Nondestructive Creation of Ordered Nanopores by Selective Swelling of Block Copolymers: Toward Homoporous Membranes

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CONSPECTUS: Pores regulate the entry and exit of substances based on the differences in physical sizes or chemical affinities. Pore uniformity, ordering, and the homogeneity of the surface chemistry of the pore walls are vital for maximizing the performance of a porous material because any scattering in these parameters weakens the capability of pores to discriminate foreign substances. Most strategies for the creation of homogeneous pores are destructive, and sacrificial components in the precursor materials must be selectively removed to generate porosities. The incorporation and subsequent removal of the sacrificial components frequently make the pore-making process complicated and inefficient and impose greater uncertainty in the control of the pore homogeneity.

Block copolymers (BCPs) have been demonstrated to be promising precursors in the fabrication of highly ordered nanoporous structures. Unfortunately, BCP-derived porosities are also predominantly dependent on destructive pore-making processes (e.g., etching or extraction). To address this problem, we have developed a swelling-based nondestructive strategy. In this swelling process, one simply needs to immerse BCP materials in a solvent selective for the minority blocks for hours. After removing the BCPs from the solvent followed by air drying, pores are generated throughout the BCP materials in the positions where the minority blocks initially dwell. This Account discusses our recent discoveries, new insights, and emerging applications of this burgeoning pore-making method with a focus on the development of ordered porosities in bulk BCP materials. The initial morphology and orientation of the minority phases in BCPs determine the pore orientation and geometry in the produced porous materials. For nonaligned BCPs, three-dimensionally interconnected pores with sizes scattering in the 10–50 nm range are produced after swelling. There is a morphology evolution of BCP materials from the initial nonporous structure to the increasingly opened nanoporous intermediates, to interconnected networks of micellar nanofibers, and finally to isolated micellar spheres with increasing degrees of swelling. When the BCP films are aligned perpendicularly or in-plane, selective swelling results in uniform “standing” (perpendicular orientation) and “sleeping” (in-plane orientation) pores, respectively. Pore sizes can be tuned by changing molecular weights of the BCPs and swelling conditions without the loss of pore uniformity. Due to the nondestructive nature of this swelling process, nothing in the BCPs is lost during the pore-forming procedure, and consequently the formed pores can be progressively closed also by selective swelling. Such reversible pore opening/closing can be repeated many times, enabling the application of these materials in drug delivery and intelligent antireflective coatings. The monodispersed pore sizes, straight pore profile, and hydrophilic pore walls particularly favor the application of the porous BCPs in separations as homoporous membranes (HOMEs) exhibiting high selectivity, permeability, and inherent stimulus responsiveness.

1. INTRODUCTION

Porous media, either naturally existing or man-made, are ubiquitous and are finding enormous applications and playing irreplaceable roles in separation, catalysis, energy storage and conversion, biomedical engineering, etc. Pores regulate the entry and exit of substances based on the differences in physical sizes or chemical affinities in reactions, separations, and other functionalities that a porous material may deliver. Pore uniformity, ordering, and the homogeneity of the surface chemistry of the pore wall are vital for maximizing the performances of porous materials, because any scattering in these parameters weakens the capability of pores to discriminate foreign substances. However, with pore sizes reduced to the nanometer scale, the fabrication of ordered pores with homogeneous sizes, shapes, and chemistries becomes increasingly challenging.

Most strategies for the creation of homogeneous pores are destructive, and some components in the precursor materials must be controllably removed to generate porosities. For example, track etching of polymer films and anodization of aluminum rely on irradiation bombardment plus alkaline etching and electrochemical oxidation to destructively “drill” pores in the corresponding substrates. The need for the selective removal of components makes the pore-making process much more complicated and imposes greater uncertainty in the control of the pore homogeneity. Even
worse, these methods frequently suffer from inadequately developed porosities because of the incomplete removal of sacrificial components.

