JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Ordered Microporous Membranes Templated by Breath Figures for Size-Selective Separation

Ling-Shu Wan,* Jun-Wei Li, Bei-Bei Ke, and Zhi-Kang Xu

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Supporting Information

ABSTRACT: Membranes with highly uniform pore size are important in various fields. Here we report the preparation and performance of ordered membranes, the pore diameter of which is on the micrometer scale. The ordered membranes fabricated at two-phase interfaces enable a high-resolution and energy-saving separation process. Moreover, a possible mechanism for the formation of through-pores has been proposed and experimentally verified.

Porous membranes are important not only in industrial applications but also in some advanced fields such as microfluidics, biosensing, and catalysis.[1−7] Microporous membranes are often employed to remove impurities or byproducts through size-selective filtration for sample pretreatment or post-treatment. For example, the sample can be that for chromatography or light scattering measurements. It is well known that the pore size and its distribution are crucial to the size-selective separation performance of the membranes. They are therefore strongly desired to have pores with narrow size distribution and ordered structures, as such membranes possess extra separation accuracy, require only low or ultralow operation pressure, and show some interesting features such as significantly enhanced mass transport rates.[8−11]

The track etch method was adapted to fabricate membranes with highly uniform pore size, but this method is limited to polycarbonate and poly(ethylene terephthalate), and the pore density is low. Self-assembly of block copolymers has attracted much attention over the past decades. Bicontinuous or cylindrical microphase separated domains can be formed in the assembled film by varying preparation conditions such as annealing and by modulating the balance of repulsive interactions between dissimilar segments of the copolymers. The domains may be selectively removed, leaving well-ordered pore channels.[8−16] Recently, the block copolymers have been advanced from polystyrene-*block*-poly(ethylene oxide)[14] to polyethylene-based copolymers;[15] the self-assembly process was combined with non-solvent-induced phase separation to fabricate asymmetric membranes.[16] It is generally believed that microphase separation of block copolymers leads to domains in the range of 10−100 nm.[17,18] In this Communication, we describe a method to prepare ordered membranes with highly uniform pore size on the micrometer scale for size-selective separation. The ordered membranes enable a high-resolution and energy-saving separation process.

An amphiphilic block copolymer, polystyrene-*block*-poly(*N*,*N*-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA), that was synthesized by atom-transfer radical polymerization,[19,20] was used to prepare ordered membranes. The copolymer was dissolved in carbon disulfide (CS_2), and 100 μL of the as-prepared solution was cast at a two-phase interface under a humid airflow. The relative humidity was controlled above 70%. During this process, condensed water droplets arrange into ordered arrays, i.e., the so-called breath figures, and act as dynamic templates for the pores.[21,22] It has been reported that properties of the interfaces (e.g., air/solid and air/water interfaces) have a great impact on the pore structures.[23−27] For example, the air/glass interface often leads to dead-end pores which may be considered as picoliter beakers[28] or microreactors.[29] Formation of through-pores is a prerequisite for preparation of ordered separation membranes. In this work, the block copolymer solution was cast at an air/ice interface. Figure 1 shows SEM micrographs of the typical ordered membrane with hexagonal pore arrays. As can be seen from the micrographs of the top, bottom, and cross section of the

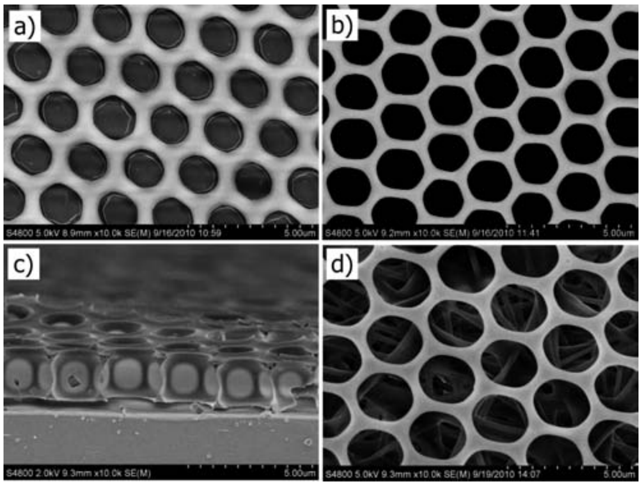

Figure 1. SEM images of the typical ordered membrane with through-pores, prepared from 1 mg/mL of PS-*b*-PDMAEMA solution in CS_2 at an air/ice interface. The airflow speed is 4 L/min. (a) Top, (b) bottom, and (c) cross section. (d) The membrane transferred onto a piece of dense nanofiber mesh.

