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Mesoporous Polystyrene Monoliths

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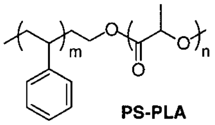
Mesoporous materials, are highly regarded for a range of applications from size/shape-selective catalysts to inner-layer dielectrics.[1] Both mesoporous organic[2] and inorganic[3] frameworks have been synthesized, however advances in the preparation of mesoporous inorganic materials have far outpaced their organic counterparts. For example, in the amphiphile templated synthesis of mesoporous metal oxides, a variety of ordered mesoscopic morphologies (e.g., hexagonally packed cylinders and bicontinuous phases) have been prepared in several macroscopic forms (e.g., powders, films, and fibers). Recently, the preparation of mesoporous silica monoliths was reported with pore sizes in the 10−20 nm range.[4] The formation of well-ordered mesopores in a bulk material is desirable for separations, anisotropic transport, high surface area catalytic monoliths, and other applications. Furthermore, this type of material could be extremely useful as a template for the formation of other nanomaterials (e.g., metal or conducting polymer nanowires).[5] In this communication we describe the preparation of a mesoporous polystyrene (**PS**) monolith through the combination of block copolymer self-assembly, the long-range order resulting from shear alignment, and mild chemical degradation.

The covalent bond connecting two immiscible segments in a diblock copolymer prevents macrophase separation of the thermodynamically incompatible materials and restricts the partitioning of the components to nanoscopic (1−100 nm) domains.[6] The exploitation of nanoscopic heterogeneities in ordered block copolymers for nanomaterial synthesis has resulted in a remarkable array of technological possibilities such as controlled growth of nanoparticles,[7] for nanolithography,[8] and as templates for the formation of mesoporous thin films wherein selective removal of the minority component leaves a matrix filled with nanoscopic voids. In 1988 Nakahama reported the preparation of functionalized **PS**−polyisoprene block copolymer thin films in which the **PS** was cross-linked through a pendant siloxane with HCl and the polyisoprene was selectively removed using a O_3/MeOH protocol.[9] Similar routes to nanoporous thin films using block copolymer precursors and approaches that cross-link the matrix and degrade the minority component have since been investigated.[10] The reported schemes are not easily applicable to bulk materials (e.g., monoliths), cross-linking of the matrix phase limits subsequent chemical and physical manipulation of the porous material, and definition of the chemical functionality at the pore wall is dictated by the degradation chemistry and thus difficult to control. To overcome these limitations we demonstrate a versatile preparation of mesoporous organic monoliths by the preparation of diblock copolymers containing oriented nanoscopic cylinders of degradable polymer (polylactide, **PLA**) embedded in **PS**, an inert, thermoplastic matrix, followed by selective and mild removal of the **PLA**.



PS-PLA

We recently reported the synthesis of **PLA**−polydiene block copolymers using a two-step polymerization sequence.[11] Following that protocol, we prepared a hydroxy-terminated **PS** (M_n = 22 kg/mol (NMR), PDI = 1.02) by anionic polymerization. This material was reacted with triethylaluminum to yield the corresponding aluminum alkoxide macroinitator that was used for the controlled polymerization of D,L-lactide. The resultant block copolymer (**PS**−**PLA**) contained 40% **PLA** by weight and had an overall molecular weight of 37 kg/mol by ^{1}H NMR spectroscopy. By size exclusion chromatography (SEC) a polydispersity index (PDI) of 1.11 was calculated for **PS**−**PLA**. The position of the reflections from small-angle X-ray scattering (SAXS) analysis of **PS**−**PLA** (Figure S1) and the composition of the block copolymer were consistent with a material containing 22 nm diameter cylinders of **PLA** packed on a hexagonal lattice in a **PS** matrix.

The as-synthesized block copolymer consisted of randomly oriented cylinders as evidenced by an isotropic 2-D SAXS pattern. Application of sinusoidal shear to a **PS**−**PLA** melt led to macroscopic alignment as seen by the 2-D SAXS analysis (Figure 1a and 1b).[12] While we have not analyzed the degree of alignment in detail,[13] the 2-D pattern shown in Figure 1a was reduced to a 1-D form by summing the intensity in a band ($\Delta q = 0.04$ nm^{-1}) centered on the principal scattering wave vector (q^*) as a function of angle. The peak-to-valley ratio was 10, and using established protocol for aligned liquid crystalline polymers we calculated an anisotropy factor of 0.7 for shear oriented **PS**−**PLA**, indicating a high degree of cylinder orientation parallel to the flow direction.[14]

A **PS**−**PLA** monolith (6.7 × 3.4 × 0.32 mm) with the cylinders of **PLA** oriented in the plane of the sample was prepared

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[1] (a) Nguyen, C. V.; Carter, K. R.; Hawker, C. J.; Hedrick, J. L.; Jaffe, R. L.; Miller, R. D.; Remenar, J. F.; Rhee, H.-W.; Rice, P. M.; Toney, M. F.; Trollås, M.; Yoon, D. Y. *Chem. Mater.* **1999**, *11*, 3080. (b) Hedrick, J. L.; Carter, K. R.; Richter, R.; Miller, R. D.; Russell, T. P.; Flores, V.; Meccereyes, D.; Dubois, P.; Jerome, R. *Chem. Mater.* **1998**, *10*, 39.

