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Communications to the Editor

Nanoporous Polystyrene Containing Hydrophilic Pores from an ABC Triblock Copolymer Precursor

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Nanoporous polymeric materials are versatile structures with a broad range of potential and realized applications;[1] they can serve as templates for the synthesis of nanoobjects[2] and for confined crystallization,[3] be utilized as membranes for selective transport,[4] and be employed as high surface area supports for catalysis applications.[5] Furthermore, nanoporous structures with hydrophilic pore environments are useful for biological applications such as antibody or enzyme immobilization[6] and selective transport and separation of biomolecules.[7] Such a diverse set of applications necessitates versatile methodologies for the preparation of nanoporous materials with wide-ranging properties. Relative to their inorganic cousins, organic/polymeric nanoporous materials[8−10] are readily amenable to controlled functionalization. In this Communication, we describe a route to nanoporous polymeric monoliths with controlled pore wall functionality from the degradation of ordered ABC triblock copolymers.

Recently, Zalusky et al.[11,12] and Wolf et al.[13] reported the synthesis of mesoporous monoliths with aligned, uniform pores from polylactide (PLA) containing diblock copolymer precursors by selective removal of the PLA. The hydrolytic degradation process leaves hydroxyl groups on the internal surface of the pores, which are accessible for further functionalization.[12] However, the concentration of these polar groups is not high enough to have a significant effect on the pore surface properties, and therefore, the internal pore environment is dictated by the properties of the matrix (e.g., polystyrene (PS)). As a result, the synthesized nanoporous materials possess hydrophobic channels inaccessible to water. One of the attempts to circumvent this limitation was recently reported by Mao et al., where an AB/AC blending strategy was used to create nanoporous PS monoliths with poly(ethylene oxide) functionalized pores.[14]

Compared to their diblock counterparts, ABC triblock copolymers possess a diverse morphological spectrum, and with appropriate molecular design can serve as versatile templates for the preparation of mesoporous structures.[15] Our approach utilizes an ABC triblock copolymer that contains a short hydrophilic middle block (B) and that forms a cylindrical morphology. Selective degradation of the sacrificial component leaves the nondegradable block B “coating” the pore walls and renders the pores hydrophilic (Figure 1).

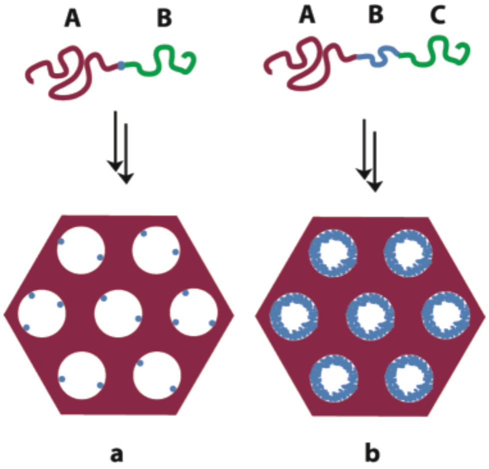
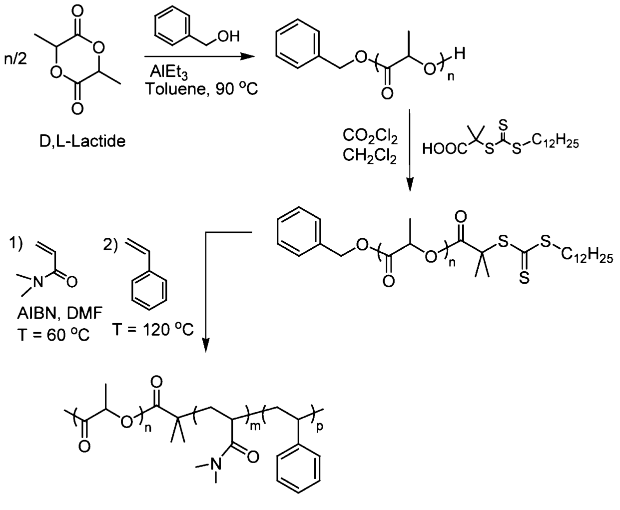


Figure 1. Schematic representation of a nanoporous material obtained from an AB diblock (a) and an ABC triblock (b) copolymer precursors, each with one degradable block (green).