Received: October 2, 2011
Published: December 5, 2011

membrane, the pores are of through structure. The membrane was further transferred onto a piece of dense electrospun nanofiber mesh.[30] Nanofibers below the ordered membrane can be clearly observed through the pores. Moreover, the pore diameter of the membranes can be facilely modulated in the range of 1−5 μm by changing the solution concentration and airflow speed (Figure S1, Supporting Information (SI)).

The thickness of the ordered membrane is about 2 μm (Figure 1c). It is not free-standing but can be easily transferred onto various supports such as silicon, gold, and porous meshes. Therefore, we fabricated composite membranes using a stainless steel woven wire mesh as the support (Figure 2). A composite membrane with ordered separation layer has been achieved (Figure 2d). As marked by the arrow in Figure 2b, a thin layer of polystyrene nanofibers was deposited on the mesh surface to enhance both the integrity of the ordered membrane and the interfacial adhesion between the membrane and the mesh.[30] The sparse nanofiber layer has irregular and large pores of tens of micrometers without affecting the separation performance of the composite membrane. Figure 2f shows photographs of the composite membrane and a permeation module. This module is a commercially available one that is often used for sample pretreatment such as in dynamic light scattering measurements.

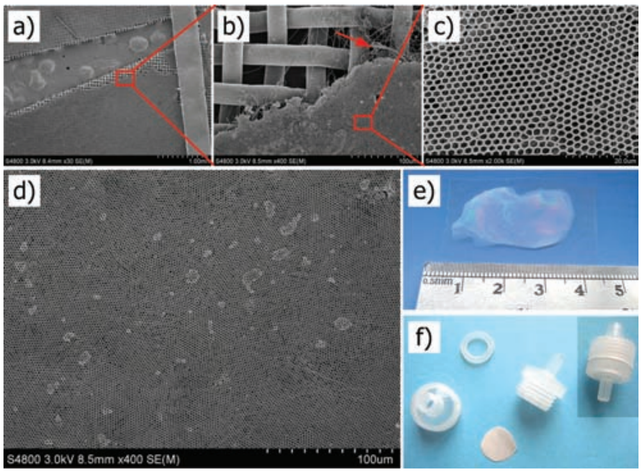

Figure 2. (a−d) SEM images of the composite membrane with different magnifications. (e) Digital photograph of a piece of ordered membrane. (f) Digital photographs of the composite membrane and the membrane module used for separation.

Figure 3 shows the size distribution of polystyrene particles before and after filtration by the composite membrane, the separation layer of which has a pore diameter of 3 μm. The feed microspheres have a bimodal size distribution peaking at 2.0 and 5.0 μm. Interestingly, the filtrates show a single peak, and the curve is accurately cut off at about 3 μm; that is, the ordered membrane shows high-resolution separation performance. Moreover, it should be mentioned that the separation can be carried out without additional pressure. As we know, traditional microfiltration processes generally need 0.1 MPa or higher additional pressure, depending on pore sizes (also the three-dimensional structure) and properties of the membrane material. Therefore, it can be concluded that this ordered membrane enables a high-resolution and energy-saving separation process.

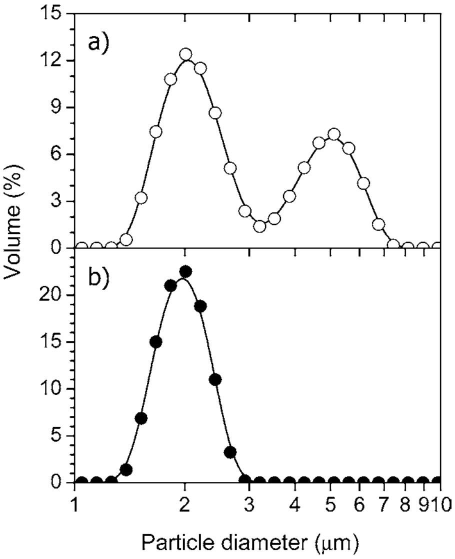

Figure 3. (a) Size distribution of the feed polystyrene microspheres with bimodal distribution at 2.0 and 5.0 μm. (b) Size distribution of the microspheres after filtration by a composite membrane, the pore diameter of which is 3 μm.

