CHEMISTRY OF MATERIALS
Communication

Chem. Mater. **2010,** *22,* 1279–1281 1279
DOI:10.1021/cm903408x

Nanoporous Materials Derived from Polymeric Bicontinuous Microemulsions

Brad H. Jones and Timothy P. Lodge*

Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Received November 7, 2009
Revised Manuscript Received January 6, 2010

Nanoporous materials are commonly used in separations, storage, catalysis, and drug delivery. These applications require the synthesis of materials with precise macroscopic shape and well-defined pore dimensions and connectivity. In particular, it is often advantageous for a material to possess a three-dimensionally continuous pore network. Such a network generally facilitates high pore densities, leading to large surface areas desired in storage and catalysis. Moreover, the increased degree of pore connectivity afforded by three-dimensional continuity can improve material lifetime in applications where pore blockage is an issue, such as separations and catalysis. Certain zeolites and related materials[1] and polymers designed to pack inefficiently[2] contain micropore (<2 nm) networks, whereas various surfactant,[3] block polymer,[4] and colloid[5] templating techniques have been extensively used to synthesize materials containing mesopore (2−50 nm) networks. However, it has been a significant challenge to synthesize materials containing pore networks with pore sizes on the order of 100 nm. We have developed a straightforward process suitable for such materials, with the sole requirement being that the material, or its precursor, be solidifiable at modest temperature.

Previous research in this area has most frequently involved colloidal templating.[5] However, the pores resulting from this technique, patterned by ordered arrays of particles, are spherical and connected by small windows. A material with pores of a uniform diameter is a desirable alternative in many cases. To this end, various phase separation processes have been exploited. Oxide aerogels, formed by the extraction of 10−100 nm liquid domains separated from condensed inorganic networks in sol−gel reactions, have been extensively studied.[6] Silica glass and cross-linked polystyrene porous beads used commonly in chromatography cover a wide range of pore sizes derived from liquid−liquid separation in alkali borosilicate melts[7] and solid−liquid separation in suspension polymerizations,[8] respectively. Such beads have also been used as templates in the synthesis of porous metals and metal oxides by nanocasting.[9] In other work, Gan and co-workers have prepared porous polymers by polymerizing methacrylate monomers within bicontinuous microemulsions comprised of the monomers, water, and surfactant.[10] Finally, porous epoxies have been prepared through polymerization-induced phase separation of the epoxy from poly(vinylmethylether)[11] and a hyperbranched polyester,[12] which are subsequently removed by oxidation and solvation, respectively. Here, we report a technique for the synthesis of nanoporous materials with uniformly sized pore networks on the order of 100 nm and with wide-ranging chemistry−an aspect the science has clearly lacked.

Our approach utilizes a solid nanoporous template derived from a polymeric bicontinuous microemulsion (BμE). A BμE is universally found in ternary blends of two chemically distinct homopolymers (A and B) and their corresponding diblock copolymer (A−B), provided that the homopolymers are of equal size and the copolymer is symmetric.[13] It is a disordered morphology, consisting of two interpenetrating, three-dimensionally continuous networks with extensive interfacial area and periodicity on the order of 100 nm. Moreover, it is thermodynamically stable, in contrast to bicontinuous morphologies formed from spinodal decomposition of binary homopolymer blends. Zhou and co-workers first demonstrated the potential of this unique morphology for nanoporous materials; using a polystyrene (PS)/polyisoprene (PI) BμE, they cross-linked the PI and removed the PS homopolymer by solvation, resulting in a nanoporous material with 20−100 nm pores.[14]

---

*Corresponding author.

