Nanoporous Polystyrene by Chemical Etching of Poly(ethylene oxide) from Ordered Block Copolymers

Huiming Mao and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431

Received January 3, 2005
Revised Manuscript Received February 23, 2005

Chemically etching the minority component from block copolymers can lead to ordered nanoporous materials with narrow pore size distributions.[1] The key to successful generation of nanoporous materials in this way is to utilize a selective etching protocol that does not compromise the integrity of the matrix material. Since this was first accomplished by ozone etching of polyisoprene from functionalized polystyrene (PS) containing block copolymers,[2] a variety of nanoporous polymers have been prepared using an assortment of etching protocols.[1] Conspicuously absent from the list of etchable materials is poly(ethylene oxide) [PEO]. Given the large variety of available block copolymers containing PEO,[3] the development of a selective PEO etching protocol could prove to have wide ranging applicability for the development of new nanoporous materials. Furthermore, given the recent work on thin films of PS−PEO block copolymers by simple spin-coating procedures,[4] an effective etching of PEO could generate nanolithographic templates[5] with unprecedented long-range order. In this Note we describe a simple procedure for the generation of nanoporous PS from ordered PS−PEO block copolymers using aqueous hydrogen iodide.

PS−PEO is a common diblock copolymer with established morphological behavior,[6] and the HI-mediated cleavage of aliphatic ether linkages (as found in PEO) is well-known.[7] We envisioned that treatment of an ordered PS−PEO block copolymer with aqueous HI would yield nanoporous PS, akin to the degradation of polylactide (PLA) from ordered PS−PLA samples[8] or poly(dimethylsiloxane) from ordered PS−PDMS samples.[9] To test this hypothesis, we prepared a PS−PEO sample with a PS molecular weight of 27 kg mol^{-1} (^{1}H NMR end group analysis and SEC), a PEO molecular weight of 13 kg mol^{-1} (^{1}H NMR spectroscopy), and a PDI of 1.04 (SEC with PS standards) using established methodologies.[10] A channel die-aligned[8] sample of this material (1 × 2 × 55 mm^3) was then prepared. Considering the volume fraction of PEO ($f_{PEO} = 0.30$)[11] and both the 1-D and 2-D small-angle X-ray scattering (SAXS) data at 25 °C, this sample contained aligned 17 nm diameter cylinders of PEO in a matrix of PS. A section of this sample (about 15 mm^3) was immersed in a 57 wt % aqueous HI solution at 60 °C for about 5 days, neutralized with an aqueous NaOH solution for 4 h, and thoroughly rinsed with methanol and water. The ^{1}H NMR spectrum of the degraded sample showed no evidence of PEO, and the SEC data were consistent with removal and preservation of the PEO and PS, respectively (Figure 1).[8,12]

* To whom correspondence should be addressed: e-mail hillmyer@chem.umn.edu.

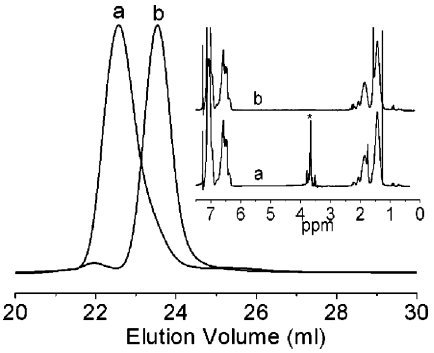

Figure 1. ^{1}H NMR spectra and SEC traces of PS−PEO before (a) and after (b) HI treatment. The * denotes that the resonance for the PEO backbone protons was truncated for clarity. The ^{1}H NMR data were acquired in $CHCl_3$ (RT), and the SEC data were acquired in THF (40 °C) using a flow rate of 1 mL min^{-1}.