[2] Johnson, S. A.; Ollivier, P. J.; Mallouk, T. E. *Science* **1999**, *283*, 963.

[3] Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

[4] (a) Melosh, N. A.; Davidson, P.; Chmelka, B. F. *J. Am. Chem. Soc.* **2000**, *122*, 823. (b) Feng, P. Y.; Bu, X. H.; Stucky, G. D.; Pine, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 994.

[5] Martin, C. R. *Science* **1994**, *266*, 1961.

[6] (a) Hamely, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998. (b) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525. (c) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.

[7] (a) Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195 ff. (b) Fogg, D. E.; Radzilowski, L. H.; Blanski, R.; Schrock, R. R.; Thomas, E. L. *Macromolecules* **1997**, *30*, 417.

[8] Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.

[9] Lee, J.-S.; Hirao, A.; Nakahama, S. *Macromolecules* **1988**, *21*, 274.

[10] (a) Liu, G. J.; Ding, J. F.; Hashimoto, T.; Kimishima, K.; Winnik, F. M.; Nigam, S. *Chem. Mater.* **1999**, *11*, 2233. (b) Hashimoto, T.; Tsutsumi, K.; Funaki, Y. *Langmuir* **1997**, *13*, 6869. (c) Chan, V. Z. H.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D.; Thomas, E. L. *Science* **1999**, *286*, 1716. (d) Hedrick, J. L.; Carter, K. R.; Richter, R.; Miller, R. D.; Russell, T. P.; Flores, V.; Meccereyes, D.; Dubois, P.; Jerome, R. *Chem. Mater.* **1998**, *10*, 39. (e) Thurn-Albrecht, T.; Steiner, R.; DeRouchey, J.; Stafford, C. M.; Huang, E.; Bal, M.; Tuominen, M.; Hawker, C. J.; Russell, T. *Adv. Mater.* **2000**, *12*, 787.

[11] (a) Schmidt, S. C.; Hillmyer, M. A. *Macromolecules* **1999**, *32*, 4794. (b) Wang, Y.; Hillmyer, M. A. *Macromolecules* **2000**, *33*, 7395.

[12] Following the protocol described in Winter, H. H.; Scott, D. B.; Gronkski, W.; Okamoto, S.; Hashimoto, T. *Macromolecules* **1993**, *26*, 7236, we sheared the **PS**−**PLA** at 160 °C, 99% strain, and 0.5 rad/s for 4 h. By both SAXS and rheological analysis, we demonstrated that this sample remained ordered up to at least 200 °C, consistent with the large incompatibility of the two components. See: Rosedale, J.; Bates, F. S.; Almdal, K.; Mortensen, K.; Wignall, G. D. *Macromolecules* **1995**, *28*, 1429.

[13] Wang, H.; Newstein, M. C.; Chang, M. Y.; Balsara, N. P.; Garetz, B. A. *Macromolecules* **2000**, *33*, 3719.

[14] (a) Cinader, D. K.; Burghardt, W. R. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 3411. (b) Tepe, T.; Schulz, M. F.; Zhao, J.; Tirrell, M.; Bates, F. S.; Mortensen, K.; Almdal, K. *Macromolecules* **1995**, *28*, 3008.

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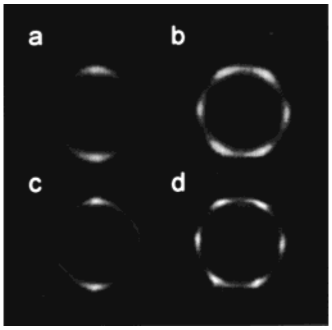

Figure 1. 2-D SAXS patterns for **PS−PLA** perpendicular to cylinder direction before (a) and after (c) degradation. The same sample oriented parallel to the cylinder direction before (b) and after (d) degradation.

and placed in an aqueous methanol mixture containing sodium hydroxide at 65 °C, a temperature below the glass transition temperature (T_g) of **PS** but above the T_g of **PLA**.[15] Under these conditions **PLA** is susceptible to main-chain cleavage,[16] and **PS** is both insoluble and inert. After 44 h the plaque was removed from the degradation solution, was thoroughly washed with water and methanol, and was dried at rt under vacuum for 16 h.