Block copolymers (BCPs) have been demonstrated to be promising precursors in the fabrication of highly ordered nanoporous structures for a variety of applications ranging from membrane separation to biomedical engineering. BCPs composed of at least two dissimilar homopolymers tend to phase-separate at the nanometer scale, resulting in well-defined nanodomains of the minority blocks with feature sizes typically in the 10−50 nm range periodically dispersed in the matrix composed of the majority block. By transforming the nanodomains of the minority blocks into voids, one can obtain porous frameworks of the majority blocks with pores present along the positions originally occupied by the minority blocks. Unfortunately, such a transformation from solid nanodomains to voids is also predominantly dependent on destructive pore-making processes and is mainly achieved by the selective etching of the labile blocks or extraction of the predosed additives incorporated into the minority blocks. To address this issue, we have developed a swelling-based, nondestructive strategy. In this swelling process, one simply needs to immerse the BCP materials for hours in a solvent selective for the minority blocks. After the removal of the BCPs from the solvent followed by drying, well-defined porosities are generated throughout the BCP materials. Among the very few methods capable of producing homogeneous pores down to <50 nm, selective swelling of block copolymers is distinguished for its extreme ease, nondestructive nature, and reversibility in the pore-forming process. This swelling process is not destructive because the minority blocks are not dissolved away, instead migrating to line along the generated pore walls, thus providing additional functionalities including enhanced hydrophilicity and stimulus responsiveness to the produced pores.

Surface reconstruction induced by selective solvents was previously observed in micellar monolayers of amphiphilic block copolymers. We extended this surface reconstruction to BCP nanofibers and nanorods. However, surface reconstruction is limited to low-dimensional BCP materials such as ultrathin films. We broke through this limitation by elevating the swelling temperatures to be comparable to the glass transition temperature (T_g) of the majority blocks in the swelling agent, and established a new pore-making strategy of selective swelling-induced pore generation that is capable of creating pores in BCPs with any dimension including bulk materials in macroscopic dimensions.

Starting in 2010, we have focused on swelling-induced pore generation in bulk BCP materials because they are expected to find many important applications beyond lithography, which is currently the main target application of ultrathin BCP films. This Account will summarize and analyze our new insights and discoveries of this burgeoning pore-making method with an emphasis on the development of ordered porosities in bulk BCP materials, mainly focused on the morphology evolution, mechanistic understanding, pore tuning, and applications of the produced porous bulk materials.

2. MORPHOLOGY EVOLUTION IN THE SELECTIVE SWELLING-INDUCED PORE FORMATION

In the selective swelling-induced pore generation, the requirements for BCPs are simple and clear: (1) the constituent blocks must exhibit a sufficient contrast in solubility or polarity, allowing the choice of selective solvents capable of strongly swelling the minority blocks but slightly swelling the majority blocks, and (2) the majority blocks should be in the glassy state or possibly in the crystalline state in order to hold the integral structure of the BCP materials during and after pore formation. Different types of BCPs are applicable in this pore-making strategy. In our studies, diblock copolymers of polystyrene and poly(2- or 4-vinylpyridine) (PS-b-PVP) are predominantly used because such BCPs are easily available with arbitrary molecular weights and narrow polydispersity indices. As-coated PS-b-PVP films are dense and nonporous. After immersion in PVP-selective solvents such as ethanol at elevated temperatures for different durations, circularly and elliptically shaped nanopores emerge in the films. These pores are enlarged and interconnected with increasing degrees of swelling by elevating the swelling temperatures or extending swelling durations or both (Figure 1a−c). Moreover, a network-like morphology of three-dimensionally interconnected nanofibers is obtained by swelling at 75 °C (Figure 1d), and a similar network-like morphology has also been observed in etched BCPs. These nanofibers are identified to cylindrical micelles with PS cores sheathed by PVP coronae. Even stronger swelling destroys the integral framework of the films, and they are progressively dissolved in the solvent as spherical micelles via the mechanism of heating enabled micellization (Figure 1e).