Scheme 1



PLA-PDMA-PS

By using a combination of controlled ring-opening and free-radical polymerizations (Scheme 1),[16] we prepared a polylactide−poly(*N*,*N*-dimethylacrylamide)−polystyrene (PLA−PDMA−PS) triblock copolymer, where PLA is the etchable component, PDMA is the hydrolytically stable hydrophilic and water-soluble component,[17] and PS is the matrix material. Size exclusion chromatography (SEC) analysis (Figure S1 of the Supporting Information) indicated high reinitiation efficiency for all segments, and the final triblock copolymer was obtained with a number-average molecular weight (M_n) of 46 kg mol^{-1} and a polydispersity index (PDI) of 1.12. From

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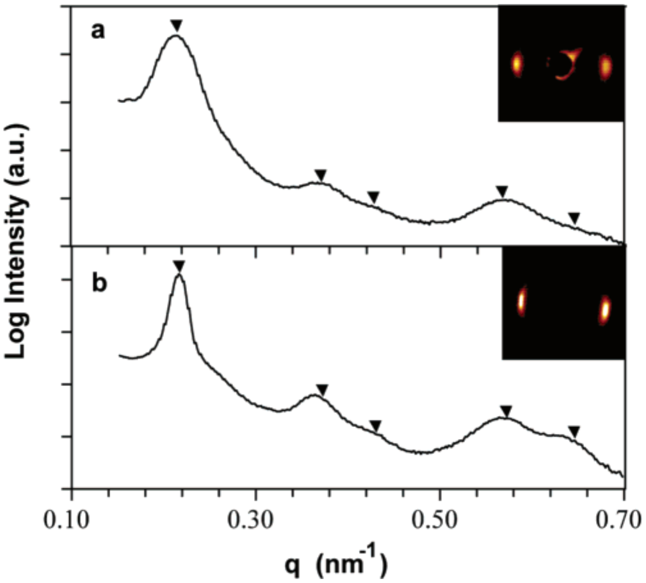

Figure 2. SAXS profiles for shear-aligned PLA−PDMA−PS triblock copolymer (a) before and (b) after PLA removal. The insets show 2D patterns taken perpendicular to the flow direction. Triangles indicate expected reflections for a hexagonally ordered structure (1:$\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$:$\sqrt{9}$).

^{1}H NMR analysis, the absolute molecular weights were calculated to be 11, 3.2, and 29 kg mol^{-1} for PLA, PDMA, and PS, respectively ($n = 156$, $m = 32$, $p = 279$ in Scheme 1).

Samples of PLA−PDMA−PS were aligned in a channel die at 160 °C and cooled to RT.[12] Small-angle X-ray scattering (SAXS) analysis of the resulting monoliths indicated the formation of a structure with hexagonal symmetry and a principal spacing (d^*) of 29 nm (Figure 2a). Anisotropic 2D-SAXS patterns taken perpendicular to the flow direction were consistent with oriented microstructure (a second-order orientation factor (F_2) of 0.83 was calculated from these patterns).[12] On the basis of the morphological behavior of the corresponding PS−PLA diblock copolymers[12] at the same PS volume fraction ($f_{PS} = 0.70$)[18] and the low molecular weight of PDMA, the morphology most consistent with the data is hexagonally packed PLA cylinders in a PS matrix with the short PDMA blocks localized at the PS−PLA interface.