The dried plaque retained its original shape, was translucent,[17] lost 40% of its original weight, and had a density of 0.6 g/cm^3. A small piece of the plaque was analyzed by SEC and ^{1}H NMR spectroscopy. By SEC the degraded **PS−PLA** had a molecular weight and a molecular weight distribution virtually identical to the hydroxy-terminated **PS** starting material (Figure S2). By ^{1}H NMR spectroscopy the degraded piece and the **PS** starting material were virtually indistinguishable (Figure S2). These data were consistent with the formation of a **PS** plaque containing nanochannels through selective etching of the **PLA**. SAXS analysis of the degraded plaque was used to confirm the existence of nanochannels. The fundamental spacing and ordered-state symmetry of the material was retained upon degradation, although the intensity of the principal peak increased by a factor of 24. This increase is consistent with the calculated increase in electron density contrast between an ordered **PS−PLA** material and the corresponding voided structure (Figure S1). Furthermore, the alignment of the nanostructure was also retained as evidenced by the 2-D SAXS pattern of the degraded material (Figure 1c and d).

A real space image of the degraded **PS−PLA** plaque provided confirming evidence for the formation of a mesoporous **PS** monolith with close-packed, aligned nanochannels. A fractured surface of the degraded **PS−PLA** was examined by high-resolution SEM.[18] An image of the fractured surface (Figure 2) is dominated by hexagonally packed holes (defects and fractures can also be observed). This image (and several other similar images) confirmed an array of ordered holes with a 16 nm average diameter and a center-to-center distance of 32 ± 2 nm, consistent with the SAXS analysis and the estimated Pt coating thickness.

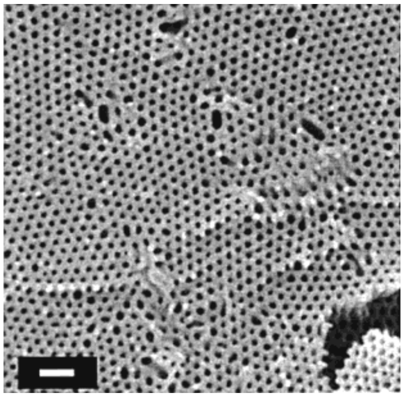

Figure 2. Scanning electron micrographs of the nanoporous materials. SEM micrographs of the degraded **PS−PLA** fractured surface. The white scale bar in the lower left corner is 100 nm.

The ability to fill the nanochannels of these mesoporous materials is important for nanotemplating applications. Furthermore, a continuous path through the material is important for transport properties. This pore fidelity was established by transport of methanol through the monolith. A porous monolith of **PS** was dipped into a colored methanol solution with the pores oriented vertically, and the solution filled the nanochannels until the entire piece was colored.[19] At this point, we cannot be sure that every pore enjoys an uninterrupted path through the entire sample. However, the fusion of two adjacent cylinders into one, a possible defect, would preserve the fidelity of the pore(s). Evidence for this type of defect (larger oval holes) can be seen in Figure 2. Further experiments to quantify the pore fidelity are currently under investigation.

The **PS** monoliths described contain nanochannels with an areal pore density of 10^{11}/cm^2 and a pore aspect ratio of 10^6 for a perfectly aligned channel. This methodology can easily be extended to different pore sizes by controlling the block copolymer molecular weight or by blending. On the basis of the degradation chemistry and preliminary NMR spectroscopy evidence (Figure S3), a single hydroxyl group for every **PS** chain resides within the pore structure, providing a chemical hook for further pore functionalization. Furthermore, the **PS** matrix can be readily manipulated (e.g., dissolution) since the preparation of these materials does not rely on cross-linking.

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Supporting Information Available: Figures S1, S2, and S3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The degradation solution was a 40/60 (v/v) mixture of methanol and water, and the sodium hydroxide concentration was 0.5 M.

(16) Tsuji, H.; Ikada, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 59.

(17) A plaque of PS homopolymer subjected to the same degradation conditions resulted in almost no change in optical clarity.

(18) SEM samples were cut and mounted on brass shims using CCC Carbon Adhesive (Electron Microscopy Sciences), sputter-coated with approximately 2 nm of Pt and analyzed by a Hitachi S-900 FE-SEM using a 5 kV accelerating voltage. The Pt-coating thickness is based on a calculated deposition rate and experimental deposition time.

(19) No transport of methanol through a nondegraded monolith or a monolith with the pores oriented horizontally was observed.