Sizeable Macroporous Monolithic Polyamide Entities Prepared in Closed Molds by Thermally Mediated Dissolution and Phase Segregation

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Received January 9, 2008. Revised Manuscript Received August 11, 2008

A simple method is presented for the preparation of macroporous monoliths from an aliphatic polyamide in closed molds, based on swelling/dissolution in benzyl alcohol at elevated temperature, followed by precipitation into a continuous monolithic structure by cooling the solution below the upper critical solution temperature. Subsequent removal of the solvent led to the formation of rigid macroporous nylon monoliths with a continuous and evenly spaced macropore system. The intended use is as supports for flow-through systems, where efficient mass transport at low flow resistance is the key optimization criterion.

Introduction

Porous monolithic polymer structures prepared from organic precursors[1] have evolved into versatile carrier materials in a wide range of flow-through applications in analytical[2] and bioseparations,[3] biocatalysis,[4] etc. Such organic monoliths are almost invariably made by direct mold polymerization of precursor monomers (commonly vinylic,[1] but more recently also based on ring-opening metathesis polymerization[5] and epoxy-based condensation systems[6−8]), in the presence of porogens[9,10] that establish flow-through and diffusive pores in the material. Direct in situ polymerization is simple and has many advantages, but thermal gradients caused by the exothermic polymerization reactions[11] disturb the formation of a spatially homogeneous network of evenly sized macropores, which is essential when large monoliths are prepared for separation purposes.[12] The nonpolymerizable porogens used in conventional direct monolith polymerizations are typically small molecules, selected to be good solvents for the starting monomers, but intermediate to bad solvents for the polymer produced,[10] and a pore formation mechanism based on this principle becomes highly sensitive to the polymerization temperature.[13]

A quite different approach for preparing a sizable monolithic entity would be to start with a ready-made polymer and create the structure by a dissolution/reprecipitation process. Most non-cross-linked polymers can be brought into solution by the action of solvents, and the parameters that determine the swelling and eventual dissolution are the solubility parameters, and the θ temperature of the polymer/solvent system in question.[14] This technique is widely used for preparing thin membranes, where one face of the cast polymer solution layer is open to procedures involving mass transfer, such as evaporation or solvent treatment.[15] The means most often used for controlling the phase separation (establishing deviation from θ conditions) are selective evaporation of the more volatile, better solvent of a solvent pair, or treatment with a nonsolvent. The latter can be accomplished either by immersion in a bath of a nonsolvent, or by depositing such solvent(s) onto the membrane by condensation from the gas phase.[15] However, in contrast to thin membranes made by open solvent casting, monolithic sorbents used for separation and catalytic purposes are typically sizable entities that are prepared in closed molds. Manipulations involving transfer of solvent to or from the precursor solution are therefore not feasible, as with membranes. The required change in solubility of the dissolved polymer must thus be established without mass transfer, and the most facile physical means for effectuating polymer precipitation is the critical solution temperature, which for a given polymer is dependent on the solvent composition.

Polyamides are among the polymers more frequently used for preparing membranes by dissolution/precipitation, and nylon membranes have found a wide range of applications

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10.1021/cm800088a CCC: $40.75
Published on Web 09/12/2008

in environmental,[16,17] biotechnological,[18−24] and medical sciences.[25] These nylon membranes can be made by either of the techniques mentioned above. Selective evaporation of the more volatile "good" solvent from the surface results in fast phase separation, producing a skin of narrow pores with gradually larger pores further away from the surface, caused by slower precipitation since diffusion of the more volatile solvent from the bottom part of the membrane dope is relatively slow.[26] The alternative approach, precipitation by immersion in or deposition of a nonsolvent from the gas phase, typically leads to more even pore distribution. Both techniques rely on increasing the upper critical solution temperature (UCST) by altering the solvent composition via the open surface, and among these techniques, precipitation by treatment with a nonsolvent seems to be most widely used. The solvent/nonsolvent system employed for solvent-induced precipitation of polyamides 6 and 66 is usually formic acid/water,[27] although in some cases more exotic solvent mixtures such as 2,2,2-trifluoroethanol with compressed CO_2 have also been used.[28]

The popularity of polyamide membranes result from a combination of the mechanical durability, the wide range of hydrophilic-hydrophobic properties available in polyamides, and the numerous possibilities that exist for surface functionalization.[29−33] These properties are equally attractive in a monolithic sorbent, and to the best of our knowledge macroporous polyamide has not yet been made as solid porous entities of larger dimensions, only as membranes. Polyamide solutions show an UCST behavior at accessible temperatures in several solvents and we therefore took the most obvious approach, a precipitation through phase separation induced by decrease in temperature. In our scouting experiments reported here, the polyamide source was a regular monofilament fishing line, which enabled us to produce macroporous monoliths in dimension up to 10 mm diameter and 15 mm length, with spatially even micrometer-sized pores of an interesting morphology.

