

#### **CB-I-4**

### **PREPARATION AND CHARACTERIZATION NANOPOROUS MONOLITHS FROM POLYLACTIDE CONTAINING BLOCK COPOLYMERS**

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Due to their unique self-assembly properties, block copolymers have attracted wide interest in applications that exploit their nanoscopic features. One of the ways in which this predictable self-assembly has been exploited is in the preparation of nanoporous materials from ordered block copolymer templates.<sup>2-6</sup> Nanoporous organic materials have potential utility as nanostructure templates, separation membranes or in controlled delivery applications. The general strategy consists of synthesizing a block copolymer that self-assembles into hexagonally packed cylinders or gyroid microstructures and then removing the minority component in a manner that permits retention of the matrix integrity. For diblock copolymers, these specific morphologies can be targeted and the size and spacing of the morphological features can be predicted with knowledge of the molecular properties of the components and the interaction parameter. The majority of the work in the preparation of nanoporous polymers from block copolymer templates has concentrated on thin films in which the matrix is crosslinked.

We have prepared nanoporous monoliths from block copolymer precursors with a degradable minority component, polylactide (PLA). Nanoporous materials were prepared following a three-step process involving synthesis (controlled polymerization) of a polystyrene (PS)-PLA block copolymer precursor, alignment of the microstructure (channel die processing), and degradation/removal of the PLA block leaving a nanoporous PS framework.<sup>7</sup> The resulting materials have well-ordered pores in the size range of 10 to 50 nm.

In the final step, the PLA block was degraded by immersing the oriented templates in a solution of NaOH in water/methanol. In this alkaline medium, the ester bonds along the PLA backbone were hydrolytically cleaved and the resulting oligomers and monomers diffused out of the newly formed pores. In this manner all of the PLA was removed leaving the desired nanoporous monolith. This process was monitored by blending the PS-PLA precursor with a dye, amaranth. PS-PLA/amaranth blends were processed in the same manner as previous templates and immersed in alkaline solution. During the PLA-removal process, amaranth was released and its concentration was measured by UV-Vis spectroscopy. The kinetic data obtained in this manner shows a square-root time dependence, which is characteristic of a Fickian diffusion process.

Scanning electron microscopy (SEM) allowed us to image both the PS-PLA template and the nanoporous PS monoliths. Both PS-PLA and nanoporous PS samples showed negative charging at the lowest working voltage (1.0 keV) of the microscope (Hitachi S-900). Thus, to facilitate observation of the PS-PLA precursor, we stained the PS matrix with RuO<sub>4</sub> and coated the sample with carbon. We were then able to image the microstructural features in the backscattered electron mode at high voltage (20-30 keV). To image the nanoporous materials, a thin coat of Pt (3-4 nm) was applied using an ion-beam sputter coater and the secondary electron mode was used to image the surface. Using these methodologies we were able to readily image both the PS-PLA precursor materials and the nanoporous PS monoliths. Images of the monoliths allowed for an estimation of the pore size, channel fidelity, and defect identity.

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