A morphology evolution of BCP films from dense films to increasingly opened porous structures, to networks of interconnected cylinders, and to isolated spherical micelles is always present upon immersion in selective solvents. It is concluded that selective swelling-induced pore generation is a series of intermediate steps in the interactions of BCPs with selective solvents. If the swelling conditions are chosen appropriately, the evolution will proceed at a moderate rate to allow several or tens of hours to finish the entire process. In these cases, the intermediate morphologies can be frozen and captured simply by removing the BCPs from the swelling bath.

3. MECHANISTIC UNDERSTANDING OF THE PORE FORMATION PROCESS

The selective swelling-induced pore generation process can be described as consisting of three steps: uptake of the solvent, swelling of the BCPs, and drying by solvent evaporation. Upon immersion of the BCPs in ethanol, which is a solvent selective for the PVP phases, ethanol diffuses into the film and is preferentially enriched in the PVP microdomains because of the much stronger affinity of ethanol toward PVP than toward PS.

Figure 1. Morphology evolution of PS-b-PVP films induced by PVP-selective solvents. Panels a−e are surface SEM images of films subjected to different swelling conditions: (a) ethanol/55 °C/6 h, (b) ethanol/55 °C/15 h, (c) ethanol/65 °C/24 h, (d) ethanol/75 °C/24 h, and (e) acetic acid/60 °C/10 min. Reproduced with permission from refs 11 and 21. Copyright 2010 Wiley-VCH and 2013 Royal Society of Chemistry.
The PVP microdomains are consequently swollen and expanded, leading to the progressive accumulation of osmotic pressure. It was found that \( T_s \) of PS homopolymers was decreased from \( \sim 100 \, ^\circ C \) in the dried state to \( 82 \, ^\circ C \) when immersed in ethanol,\(^{26} \) revealing the moderate plasticization/swelling effect of ethanol toward PS. Considering that the swelling process is performed at elevated temperatures (typically at \( 60\)–\(75 \, ^\circ C \)) that are slightly lower than the \( T_s \) of PS in ethanol, plastic deformation of the PS matrix will occur, driven by the accumulated osmotic pressure in the PVP microdomains.

Upon drying, the swelling PVP chains collapse with the evaporation of ethanol. However, the spaces initially occupied by the expanding PVP microdomains are highly swollen, and consequently adjacent PVP domains contact and are merged to form a continuous phase of swelling PVP chains, corresponding in an interconnected porosity in the subsequent drying process. We note that the drying step does not noticeably influence the pore sizes. This is because for a fixed BCP film the pore size is determined by the amount of the swelling solvent taken up by the PVP microdomains. Once the solvent is completely evaporated the pores will be fixed at the same size regardless of how fast the film is dried.

Both BCP compositions and the swelling conditions including swelling agents, temperatures, and durations influence the swelling behaviors and consequently the morphologies of the obtained porous BCP materials. According to the phase diagram of BCPs\(^{26} \), for PS-\( b \)-PVP films with PS as the majority block, the PVP phases in the morphology of spheres,\(^{25} \) cylinders,\(^{27} \) and gyroids\(^{28} \) are suitable to be converted into the corresponding nanoporous structures through this swelling mechanism. Therefore, BCPs with volume fractions \( f \) of the minority approximately in the 5–38\% range can be converted to porous structures by this selective swelling strategy, while BCPs with \( f > 38\% \) may be directly dissolved in the selective solvent.

Increases in film thicknesses and the surface segregation of PVP chains always accompany the selective swelling-induced pore generation process. As shown in Figure 2, swelling of PS-\( b \)-PVP in ethanol at \( 60 \, ^\circ C \) followed by air drying leads to a fast and nearly linear increase in the film thickness by \( \sim 100\% \) in the initial 1 h and subsequently a lower but continuous increase from 1 to 15 h due to the reduced concentration gradient of ethanol with a total increase of \( \sim 150\% \) relative to the initial as-coated films.\(^{29} \) Increasing film thicknesses is caused by the vertical stretching of the PS matrix, which is plasticized to some degree at elevated temperature in ethanol. Because the BCP films do not change their lateral dimensions upon swelling, the volume expansion leads solely to the increase in the film thickness. That is, the increase in the film thickness is linearly proportional to the volume expansion and consequently the porosities of the films. Swelling in ethanol at \( 60 \, ^\circ C \) for 10 min produces a porosity of \( 28\% \), and the porosity is significantly increased to \( >60\% \) with prolonged swelling durations, for example, 15 h. Thus, despite our previous concerns,\(^{12} \) the porosities of the selective swelling-induced porous materials are not limited to the volume fractions of the minority blocks and in fact can be several times higher.