(1) Thomas, J. M.; Klinowki, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7160–7163.
(2) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230–231.
(3) Meynen, V.; Cool, P.; Vansant, E. F. *Microporous Mesoporous Mater.* **2009**, *125*, 170–223.
(4) Olson, D. A.; Chen, L.; Hillmyer, M. A. *Chem. Mater.* **2008**, *20*, 869–890.
(5) Li, Q.; Retsch, M.; Wang, J.; Knoll, W.; Jonas, U. *Top. Curr. Chem.* **2009**, *287*, 135–180.
(6) Hüsing, N.; Schubert, U. *Angew. Chem., Int. Ed.* **1998**, *37*, 22–45.
(7) Haller, W. *Nature* **1965**, *206*, 693–696.
(8) Kun, K. A.; Kunin, R. *J. Polym. Sci., A1* **1968**, *6*, 2689–2701.
(9) Wang, Y.; Price, A. D.; Caruso, F. *J. Mater. Chem.* **2009**, *19*, 6451–6464.
(10) (a) Chieng, T. H.; Gan, L. M.; Chew, C. H.; Lee, L.; Ng, S. C.; Pey, K. L.; Grant, D. *Langmuir* **1995**, *11*, 3321–3326. (b) Chieng, T. H.; Gan, L. M.; Chew, C. H.; Ng, S. C.; Pey, K. L. *Langmuir* **1996**, *12*, 319–324. (c) Chieng, T. H.; Gan, L. M.; Chew, C. H.; Ng, S. C.; Pey, K. L. *Polymer* **1996**, *37*, 2801–2809. (d) Chieng, T. H.; Gan, L. M.; Chew, C. H.; Ng, S. C.; Pey, K. L. *Polymer* **1996**, *37*, 4823–4831. (e) Chieng, T. H.; Gan, L. M.; Teo, W. K.; Pey, K. L. *Polymer* **1996**, *37*, 5917–5925. (f) Chew, C. H.; Li, T. D.; Gan, L. H.; Quek, C. H.; Gan, L. M. *Langmuir* **1998**, *14*, 6068–6076.
(11) Loera, A. G.; Cara, F.; Dumon, M.; Pascault, J. P. *Macromolecules* **2002**, *35*, 6291–6297.
(12) Guo, Q.; Habrard, A.; Park, Y.; Halley, P. J.; Simon, G. P. *J. Polym. Sci., Polym. Phys.* **2006**, *44*, 889–899.
(13) (a) Bates, F. S.; Maurer, W. W.; Lipic, P. M.; Hillmyer, M. A.; Almdal, K.; Mortensen, K.; Fredrickson, G. H.; Lodge, T. P. *Phys. Rev. Lett.* **1997**, *79*, 849–852. (b) Hillmyer, M. A.; Maurer, W. W.; Lodge, T. P.; Bates, F. S.; Almdal, K. *J. Phys. Chem. B* **1999**, *103*, 4814–4824.
(14) Zhou, N.; Bates, F. S.; Lodge, T. P. *Nano Lett.* **2006**, *6*, 2354–2357.

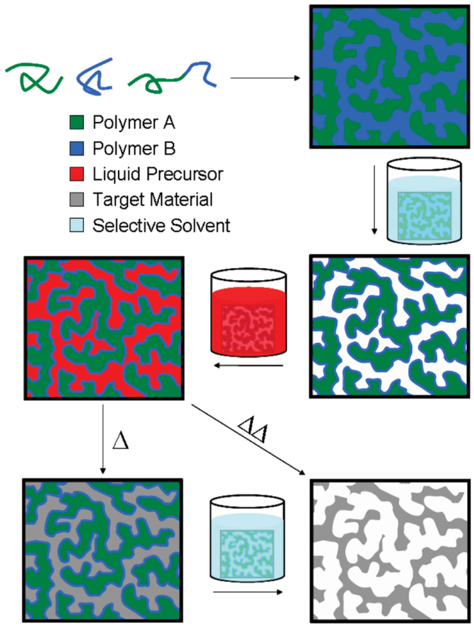

Figure 1. Schematic illustration of the general process for the preparation of nanoporous materials from BμEs.

Our aim was to build upon this work by replicating the inverse structure of such a BμE-derived nanoporous material through nanocasting, as shown in Figure 1. The pores are impregnated with a liquid precursor, which is then solidified and converted to the final product by increasing temperature. Finally, the original material is selectively removed by thermal degradation or solvation, yielding the desired pore structure. The aforementioned cross-linked PI material is not suitable as a template in this process since the cross-linking does not permit facile removal by thermal or chemical means. However, because the BμE is universal in A/B/A$-$B blends, we simply chose a new combination of A and B$-$polyethylene (PE) and poly(ethylene-*alt*-propylene) (PEP).

