and that the approach may be particularly valuable for the preparation of specialized cross-linked porous materials for applications that involve subsequent reexposure to supercritical fluid solvents.

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