In the swelling process, the PVP chains are progressively enriched on the film surface and pore walls that can be traced by monitoring the change in the water contact angles (WCAs). As shown in Figure 2, the WCA of the as-coated PS-\( b \)-PVP films is in the 80–90° range, which is close to that of PS homopolymers, implying that the surfaces are preferentially enriched with PS blocks. A short exposure to ethanol for 10 min leads to a reduction of the WCA to \( \sim 62^\circ \). Longer swelling of up to 15 h further reduces the WCA to 55°. As the evolution of surface morphology with swelling duration may also contribute to the change in the WCAs, the surface segregation of PVP chains was further confirmed by X-ray photon spectroscopy.\(^{25} \)

4. PORE CLOSING INDUCED BY SOLVENTS SELECTIVE FOR THE MAJORITY BLOCKS

This swelling-based pore-making strategy is nondestructive because it is purely a physical process and does not involve any chemical reactions. The chemical composition of BCPs remains unchanged during the swelling and the subsequent drying process. A very interesting characteristic inherent to the nondestructive nature of the pore-making method is that the pore-opening process is reversible and the opened pores can be closed by exposure to solvents selective for the majority blocks. We first prepared porous PS-\( b \)-PVP films by swelling in warm ethanol and then immersed the porous films into different nonpolar solvents. Nonpolar PS-selective solvents, for example, cyclohexane, can be used to close the pores in the ethanol-treated PS-\( b \)-PVP films.\(^{29} \) When immersed in cyclohexane, the porous films were progressively closed until they were completely sealed, recovering to their initial nonporous morphology. Moreover, the rate of pore closing can be controlled by the affinity of solvents to the PS blocks.

The mechanism for the pore closing by exposure to PS-selective solvents is similar to that of the pore opening process, and both are driven by the selective swelling of one block in the BCP. With the continuous uptake of cyclohexane, the mobility of the PS chains is significantly enhanced, eventually resulting in the deformation of the originally glassy PS framework. Driven by the locomotion of the PS chains, the PVP chains originally lined on the pore wall are forced to migrate inward to prevent the energetically unfavorable contact with cyclohexane. The PVP chains are aggregated to form isolated PVP microdomains embedded in the PS matrix. Because of the squeezing effect of the swelling PS chains, the size of the pores

Figure 2. Changes in the thickness and water contact angles of PS-\( b \)-PVP films after swelling treatment in ethanol at 60 °C for different durations.
in the films is progressively reduced until the pores are completely sealed. The closed films can be reopened by exposure to PVP-selective solvents, and the pore-opened films can once again be closed by PS-selective solvents. Such a pore opening/closing process can be repeated at least dozens of times by alternatively exposing the films to PVP- and PS-selective solvents, producing nanoporous and nonporous films, respectively.

5. ORDERED POROSITIES THROUGH SELECTIVE SWELLING OF PRE-ALIGNED BLOCK COPOLYMERS

Swelling of the as-coated BCP films leads to interconnected porosities with scattering pore sizes because the microdomains of the minority blocks are randomly oriented. Ordered porosities can be obtained by introducing a prealignment treatment of the BCP films prior to the swelling. Swelling and subsequent drying can faithfully convert the minority microdomains aligned in any orientation into the correspondingly oriented pores without weakening their ordering. This is because pore orientation (by alignment) and pore formation (by swelling) are separate and consecutive steps that can be independently controlled and tuned. We recently fabricated uniform “standing” and “sleeping” nanochannels by selective swelling of perpendicularly and in-plane aligned BCP films, respectively.27,30

