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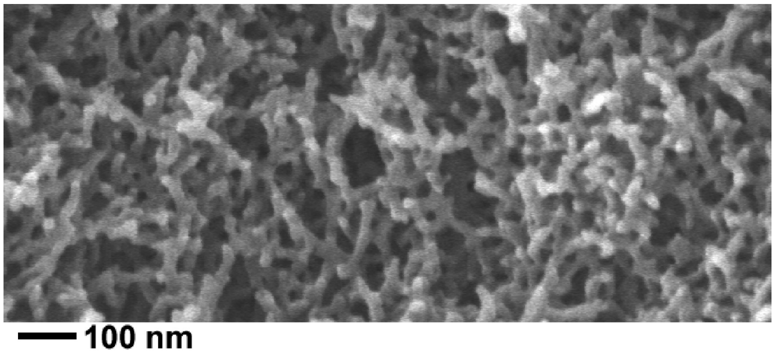

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Robust Nanoporous Membranes Templated by a Doubly Reactive Block Copolymer

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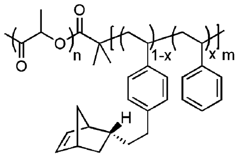
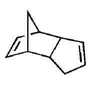
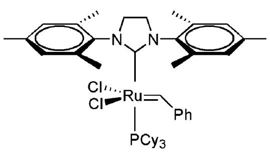
Block copolymers are versatile hybrid macromolecules that have been used in the preparation of a wide variety of nanoporous materials. The incompatibility of distinct chemical segments leads to their nanoscopic self-organization and utility as structure directing agents.[1] Syntheses of nanoporous ceramics,[2] nanofoams,[3] and various nanoporous plastics have been demonstrated using block copolymers as key components.[4] For example, several groups have shown that removal of the minority component from a self-assembled block copolymer that adopts a hexagonally packed cylindrical or bicontinuous gyroid morphology leads to the formation of an ordered array of nanopores in the majority (matrix) component.[5−8] Nanoporous separation membranes can be prepared in this way, and recent examples demonstrating the promising potential of such membranes have appeared.[9] In this communication, we describe a method that combines polymerization-induced phase separation (PIPS)[10] and a "doubly reactive" block copolymer to give nanoporous membranes with two desirable features: a percolating pore structure and significant mechanical strength.



PLA-*b*-P(N-*s*-S)



DCPD



2nd generation Grubbs catalyst

The ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) yields a thermosetting material that exhibits chemical robustness, mechanical toughness, and thermal stability.[11] Macroporous variants of polyDCPD prepared by ROMP of DCPD in the presence of a porogen (via PIPS) have been demonstrated to be useful as chromatographic supports.[12] To evaluate our hypothesis that PIPS during the ROMP of DCPD could be used to prepare nanoporous materials by including a block copolymer containing a DCPD compatible segment and a chemically etchable segment, we explored the ROMP of DCPD in the presence of a poly(styrene)-*b*-poly(lactide) (PS-*b*-PLA) diblock copolymer. Composites with little mechanical integrity resulted, and macrophase separation was evident. This observation led us to the design and synthesis of a block copolymer that contained two reactive constituents: a metathesis reactive block and a chemically etchable block (i.e., doubly reactive). Incorporation of the reactive block into the thermosetting matrix during the PIPS should help arrest phase separation. Furthermore, the incompatibility of the PLA block and polyDCPD would likely result in nanoscopic organization of these two components.

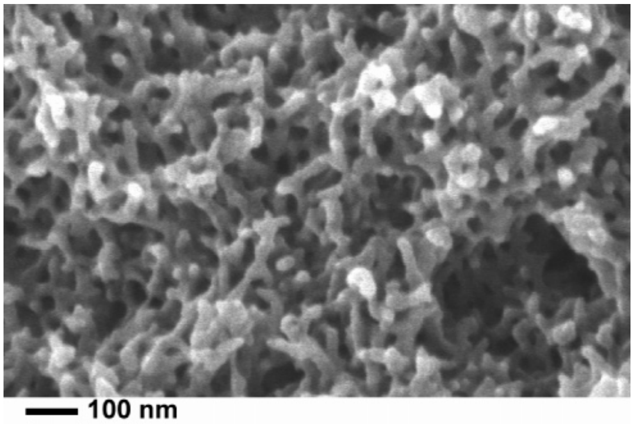


Figure 1. SEM image of the fractured composite membrane surface after PLA removal. The surface was coated with 1.5 nm of Pt to prevent charging.