We tried some other block copolymers, including polystyrene-*block*-poly(2-hydroxyethyl methacrylate) (PS-*b*-PHEMA)[31] and polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA),[32] and compared their membrane-forming properties at the air/ice and air/water interfaces (Figure S2, SI). We found that the polymer solution spreads better at the air/ice interface than at the air/water interface. The spreading leads to larger membrane areas with hexagonal arrays of monodisperse through-pores instead of dead-end pores. By contrast, the cast solution on water surface tends to form ellipsoid and hence provides longer time to grow for water droplets condensed in the thicker center area. After complete evaporation of water and the organic solvent, pores at the membrane center are larger than those at the edge area. Apart from the spreading behavior, low temperature may be another reason for the regular structure at the air/ice interface. It has been reported that evaporation of the solvent rapidly cools the solution, which is important to the formation of regular arrays of water droplets because the cooling induces a temperature gradient.[33] Our results show that water with lower temperature leads to higher regularity (Figure S3, SI). Therefore, the membrane with through-pores is more regular when prepared at the air/ice interface than at the air/water interface. This finding makes it possible to prepare ordered membranes from some commonly used polymers.

The pore structure may be affected by the vertical position of water droplets in the polymer solution at the moment of membrane hardening (Figure 4a). Besides the thermocapillary and Marangoni forces,[33] the density of the solvent can affect the position of water droplets. When benzene is used as the solvent for the polymer solution, through-pore structures are obtained with smaller round pores on the top and larger ones on the bottom.[23] Chloroform solutions, by contrast, generate pores with larger diameter on the top and smaller diameter on the bottom.[27] What we envisage is that low-density benzene (ρ = 0.87 g mL^{-1}) allows the condensed water droplets (ρ = 1.00 g mL^{-1}) to submerge into the bottom of the polymer solution, leading to larger pore size on the bottom, while in the case of

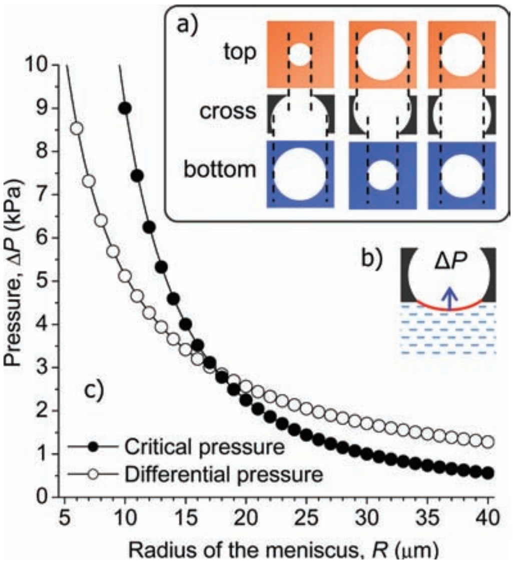

Figure 4. (a) Pore structures of ordered membranes prepared from solutions using benzene, chloroform, and CS_2 (from left to right) as the solvent. (b) Illustration of the formation of through-pores. (c) Calculated curves of differential pressure and critical differential pressure vs the radius according to eqs 1 and 2.

chloroform (ρ = 1.48 g mL^{-1}) the pores are the opposite of those found in the benzene system. In the present work, the density of CS_2 (ρ = 1.26 g mL^{-1}) is between those of benzene and chloroform, and hence, the through-pores show almost the same diameter on the top and the bottom.

It is clear that the density of the solvent can influence the pore structure, which implies water droplets are falling in the polymer solution during the film formation. The through-pore structure is proposed to be induced by fusion of water droplets in the polymer solution with the substrate, i.e., thin water layer on the ice surface or bulk water in our case.[23,27] However, how the pores become through-pores is still unclear. There should be a very thin film between the water droplets and the substrate because phase inversion takes place when polymer solution and non-solvent meet.[34] Such thin films can be sometimes observed in films cast from solutions with high polymer concentration (Figure S4, SI). Differing from hard substrate, soft substrate such as water allows further falling of the water droplets, which leads to the deformation of the thin film and induces meniscuses toward the substrate (Figure 4b). With the evaporation of the water droplets, there is a differential pressure, ΔP, induced by the surface tension of the substrate liquid across the meniscus, and the relationship is given as[35]