Experimental Section

Reagents and Materials. Spin Abulon 0.70 mm monofilament fishing line (ABU Garcia, Marignier, France; exact composition unknown) was used as initial polyamide source in this work. The benzyl alcohol (p.a.) was from Merck (Darmstadt, Germany) and the methanol used for flushing the benzyl alcohol out of the materials was of "pure grade" from Prolabo (Paris, France).

Macroporous Material Preparation. Polyamide solutions were prepared by adding fishing line chopped into ∼5 mm long pieces (∼100−300 mg) to 1 g benzyl alcohol aliquots in 2 mL borosilicate glass vials, which were crimp-sealed with PTFE-faced septa. Dissolution took place by heating the vials in a convective laboratory oven (Electrolux, Sweden) set at 140 °C, until clear solutions were obtained. The dissolution was facilitated by gentle manual shakes (5−10 s each time). After ∼30 min with 4−5 shaking cycles, the solutions appeared homogeneous and were then kept in the dissolution oven, which was turned off and left closed to retard the cooling process. When the temperature had reached the ambient, the vials were carefully broken to recover the resulting gels as intact as possible. These gels were then subjected to Soxhlet extraction in methanol for 24 h to remove the benzyl alcohol, and then left to dry in air before scanning electron microscopy (SEM) images were taken.

In an experiment designed to investigate the effect of cooling rate, the phase separation of 12% solutions of polyamide (PA) took place in 530 μm i.d. polyimide-coated fused silica capillaries (Polymicro Technologies, Phoenix, AZ) to ensure a fast heat transfer. The ∼10 cm long capillaries used in these experiments were first etched and then treated with 3-glycidoxypropyl-trimethoxysilane (GLYMO) following a procedure similar to that described in ref.[34] This step was implemented to ensure immobilization of the polyamide to the capillary walls through the amino terminals. The hot polyamide solution prepared according to the procedure above was filled into the treated capillaries by piercing one end through the vial septum and applying nitrogen gas pressure to the vial (temporarily removed from the oven in a hot sand bath) through a hypodermic syringe to ensure rapid filling. A sufficient excess of hot solution was flushed to ascertain that the temperature of capillary was above UCST before its ends were closed by pieces of silicone rubber septa. The filled capillaries were thereafter rapidly transferred back to the oven and further heated for 2 h at the dissolution temperature to promote the reaction of the amino end groups with the oxirane groups on the capillary inner wall before the cooling was initiated. Slow cooling took place from 135 to 85 °C at a rate of 0.1 °C/min, controlled by programming the oven of an HP 5890 gas chromatograph. When the lower temperature was reached, the oven was switched off and the vials allowed to remain in the closed oven until it reached room temperature. Fast cooling was accomplished by moving the capillary from the oven directly to the laboratory bench at room temperature. After cooling, the benzyl alcohol was removed from both capillaries by applying partial vacuum (∼100 Pa) at room temperature, with both ends open. Since the solvent had to evaporate through the entire monolithic structure, the capillaries were left under partial vacuum for 4 weeks (a time set by a convenient vacation period)