Using a PLA ($M_n = 34$ kg mol^{-1}) end-capped with a reversible addition fragmentation transfer (RAFT) chain transfer agent,[5b] we performed the controlled radical polymerization of a mixture of styrene and *p*-norbornenylethylstyrene (N) to give a PLA-*b*-P(N-*s*-S) block copolymer with an overall molecular weight of 50 kg mol^{-1} and a polydispersity index of 1.4. The P(N-*s*-S) block contained 30 mol % of N. We combined this block copolymer (133) with DCPD (67), THF (625), and the second generation Grubbs metathesis catalyst[13] (1) at room temperature to give an optically homogeneous solution (the relative weight ratios are given in parentheses). Preliminary dynamic light scattering analysis of a mixture without the catalyst did not reveal any supramolecular aggregation. A cast film of this solution formed a gel in about 2 min, was allowed to react at room temperature for 6 h, and was then cured at 100 °C for 1 h. During the room temperature processing, much of the THF evaporated from the film, and the 100 °C treatment led to nearly complete removal of the THF (as determined by mass loss). The resultant optically transparent films could be easily peeled from a silica or glass substrate, and exposure of these films to a 0.5 M solution of NaOH (in methanol/water) removed the PLA component as confirmed by mass loss and IR spectroscopy (Figure S1). The films remained optically transparent after PLA removal, and a 0.5 mm thick, 10 mm × 3 mm piece of such a film could be bent 90° without breaking.

A TEM image of the composite prior to etching (Figure S3) supported the templating role of the PLA blocks. After PLA removal, the films were analyzed by SAXS (Figure S2) and scanning electron microscopy (SEM) (Figures 1 and S4). The one-dimensional SAXS data showed a single peak at 0.19 nm^{-1} consistent with a microphase separated but disorganized structure on a 33 nm length scale. The SEM images of a fractured piece of the film revealed a bicontinuous structure containing percolating pores; the average diameter of the pores estimated from the SEM image was about 20 nm, comparable to the SAXS data. However, the scattered intensity in the films without PLA was about 30 times

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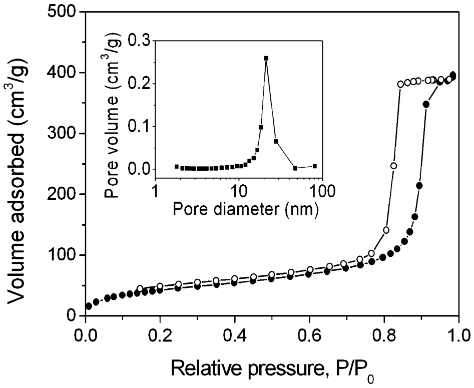

Figure 2. Nitrogen adsorption (filled circles)−desorption (open circles) isotherms of the nanoporous films. Inset: pore size distribution from adsorption data.

greater than that of the precursor film, consistent with the increased electron density contrast. Nitrogen adsorption experiments confirmed the mesoporosity of the films; BET analysis showed a type IV isotherm and gave a specific surface area of 160 $\mathrm{m}^2\ \mathrm{g}^{-1}$, and BJH analysis gave a peak pore diameter of 20 nm, an average pore diameter of 17 nm, and a peak width at half-height of 7 nm (Figure 2).[14]

Combined, these data confirm the formation of a robust thermoset with nanopores templated by the PLA-*b*-P(N-*s*-S) block copolymer. The inclusion of the reactive norbornene-containing block results in control of the PIPS process, leading to nanoscopic organization of the PLA segments in the polyDCPD/poly(N-*s*-S) composite. The nanoporous films retained their structure after annealing at 140 °C for 1 h or after swelling in THF followed by slow drying as revealed by both SAXS and SEM (Figure S5). Furthermore, the nanoporous films also retained >95% of their mass upon heating to 450 °C in air (Figure S6).