PE and PEP homopolymers (M_n = 23 kg/mol) and a symmetric poly(ethylene-*block*-ethylene-*alt*-propylene) (PE-PEP) diblock copolymer (M_n = 101 kg/mol) were synthesized by anionic polymerization, as previously described.[15] Blends were prepared by dissolving the polymers in benzene at 70 °C, followed by freeze-drying. In previous work, the BμE morphology was confirmed by transmission electron microscopy (TEM) and small angle neutron scattering (SANS).[15] An additional TEM image is provided in the Supporting Information. The BμE can be captured in the solid state by inducing crystallization of the PE domains. Therefore, the blends were loaded into ampules, annealed at 127 °C for 2 h, and then quenched in liquid nitrogen. The quench ensures that there is no large-scale PE crystallization which would otherwise disrupt the structure.[16] The resultant solid monoliths were removed from the ampules, soaked in THF at room temperature overnight, and dried under a vacuum. This procedure completely removes the PEP homopolymer from the material, as was readily confirmed by weight measurements and the known density[17] and volume fraction of PEP homopolymer in the starting blends.

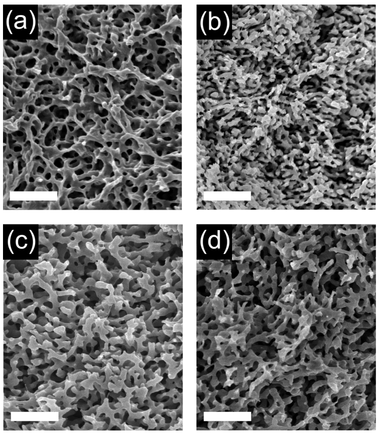

Figure 2. SEM images of (a) nanoporous PE material derived by extraction of PEP homopolymer from PE/PEP BμE, subsequently used as a template for the synthesis of nanoporous (b) ceramic, (c) epoxy, and (d) polyurethane. Scale bars are 1 μm.

The nanoporous PE monoliths were analyzed by scanning electron microscopy (SEM). Samples were prepared by submerging and fracturing small pieces cut from the monoliths in liquid nitrogen. The structure of the nanoporous PE is seen in part a of Figure 2. As expected, the pores form a three-dimensionally continuous network and the pore sizes are on the order of 100 nm. The SANS data (see the Supporting Information) for the BμE indicate an average domain spacing, i.e., the sum of the diameters of adjacent PE and PEP domains, of ~160 nm. Therefore, to a first approximation, one would expect the nanoporous PE to have an average pore diameter of around 80 nm. The porosity of the material is 40%, evaluated by infiltrating the pores with the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide and measuring the resultant change in weight.

Previously, we have demonstrated that the nanoporous PE can be used as a template for the synthesis of nanoporous silicon carbonitride ceramic, according to the process depicted in Figure 1.[15] In that work, a commercially available polysilazane was impregnated into the PE pores and converted to a ceramic at high temperature, whereas the PE template was simultaneously removed by degradation. Here, we have extended this work to a completely different class of materials, polymer thermosets. In this case, by using chemical means to remove the PE template, we demonstrate the universality of our approach for synthesizing nanoporous materials at both high and low temperature.

Two different nanoporous polymer thermosets, an epoxy and a polyurethane, were synthesized. In both cases, the nanoporous PE monoliths were impregnated with difunctional and multifunctional monomers. For the epoxy, glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) (M_n = 348 Da) and 4,4′-methylenedianiline were the

---

(15) Jones, B. H.; Lodge, T. P. *J. Am. Chem. Soc.* **2009**, *131*, 1676–1677.

(16) Khandpur, A. K.; Macosko, C. W.; Bates, F. S. *J. Polym. Sci., Polym. Phys.* **1995**, *33*, 247–252.

(17) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639–4647.

monomers, and for the polyurethane, toluene diisocyanate and glycerol propoxylate (M_n = 266 Da). In the epoxy case, the monomers were mixed in stoichiometric proportions by dissolving in chloroform at ~50% by weight. The nanoporous PE monolith was submerged in the monomer solution and the solution was exposed to vacuum for 2 days, hence the impregnation of monomer into the PE pores was accomplished concurrently with the removal of chloroform. In the polyurethane case, the monomers were directly mixed by stirring and the nanoporous PE monolith was submerged in the mixture and exposed to vacuum for several hours. In both cases, the monoliths were removed, cleansed of excess monomer on the surface, and heated to 90 °C overnight to cure the material within the pores. Finally, the PE template was removed by soaking the monoliths in toluene at 70 °C and drying under vacuum.