Ordered bulk samples of PLA−PDMA−PS were degraded in a 0.5 M water/methanol solution of sodium hydroxide. After 4 days at 65 °C, the samples were removed, washed with water and methanol, and thoroughly dried under vacuum. Dried pieces lost 26% of their original weight, consistent with the fraction of PLA in the triblock copolymer precursor (25%), and had a density of approximately 0.74 g cm^{-3}. ^{1}H NMR analysis indicated complete removal of PLA, and the ratio of PS to PDMA in the degraded sample was virtually identical to the precursor material (Figure S2). SEC of the degraded PLA−PDMA−PS monoliths showed a monomodal peak with $M_n = 38$ kg mol^{-1} and PDI = 1.16, corresponding to the remaining PDMA−PS diblock copolymer. SAXS analysis of the degraded monoliths confirmed the retention of the principal spacing, hexagonally ordered structure, and degree of orientation ($d^* = 29$ nm, $F_2 = 0.93$, Figure 2b). The principal peak was a factor of 26 more intense for the porous sample consistent with the expected increase in electron density contrast upon removal of PLA.[9,12]

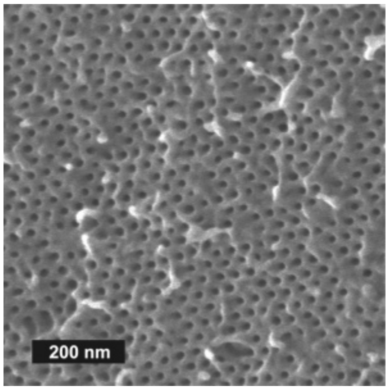

Figure 3. Scanning electron micrograph of the fractured surface of nanoporous material prepared from the PLA−PDMA−PS triblock copolymer precursor.

Figure 3 shows a typical scanning electron microscopy (SEM) image of a nanoporous PDMA−PS fractured surface and demonstrates the existence of a nanoporous structure arranged on a hexagonal lattice, with an average pore diameter of 19 ± 2 nm and an average principal spacing of 29 ± 2 nm, in agreement with the SAXS data.

Nanoporous monoliths prepared by this protocol contain hydrophilic PDMA, and the PDMA is presumably coating the pore walls based on the connectivity of the blocks. Consistent with this hypothesis, when the nanoporous PDMA−PS monoliths were placed in water, they sank to the bottom of the vessel within a few minutes, indicating efficient water uptake into the pores. (The densities of PS and PDMA are both larger than that of water.[18]) In contrast, nanoporous polystyrene monoliths obtained from PS−PLA diblock copolymers remain on the surface of water for several months.[19] After soaking in water for 1 h, nanoporous PDMA−PS pieces showed a 22% increase in weight, consistent with the calculated pore volume. The amount of absorbed water was confirmed by thermogravimetric analysis of the water soaked monoliths (Figure S3). Additional evidence for the presence of water inside the nanopores was obtained by differential scanning calorimetry. A significant melting point depression (ΔT_m) of −6 °C was observed for ice formed by cooling water soaked monoliths to −30 °C (Figure S4). Such a decrease in melting temperature (T_m) cannot be solely explained by the presence of PDMA chains inside the pores. (A ΔT_m of −0.2 °C was calculated for a solution with the same concentration of PDMA in water.) We propose confinement of water inside the nanopores is the major contributor to the melting point depression.[20−22]

By combining new controlled polymerization methodologies, ABC block copolymer self-assembly, and selective etching protocol, we have demonstrated that nanoporous polystyrene can be prepared with aligned, narrow-size-distribution hydrophilic pores that render the materials water-comaptible. This development will enable many applications of these materials that require access of the pore structure by aqueous solutions including biocatalysis, water purification, and biomolecule separations.

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Supporting Information Available: Figures S1−S4 and the experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) According to the Gibbs−Thompson relationship, ΔT_m for water confined inside the pores with 19 nm diameter is predicted to be −2 °C.[21] This and related findings (Ha, J.-M.; Hillmyer, M. A.; Ward, M. D. *J. Phys. Chem. B,* in press) suggest that the interaction between the substances and the pore walls in confined crystallization may play a significant role in the observed melting point depression.

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