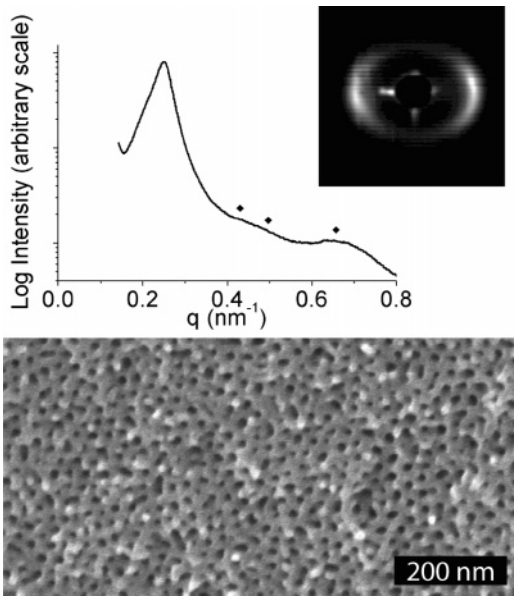

Figure 2. 1-D and 2-D SAXS data of PS−PEO sample after HI treatment and a SEM image of the nanoporous PS sample. Expected reflections for a cylindrical microstructure are marked by diamonds ($\sqrt{3}$, $\sqrt{4}$, and $\sqrt{7}$). The SAXS data were acquired using Cu Kα X-rays ($\lambda = 1.542$ Å) from a Rigaku RU-200BVH rotating anode equipped with a 0.2 × 2 mm microfocus cathode and Franks mirror optics. 2-D scattering data were recorded on a Siemens multiwire area detector. The SEM sample was mounted onto a brass shim and sputter-coated with Pt before analysis using a high-resolution Hitachi S-900 FE-SEM at an accelerating voltage of 3 keV.

Analysis of the HI-treated sample by SAXS showed essentially no change in alignment (as determined by the second-order orientation factor[8]) or principal spacing compared to the PS−PEO starting material. The intensity of the primary scattering peak for the degraded sample was 40 times larger than the parent PS−PEO, consistent with expected increased scattering contrast. 1-D and 2-D SAXS data of the degraded sample are shown in Figure 2 along with a scanning electron microscopy (SEM) image, confirming the nanoporous structure. The pores in the SEM image are about 15 ± 1 nm in diameter, consistent with the PEO cylinder diameter in the original PS−PEO considering the Pt

10.1021/ma050008z CCC: $30.25
Published on Web 04/05/2005

coating used to prevent sample charging.[8] This simple and effective PEO degradation protocol can, in principle, be applied to a wide range of PEO-containing diblock copolymers.

Acknowledgment. The National Science Foundation (DMR-0094144) and the David and Lucile Packard Foundation supported this research.

References and Notes

(1) Hillmyer, M. A. *Adv. Polym. Sci.* **2005**, in press, and references therein.
(2) Lee, J.-S.; Hirao, A.; Nakahama, S. *Macromolecules* **1988**, *21*, 274.
(3) Xie, H.-Q.; Xie, D. *Prog. Polym. Sci.* **1999**, *24*, 275.
(4) Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 226.
(5) Thurn-Albrecht, T.; Schotter, J.; Kästle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.
(6) For example see: Huang, P.; Zhu, L.; Cheng, S. Z. D.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Lotz, B.; Hsiao, B. S.; Liu, L.; Yeh, F. *Macromolecules* **2001**, *34*, 6649. Sun, L.; Zhu, L.; Ge, Q.; Quirk, R. P.; Xue, C.; Cheng, S. Z. D.; Hsiao, B. S.; Avila-Orta, C. A.; Sics, I.; Cantino, M. E. *Polymer* **2004**, *45*, 2931.
(7) Burwell, R. L., Jr. *Chem. Rev.* **1954**, *54*, 615.
(8) Zalusky, A. S.; Olayo-Valles, R.; Wolf, J. H.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 12761.
(9) Ndoni, S.; Vigild, M. E.; Berg, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 13366.
(10) For example see: Bailey, T. S.; Pham, H. D.; Bates, F. S. *Macromolecules* **2001**, *34*, 6994.
(11) At 140 °C using $\rho_{PS} = 0.969$ g cm^{-3} and $\rho_{PEO} = 1.064$ g cm^{-3}. See: Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
(12) The high molecular weight peak present in the HI-treated sample is approximately double the molecular weight of $PSCH_2CH_2OH$ starting material used for the PS−PEO synthesis and is likely a result of a low level of coupling (i.e., $PSCH_2CH_2OCH_2CH_2PS$) mediated by HI.

MA050008Z