$$\Delta P = \frac{2\gamma}{R} \tag{1}$$

where γ is the interfacial tension of the substrate/thin film (liquid/solid) interface, and R is the radius of the meniscus. Interfacial tension of polystyrene/water is about 25.6 mN m^{-1},[36] and R is always larger than the radius of the pore diameter. The curve of ΔP vs R can therefore be plotted according to eq 1. However, for an ultrathin polymer film it is very difficult to measure or accurately calculate the critical differential pressure, ΔP_c, at which the film ruptures. Through-pores can be formed only when ΔP is larger than ΔP_c. It has been reported that for a polymer hollow microsphere with a wall thickness of δ, ΔP_c is expressed as[37,38]

$$\Delta P_c = \frac{4E}{3}\left(\frac{\delta}{R}\right)^2 \tag{2}$$

where E is Young's modulus of the polymer. The Young's modulus of dry polystyrene is about 3000 MPa, which slightly changes with the molecular weight and temperature[39] and drastically decreases with the presence of solvent. The thickness of the thin film, which is generated by phase inversion as mentioned above, is estimated from SEM images to be about 15 nm (Figure 1c). Therefore, a curve of ΔP_c vs R can be obtained according to eq 2. As can be seen from the two calculated curves (Figure 4c), ΔP induced by the interfacial tension exceeds ΔP_c of the film when $R > 18$ μm. In other words, the possible thin film can be easily broken by the differential pressure, forming through-pores. It should be noted that the values of film thickness, interfacial tension, and the Young's modulus do not change the trends of ΔP and ΔP_c.

Based on the above-mentioned mechanism, other liquids that provide enough interfacial tension may theoretically be considered as substrates for the preparation of ordered membranes with through-pores. Membranes prepared on the surface of glycerol and formic acid support our hypothesis (Figure S5, SI). However, through-pore membranes cannot be fabricated on the surface of acetic acid, tetraethyl orthosilicate, ethyl acetate, ethanol, isopropanol, and methanol, which are of low surface tension and low density. Experimentally, the cast solution was observed sinking into the soft substrates with low density. Besides, our preliminary results show that an ordered membrane with through-pores can be prepared from a commercially available polymer, polystyrene, although the membrane-forming window is very narrow (Figure S6, SI). The use of other substrates and commercial available polymers not only extends the application range of the ordered membranes but also increases the easy availability of this method.

In summary, this Communication reports ordered microporous membranes with highly uniform pore size. The membranes were prepared at the interface of air/ice, which can be extended to the interfaces of air/glycerol and air/formic acid. A static model has been proposed for the calculation of critical pressure for rupture of the thin film and the applied pressure. If the applied pressure exceeds the critical pressure, the formation of through-pores becomes possible. We demonstrated the capability of the corresponding composite membranes for high-preciseness separation of polystyrene microspheres with close sizes. The membranes only require ultralow operation pressure, enabling an energy-saving separation process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and effects of substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

lswan@zju.edu.cn

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51173161, 50803053), and partially supported by the Zhejiang Provincial Natural Science

Foundation of China (Y4110076), the Program for Zhejiang Provincial Innovative Research Team (2009R50004), and the Open Fund of Zhejiang Provincial Top Key Discipline of New Materials and Process Engineering (20110932). J.-W.L. thanks the Zhejiang Provincial Undergraduate Scientific and Technological Innovation Project (2011R401163) for support.