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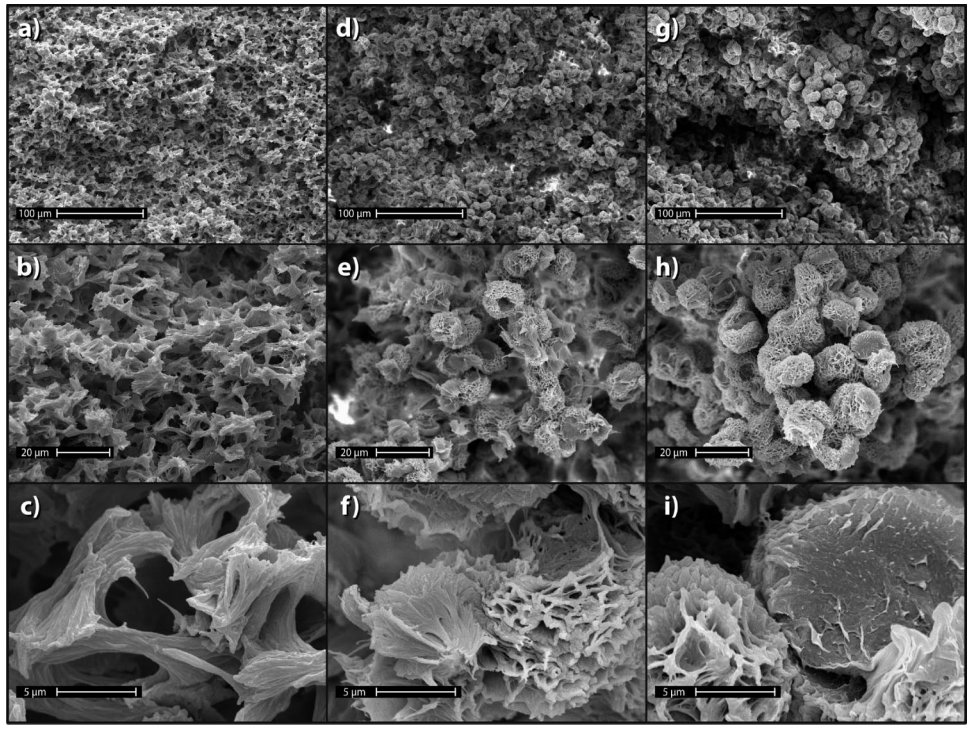

Figure 1. Scanning electron micrographs of random cryogenic fracture surface areas for materials prepared by reprecipitation of polyamide from their benzyl alcohol solutions at (a−c) 10, (d−f) 15, and (g−i) 30% polymer concentration with slow cooling. Images of each sample were acquired at three different magnifications to illustrate the pore homogeniety and skeleton structure.

to ensure complete drying. They were thereafter flushed with methanol using an HPLC pump.

Surface Area Determination. For surface area determination, the gels were divided into cubes with sides of 2−3 mm and exhaustive removal of benzyl alcohol was carried out by renewed methanol Soxhlet extraction for 24 h. Following initial drying in air, the materials were purged by dry nitrogen at 50 °C for 3 h before their specific surface areas were determined by N_2 adsorption−desorption by a Micromeritics (Norcross, GA) Tristar 3000 automated gas adsorption analyzer. Multipoint surface areas and average pore widths of the monoliths were measured, based on the Brunauer−Emmett−Teller (BET) equation.[35]

Scanning Electron Microscopy. Samples for scanning electron microscopy were prepared by freezing the structures in liquid nitrogen and fractioning the pieces by impact or snapping the fused silica capillaries to obtain cryogenic fracture surfaces. The fragments thus obtained were placed on sticky carbon foils (used to increase conductivity), attached to standard aluminum specimen stubs, and coated with a ∼20 nm thick gold layer by using a combination of sputter coating by an Edwards (Crawley, U.K.) model S150A sputter coating unit, and evaporation by a modified Edwards E14 vacuum coating unit, incorporating an automatic tilt and rotate device. Microscopic analysis of all samples was carried out by an S-360 iXP SEM (Leica Cambridge Ltd., Cambridge, U.K.) operated at 10 kV, 100 pA probe current, and 0° tilt angle. Final images were recorded from randomly chosen areas at the magnifications indicated in each SEM.

Results and Discussion

Numerous nonacidic solvents or solvent mixtures have been described in the literature for dissolution of linear aliphatic polyamides.[36−38] Among these are dimethylsulfoxide, dichloromethane, trichloromethane, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, and benzyl alcohol. For the first tests, our choice fell on benzyl alcohol, because it is one of the relatively few solvents capable of dissolving several polyamides, that requires elevated temperature to work; in other words, where the polyamide will undergo the required UCST transition above ambient temperature and thus enable a monolithic structure to be formed without supercooling. Additional selection criteria in favor of benzyl alcohol were low cost and low toxicity. The initial dissolution conditions were chosen based on the work of Robert et al.,[38] who investigated conditions for separation of polyamides for size exclusion chromatography in various solvents.