The pore structures of the resultant epoxy and polyurethane materials are shown in parts c and d of Figure 2, respectively. For comparison, the pore structure of silicon carbonitride ceramic synthesized as previously described[15] is shown in part b of Figure 2. The procedure clearly gives a three-dimensionally continuous pore network and the disordered, BμE mophology is preserved in all three cases. Furthermore, the pore walls of the ceramic are noticeably thinner than those of the epoxy or polyurethane. This is to be expected, because there is a significant increase in density during the ceramic synthesis, which is not the case during either thermoset synthesis. The porosities of the ceramic, epoxy, and polyurethane are 66, 62, and 54%, respectively, evaluated by the same procedure as the PE template.

To characterize the pore sizes of these materials, we employed differential scanning calorimetry (DSC) thermoporometry using cyclohexane as a probe liquid. DSC thermoporometry is based on the phenomenon that a liquid confined to a pore exhibits a depressed freezing temperature relative to the bulk.[18] We have followed the procedure described by Landry[19] with appropriate modifications (see the Supporting Information). The pore size distributions of the nanoporous ceramic, epoxy, and polyurethane are presented in Figure 3. All three materials possess a well-defined and moderately narrow distribution of pore sizes, spanning approximately 50−150 nm in the ceramic and 60−200 nm in the thermosets. In a separate experiment, nonporous pieces of the epoxy and polyurethane were immersed in cyclohexane for several days, after which there is no visual evidence of swelling and no appreciable increase in weight. Consequently, we feel the pore size distributions presented are unaffected by any material−cyclohexane interactions. The average pore diameter and total surface area calculated from Figure 3 are 74, 106, and 103 nm and 32, 36, and 31 m^2/g for the ceramic, epoxy, and polyurethane, respectively. As with the pore walls, the lower average pore diameter of the ceramic is expected due to the increase in density during synthesis. Furthermore, a rough calculation (see the Supporting Information) gives an expected pore size of 104 nm for the epoxy and polyurethane, in good agreement with the measured values. This further confirms the excellent retention of the BμE structure throughout the procedure.

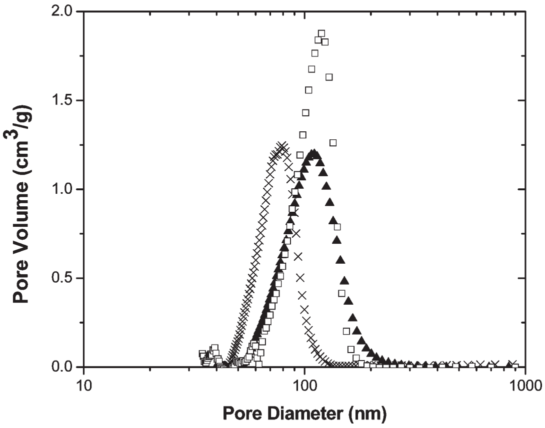

Figure 3. Pore size distributions of nanoporous (×) ceramic, (□) epoxy, and (▲) polyurethane, calculated by DSC thermoporometry with cyclohexane as a probe liquid.

Collectively, the results presented here demonstrate that the structure of a BμE can be replicated with high precision in materials formed at both high and low temperatures, resulting in nanoporous materials with three-dimensionally continuous pore networks and pore sizes on the order of 100 nm. We propose that our method can be applied in the synthesis of nanoporous materials with arbitrary chemistry, provided the material, or its precursor, be solidifiable at a temperature at which the BμE-derived template retains structural integrity. In this case, we have used a hydrophobic PE template that requires solidification at a temperature below ~105 °C. However, the universal existence of BμEs should allow for selection of starting polymers so as to achieve templates with increased thermal stability or hydrophilic pore walls. In addition, the characteristics of BμEs, such as domain size, can be tuned by changing temperature and composition, thereby providing control of pore size and surface area.

Acknowledgment. This work was supported partially by the MRSEC program of the National Science Foundation under Award DMR-0819885, and by University of Minnesota Graduate School and Doctoral Dissertation Fellowships (B.H.J.). EM instrumentation was provided by the Institute of Technology Characterization Facility. We thank Michael Bluemle, Melissa Fierke, Chris Frethem, Chun Liu, Ameara Mansour, and Rajiv Taribagil for their assistance.

Supporting Information Available: TEM and SANS data of BμE, discussion of DSC thermoporometry technique used, pore size calculation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(18) Brun, M.; Lallemand, A.; Quinson, J.-F.; Eyraud, C. *Thermochim. Acta* **1977**, *21*, 59–88.

(19) Landry, M. R. *Thermochim. Acta* **2005**, *433*, 27–50.