■ REFERENCES

(1) Ulbricht, M. *Polymer* **2006**, *47*, 2217.
(2) de Jong, J.; Lammertink, R. G. H.; Wessling, M. *Lab Chip* **2006**, *6*, 1125.
(3) Baker, L. A.; Choi, Y. S.; Martin, C. R. *Curr. Nanosci.* **2006**, *2*, 243.
(4) Weder, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 448.
(5) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. *Nature* **2008**, *452*, 301.
(6) Wan, L. S.; Liu, Z. M.; Xu, Z. K. *Soft Matter* **2009**, *5*, 1775.
(7) Huang, J. X.; Pradel, K. C.; Sohn, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3412.
(8) Wei, Q. H.; Bechinger, C.; Leiderer, P. *Science* **2000**, *287*, 625.
(9) Kim, J. K.; Yang, S. Y.; Ryu, I.; Kim, H. Y.; Jang, S. K.; Russell, T. P. *Adv. Mater.* **2006**, *18*, 709.
(10) Yang, S. Y.; Park, J.; Yoon, J.; Ree, M.; Jang, S. K.; Kim, J. K. *Adv. Funct. Mater.* **2008**, *18*, 1371.
(11) Yang, S. Y.; Yang, J. A.; Kim, E. S.; Jeon, G.; Oh, E. J.; Choi, K. Y.; Hahn, S. K.; Kim, J. K. *ACS Nano* **2010**, *4*, 3817.
(12) Chen, L.; Phillip, W. A.; Cussler, E. L.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 13786.
(13) Li, X. F.; Fustin, C. A.; Lefevre, N.; Gohy, J. F.; De Feyter, S.; De Baerdemaeker, J.; Egger, W.; Vankelecom, I. F. J. *J. Mater. Chem.* **2010**, *20*, 4333.
(14) Kim, S. H.; Misner, M. J.; Xu, T.; Kimura, M.; Russell, T. P. *Adv. Mater.* **2004**, *16*, 226.
(15) Pitet, L. M.; Amendt, M. A.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 8230.
(16) Peinemann, K. V.; Abetz, V.; Simon, P. F. W. *Nat. Mater.* **2007**, *6*, 992.
(17) Bernards, D. A.; Desai, T. A. *Soft Matter* **2010**, *6*, 1621.
(18) Wang, Y.; Li, F. B. *Adv. Mater.* **2011**, *23*, 2134.
(19) Ke, B. B.; Wan, L. S.; Chen, P. C.; Zhang, L. Y.; Xu, Z. K. *Langmuir* **2010**, *26*, 15982.
(20) Wan, L. S.; Lv, J.; Ke, B. B.; Xu, Z. K. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3759.
(21) Widawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387.
(22) Srinivasarao, M.; Collings, D.; Philips, A.; Patel, S. *Science* **2001**, *292*, 79.
(23) Nishikawa, T.; Ookura, R.; Nishida, J.; Arai, K.; Hayashi, J.; Kurono, N.; Sawadaishi, T.; Hara, M.; Shimomura, M. *Langmuir* **2002**, *18*, 5734.
(24) Bunz, U. H. F. *Adv. Mater.* **2006**, *18*, 973.
(25) Stenzel, M. H.; Barner-Kowollik, C.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2363.
(26) Gugliuzza, A.; Aceto, M. C.; Macedonio, F.; Drioli, E. *J. Phys. Chem. B* **2008**, *112*, 10483.
(27) Ma, H. M.; Cui, J. W.; Song, A. X.; Hao, J. C. *Chem. Commun.* **2011**, *47*, 1154.
(28) Erdogan, B.; Song, L. L.; Wilson, J. N.; Park, J. O.; Srinivasarao, M.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2004**, *126*, 3678.
(29) Li, X.; L., X. F.; Zhang, L. A.; Wang, Y. X.; Yang, X. L.; Zhao, N.; Zhang, X. L.; Xu, J. *J. Am. Chem. Soc.* **2011**, *133*, 3736.
(30) Wan, L. S.; Ke, B. B.; Wu, J.; Xu, Z. K. *J. Phys. Chem. C* **2007**, *111*, 14091.
(31) Ke, B. B.; Wan, L. S.; Xu, Z. K. *Langmuir* **2010**, *26*, 8946.
(32) Chen, P. C.; Wan, L. S.; Ke, B. B.; Xu, Z. K. *Langmuir* **2011**, *27*, 12597.
(33) Maruyama, N.; Koito, T.; Nishida, J.; Sawadaishi, T.; Cieren, X.; Ijiro, K.; Karthaus, O.; Shimomura, M. *Thin Solid Films* **1998**, *327*, 854.
(34) Guillen, G. R.; Pan, Y. J.; Li, M. H.; Hoek, E. M. V. *Ind. Eng. Chem. Res.* **2011**, *50*, 3798.
(35) Youngblood, J. P.; McCarthy, T. J. *Macromolecules* **1999**, *32*, 6800.
(36) Absolom, D. R.; Neumann, A. W. *Colloids Surf.* **1988**, *30*, 25.
(37) Gao, C. Y.; Leporatti, S.; Moya, S.; Donath, E.; Mohwald, H. *Langmuir* **2001**, *17*, 3491.
(38) Gao, C. Y.; Donath, E.; Moya, S.; Dudnik, V.; Mohwald, H. *Eur. Phys. J. E* **2001**, *5*, 21.
(39) Ellis, B.; Smith, R., *Polymers: A Property Database*, 2nd ed.; CRC Press: Boca Raton, FL, 2009.