Duplicate vials with hot polymer solutions at different PA concentrations (10−30%) in benzyl alcohol were divided into two groups; one set was cooled quickly by submersing into an ice bath, whereas the other was kept in the dissolution oven, which was turned off and left closed to retard the cooling process. The SEM images of the monolithic structures produced by slow cooling (Figure 1) show that varying polyamide concentration resulted in clearly different morphologies. At 10% PA (Figure 1a−c), the materials consisted of an evenly spaced macropore system made up by slim, bitapered rods[39] forming interconnects between nodes of

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higher material thickness, making up a three-dimensional polyamide network. The shapes of the structures and the voids indicate that phase segregation and partial crystallization had taken place by the formation of a bicontinuous system, with the polymeric material deposited in the interstices between interconnected solvent droplets. At 15% polyamide concentration (Figure 1d−f), the nodes had grown larger and their surfaces started to turn into coral-like structures; the macropores became irregular, and the bitapered interconnecting rod morphology was clearly less pronounced. At 30% polyamide concentration (Figure 1g−i), the interconnecting rods had completely disappeared, and the rather dense porous material showed irregular macropores of a fused spherulite character, with a highly reticulated surface. Similar structures have also observed in membranes prepared by solvent-induced phase separation.[26,28,39]

The cooling process and/or the way the solvent was removed also had an impact on the morphologies of the monolithic structures produced. The SEMs in Figure 2 reveal that slow cooling of a 12% PA solution followed by Soxhlet extraction with methanol produced a material with relatively small domain size, but with coarse skeleton structure (note the different scales in the SEMs). Fast cooling with subsequent slow evaporation of solvent yielded an evenly distributed filigrain network with a domain size about 2−3 times larger than that seen with slow cooling. The bicontinuous structure was also more pronounced in the rapidly cooled monolith. Note also in Figure 2d that the GLYMO-activation was successful in establishing an attachment of the polyamide to the surface of the fused silica capillary.

Surface area and pore characterization by BET measurements could only be realized for monoliths prepared in vials, and the specific surface area of the monolith prepared with 12% PA (images a and b in Figure 2) was determined to be 6.7 m^2/g. Considering the domain size evident from the SEMs, this indicates that there is little, if any porosity present apart from the external surface of the primary monolithic network. The virtual absence of a mesoporous network would be problematic in applications requiring a high surface loading, such as in the separation of small molecules. However, as we foresee the primary application area of these monoliths in separations of biomacromolecules, the lack of internal mesoporosity is of less concern, as biomacromolecules diffuse slowly and are known to be largely excluded from the internal pore space. On particulate separation materials, proteins separate equally on materials where the functional surface in confined to the perimeter only.[40] Concerning stability, these monoliths should be similar to solvent-cast nylon filters, which have been in use for a long time. The amount of material produced in the capillaries was too low to enable BET measurements and it was also impracticable to recover the structures from the capillary mold.

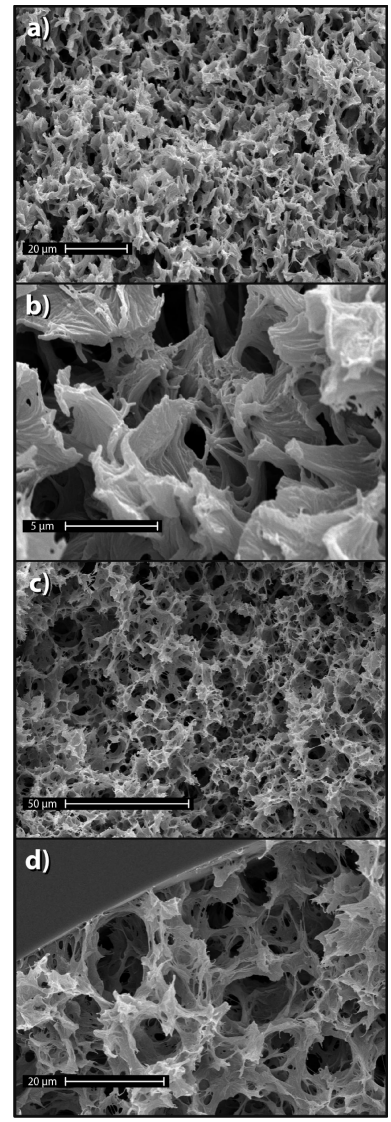

Figure 2. Scanning electron micrographs of monoliths prepared in GLYMO-activated fused silica capillaries by cooling of 12% PA solutions in benzyl alcohol at two different rates; slowly at 0.1 °C/min from (a, b) 135 to 85 °C, and (c, d) direct transfer to room temperature. Note the different magnifications used in the SEMs from the two procedures.

In summary, we describe here an exceptionally simple way of preparing sizable monolithic structures with attractive chemical, physical and porous properties by a simple thermally controlled dissolution and phase segregation process. Preparation and further characterization of macroporous entities based PA6 and several other polyamides of well-defined composition and molecular weight are in progress.

Acknowledgment. The authors are grateful for financial support from the Swedish Foundation for Strategic Research, the Swedish Science Research Foundation, and the Ministry of Training and Education of Vietnam. We are also grateful to Per Hörstedt for preparing the SEMs.

CM800088A

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