5.1. Standing Pores

Standing pores are referred to pores oriented perpendicularly to the substrate surface. In the fabrication of standing pores, we used chloroform to anneal the PS-b-PVP films.27 A short exposure to chloroform vapor for several minutes followed by instant vapor evaporation31 led to the perpendicular orientation of the PVP cylinders hexagonally arranged in the PS matrix. The aligned films were then immersed in ethanol for several hours, and the initially solid PVP cylinders were converted into empty cylindrical pores while the ordering and spacings of the pores were unchanged compared with those of the PVP cylinders (Figure 3a). Close observations of the cross sections of the swelling-treated films reveal that the pores are straight and traverse the entire film (Figure 3b).

The diameters of the straight pores are determined by the sizes of the initial PVP cylinders as well as the degree of swelling. Correspondingly, we can tune the pore sizes by changing the molecular weights of BCPs or by changing the swelling conditions. For example, the pore size was increased from 12 to 35 nm with the molecular weight increased from 56000 Da (PS)-b-16500 Da (PVP) to 290000 Da (PS)-b-72000 Da (PVP) by ethanol swelling at 50 °C for 3 h. The pore size was further enlarged to 46 nm by swelling at 60 °C for 3 h (Figure 3c).27 Alternatively, the pore sizes could be tuned in a wider range by the incorporation of additives into the PVP cylinders followed by ethanol treatment.28,32 In this case, ethanol has dual effects (swelling of the PVP blocks and dissolution of the additives) to transform the PVP cylinders with the incorporated additives into empty pores. We note that the incorporation of additives into the BCP systems makes the pore-forming process not completely nondestructive because the additives have to be removed and are left in ethanol.

5.2. Sleeping Pores

Pores in other orientations can be similarly obtained by selective swelling of BCP films with corresponding orientations. By annealing with 1,1,2-trichloroethane followed by instant evaporation, we obtained the in-plane orientation of PS-b-PVP films. Subsequent swelling in ethanol at 50 °C for 3 h produced densely packed, long and narrow channel-like pores winding in the surface of the films (Figure 3d). These pores are parallel to the film surface and can therefore be termed as “sleeping” pores. The pores exhibited a uniform pore width of 12 nm, which is equal to the diameter of the standing pores prepared from the same BCP under identical swelling conditions. The only difference between the standing pores and the sleeping pores is their orientation, while their pore sizes and chemistry of the pore wall are identical because these features are determined by the original PVP cylinders as well as the swelling conditions.

6. APPLICATIONS OF THE NANOPOROUS BULK BLOCK COPOLYMER MATERIALS

The ordered, flexibly tunable nanoporous BCP bulk materials such as the active pore walls, suggest interesting applications of the selective swelling-induced nanoporous BCP bulk materials such as separation membranes, optical coatings, and precursors for the syntheses of functional materials.

6.1. Applications as Separation Membranes

As we predicted several years ago,12 membrane separation is a straightforward application of the swelling-induced porous films. First, their pore sizes fall in the ~10–50 nm range, making them particularly suitable for ultrafiltration; second, the uniform pore sizes are highly desired to ensure high separation selectivities; third, the pore walls covered with polar blocks exhibit a strong hydrophilicity as well as inherent stimulus responsiveness; finally, the nondestructive pore-making strategy in which both the polymers and the swelling agents can be directly recycled is highly desirable for improving the ecofriendliness in the production of separation membranes. The first work on membrane separations of the selective swelling-induced nanoporous structures was performed on interconnected porous films obtained from as-coated, non-aligned PS-b-PVP films.33 Dilute BCP solutions were coated on water-filled macroporous poly(vinylidene fluoride) (PVDF) substrates that were then dried to form dense BCP layers.
adhering to the substrates. Subsequent swelling treatment in warm ethanol produced composite membranes with nano-porous top layers with a thickness of a few micrometers (Figure 4a). Because the BCP layers were tightly adhered to the PVDF substrates, the composite membranes were sufficiently mechanically robust for use in pressure-driven ultrafiltration (inset in Figure 4b).