For use as separation membranes, these nanoporous thin films should ideally exhibit robust mechanical properties and a percolating pore structure. To demonstrate the porosity in a macroscopic measurement, we filled the nanoporous films with an ionic liquid[8,15] and measured an ionic conductivity of 1.49×10^{-3} S cm^{-1} across a 510 μm thick film by AC impedance spectroscopy. This conductivity compares well to the pure ionic liquid (9.0×10^{-3} S cm^{-1}) accounting for a calculated porosity (the ratio of the void volume to total sample volume) of 0.41 and a tortuosity of 2.48 (Figure S7). These data confirm that the bicontinuous structure percolates through the entire film. Additionally, we made gas diffusion measurements on a set of membranes with a 23 nm average pore size (BET) as in previously reported block-copolymer-based nanoporous membranes.[9c] From the measured absolute permeabilities of He, N_2, and Ar, we extracted effective diffusion coefficients and separation factors for these gases (accounting for a porosity of 0.40 and an estimated tortuosity of 2.29) consistent with simple Knudsen theory using an average pore diameter of 23 nm (Figure S9). We also prepared “dog bone” samples by cutting the cross-linked thin films for mechanical testing before (Figure S8) and after (Figure 3) removal of the PLA. The average ultimate elongation of the nanoporous membrane (ca. 10%) was similar to the PLA-containing precursor (ca. 15%), and the average tensile strength was 32 MPa, comparable to the films before removal of the PLA (45 MPa) and pure polyDCPD (55 MPa). The remarkable mechanical strength of these nanoporous membranes is contrasted with other block-copolymer-templated membranes that are typically too brittle to practically evaluate.

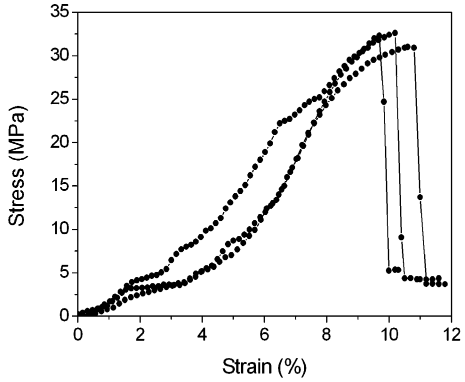

Figure 3. Tensile tests on cross-linked nanoporous membranes (tested three times).

In sum, we have demonstrated that, by combination of thermosetting monomer, a functional group tolerant metathesis catalyst, and a doubly reactive block copolymer, new robust nanoporous membranes can be generated that contain a percolating pore structure and a narrow pore size distribution. These membranes may have utility as high surface area catalysts supports, size selective membranes, and nanomaterial templates.

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Supporting Information Available: Figures S1−S9 (PDF) and a description of the experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998.
(2) For a relevant review, see: Soler-Illia, G. J. de A. A.; Crepaldi, E. L.; Grosso, D.; Sanchez, C. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 109−126.
(3) For example, see: Li, L.; Nemoto, T.; Sugiyama, K.; Yokoyama, H. *Macromolecules* **2006**, *39*, 4946−4755.
(4) Hillmyer, M. A. *Adv. Polym. Sci.* **2005**, *190*, 137−181.
(5) (a) Zalusky, A. S.; Olayo-Valles, R.; Wolf, J. H.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 12761−12773. (b) Rzayev, J.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 13373−13379.
(6) Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126−2129.
(7) Chan, V. Z.-H.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D.; Thomas, E. L. *Science* **1999**, *286*, 1716−1719.
(8) For related work, see: Zhou, N.; Bates, F. S.; Lodge, T. P. *Nano Lett.* **2006**, *6*, 2354−2357.
(9) (a) Yang, S. Y.; Ryu, I.; Kim, H. Y.; Kim, J. K.; Jang, S. K.; Russell, T. P. *Adv. Mater.* **2006**, *18*, 709−712. (b) Uehara, H.; Yoshida, T.; Kakiage, M.; Yamanobe, T.; Komoto, T.; Nomura, K.; Nakajima, K.; Matsuda, M. *Macromolecules* **2006**, *39*, 3971−3974. (c) Phillip, W. A.; Rzayev, J.; Hillmyer, M. A.; Cussler, E. L. *J. Membr. Sci.* **2006**, *286*, 144−152.
(10) For two relevant reviews, see: (a) Inoue, T. *Prog. Polym. Sci.* **1995**, *20*, 119−153. (b) Kiefer, J.; Hedrick, J. L.; Hilborn, J. G. *Adv. Polym. Sci.* **1999**, *147*, 161−247.
(11) Trimmer, M. S. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 3, pp 407−418.
(12) Martina, A. D.; Hilborn, J. G.; Mühlebach, A. *Macromolecules* **2000**, *33*, 2916−2921.
(13) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.
(14) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.
(15) After PLA removal, the films generally were treated by an oxygen-reactive ion etch to remove a thin “skin” that formed at the surface of the films.

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