The water flux of the composite membranes can be regulated from ∼100 to 313 L/(bar·m²·h) by increasing the swelling duration from 1 to 30 h, whereas the retention of bovine serum albumin (BSA) was still maintained at >60%. The flux can be significantly upgraded to >2000 L/(bar·m²·h) by reducing the thickness of the nanoporous BCP layers down to a few hundreds of nanometers.34 This swelling process on as-coated BCP films was also used to prepare nanoporous membranes of PS-block-poly(methyl methacrylate) (PMMA), and good separation performances were also achieved.19 Similarly, a swelling treatment known as collective osmotic shock was performed on the cross-linked PS-b-PVP, and ordered porous membranes were obtained.35 Interestingly, in the presence of weak-polyelectrolyte-natured PVP blocks on the pore walls, the membranes exhibit a sensitive, pH-dependent water permeability, because PVP chains change their conformation in response to the changes in environmental pH (Figure 4b). It should be noted that this smart stimulus responsiveness was achieved simultaneously with the pore formation, and in stark contrast to postmodification of preformed membranes,36 it is therefore inherent to the swelling-induced porous membranes of amphiphilic block copolymers.

Straight pores with uniform pore diameters are particularly desired in membrane separation because uniform pore diameters promise sharp selectivity,37 while a straight pore profile guarantees an enhanced permeability because the flow resistance in straight pores is smaller than that in tortuous pores. Moreover, straight pores have a better fouling resistance than tortuous pores. We have termed membranes composed of uniform and straight pores as “homoporous membranes” (abbreviated as “HOMEs”).32,38 The pores in a homoporous membrane do not necessarily need to be isotropic or cylindrical in shape.38 Pores in other geometries, such as the sleeping pores discussed above, may also constitute homoporous membranes delivering excellent separation performances.

Homoporous membranes with standing pores were prepared by swelling the perpendicularly aligned PS-b-PVP films.39 The BCP films as thin as 70 nm deposited on smooth substrates were perpendicularly aligned and then transferred to macro-porous PVDF membranes. The substrates must have a

Figure 4. Morphology and the stimulus responsiveness of swelling-induced PS-b-PVP membranes. (a) Cross-sectional SEM image of the nanoporous BCP membrane composited on a PVDF macroporous substrate. (b) pH-responsive water fluxes of a membrane prepared with a swelling duration of 24 h. Inset in panel b is a photograph of a composite membrane. Reproduced with permission from ref 33. Copyright 2012 Royal Society of Chemistry.

Figure 5. Schematic of the fabrication of homoporous membranes with standing pores supported on macroporous PVDF substrates. Reproduced with permission from ref 39. Copyright 2014 Elsevier B. V.
hydrophobic surface, which can be achieved by grafting with PS homopolymers to obtain pores that are open at both ends after swelling. Subsequent immersion of the composite membranes in warm ethanol converted the perpendicular cylinders into straight pores in the BCP layer (Figure 5). The obtained membranes exhibited a permeability as high as \( \sim 1700 \text{ L/(bar \cdot m}^2\cdot \text{h)} \), which is approximately 10 times higher than that of commercial membranes with similar rejections. Furthermore, the alignment of the BCP films can also be done directly on porous substrates, thus avoiding the cumbersome transfer operations.

In-plane oriented pores with high ratios of pore length to pore width are of particular interest in membrane separations. It has been theoretically and experimentally demonstrated that slit-shaped pores that have high aspect ratios deliver enhanced selectivities as well as permeabilities and also better fouling resistance than cylindrical pores. However, it remains extremely challenging to create such pores with pore width down to the nanometer scale at an affordable cost. The densely packed sleeping pores with pore widths down to 12 nm produced by swelling the in-plane aligned BCPs are an excellent solution to this problem. We transferred the prealigned BCP films onto macroporous poly(ether sulfone) (PES) substrates followed by ethanol swelling and obtained homoporous membranes with sleeping pores deposited on PES substrates (Figure 6a,b). This homoporous membrane exhibited a porosity as high as 34.8%, which was more than twice that of the membranes with cylindrical standing pores with a pore diameter identical to the pore width of the sleeping pores. Because of the high porosity, ultrathin selective layers, and the hydrophilic surface, the homoporous membranes with sleeping pores exhibited a remarkable water permeability of \( \sim 3400 \text{ L/(bar \cdot m}^2\cdot \text{h)} \) at BSA retention of 75% (Figure 6c). Furthermore, the membrane showed an excellent size-selective separation in discriminating 2 and 10 nm colloidal gold nanoparticles (Figure 6d). Homoporous membranes composed of either standing pores or sleeping pores also exhibit an inherent pH-responsive functionality.

6.2. Other Applications

The swelling-induced porous membranes have also been explored in a number of other applications. We coated PS-b-PVP films on glass substrates followed by swelling treatment to introduce nanopores. Because of the presence of nanopores and film thicknesses that can be easily tuned to be one-quarter of the light wavelength, the coated glasses exhibited excellent antireflective properties with light transmittance higher than 99% under optimized conditions. Considering the reversible nature of the swelling-induced nanoporous BCPs, they can potentially be used in controlled release. Drugs, either small molecules or proteins, can be loaded into the pores, and then the pores are (partially) closed by exposing the films to solvents selective to the majority blocks, thus allowing the stable and long-term release of the loaded drugs. By using these porous membranes as templates, different structures copying the porosities of the templates can be produced with the replicas possibly delivering new functionalities. Using atomic layer deposition (ALD) of metal oxides along the pore walls followed by the combustion of the polymeric templates, we produced arrays of nanotubes and networks of three-dimensionally interconnected nanotubes using standing pores and interconnected pores, respectively, as templates (Figure 7a). Although the tube walls were as thin as a few nanometers, the obtained networks were highly porous and also robust due to their interconnected structure (Figure 7b). These networks of nanotubes showed excellent antireflective and humidity-sensing performance because of their highly porous nature and large surface areas. Furthermore, the uses of the swelling-
induced nanoporous BCPs as precursors for supercapacitors, solar cells, biosensors, etc., are also expected and are currently under investigation.

7. CONCLUSIONS

Selective swelling of block copolymers is distinguished from other pore-making strategies for its nondestructive nature, extreme simplicity, and reversibility in the pore forming process. In this method, pores are formed strictly along the microdomains of the minority blocks, and therefore, a rich library of ordered morphologies of block copolymers can be converted precisely to empty voids without the loss of the ordering and uniformity as well as integral stabilities. Thus, obtained porous materials are finding important applications in various fields, with their use in separations as homogenous membranes as one of the most promising applications because their uniform pore sizes, straight pore profiles, and hydrophilic pore walls are an exact match for the requirements of the next-generation advanced membranes. Future efforts are suggested for the following; (i) expanding the range of pore sizes beyond the currently available 10–50 nm, thus extending applications such as nanofiltration, nanofluidics, adsorption, and tissue engineering; (ii) developing low-cost sources of copolymers suitable for this method for the sake of upscaling and practical applications, which are the focus of our current research; (iii) design of pores with other geometries by taking advantage of the rich morphologies of block copolymers, especially multi-block copolymers, because this swelling method has very recently been demonstrated to also be applicable to ABC-type triblock terpolymers, and (iv) creation of graded porosities to further improve the performance in membrane separations by controlling the swelling process. Moreover, because separation performances are not merely dependent on pore sizes and the interactions between the species to be separated and the pore surfaces are also playing a significant role, more studies are therefore expected to functionalize and modify the surfaces of thus produced porous membranes to further enhance the separation. With continuous progress in these areas, this pore-making methodology is foreseen to further expand its range of applications to provide porous materials with well-defined porosities for both research and industry purposes.

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**Notes**

The authors declare no competing financial interest.

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