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Thin Isoporous Block Copolymer Membranes: It Is All about the Process

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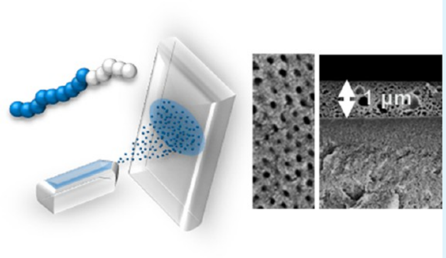

ABSTRACT: The combination of the self-assembly of amphiphilic block copolymers and the nonsolvent induced phase inversion process offers an efficient way to isoporous integral-asymmetric membranes. In this context we report fast, easily upscalable and material reducing ways to thin self-assembled membranes. Therefore, we succeeded to implement a spray or dip coating step into the membrane formation process of different diblock copolymers like polystyrene-*block*-poly(4-vinylpyridine), poly(α-methylstyrene)-*bock*-poly(4-vinylpyridine), and polystyrene-*block*-poly(*iso*-propylglycidyl methacrylate). The formation of hexagonal pore structures was possible using a highly diluted one solvent system allowing the reduction of diblock copolymer consumption and therefore the production costs are minimized compared to conventional blade casting approaches. The broad applicability of the process was proven by using different flat and hollow fiber support materials. Furthermore, the membranes made by this new method showed a more than 6-fold increase in water flux compared to conventional polystyrene-*block*-poly(4-vinylpyridine) membranes with similar pore sizes prepared by blade casting. The membranes could be proven to be stable at transmembrane pressures of 2 bar and showed a pH responsive flux behavior over several cycles.

KEYWORDS: *block copolymer, self-assembly, nanoporous membranes, spray coating, dip coating, pH responsive*

INTRODUCTION

Isoporous membranes have gained growing importance due to their versatile structures with many promising applications including micro- and nanofiltration, cell separation, controlled drug delivery, optics and gas separation in the last couple of years.[1] In particular integral asymmetric, isoporous membranes made from amphiphilic block copolymers have attracted increasing scientific interests because they can be prepared in a fast membrane casting process using a combination of the self-assembly ability and the nonsolvent induced phase-separation process (SNIPS).[2−8] A unique feature is that the open pores are directly formed within the process. The first and most understood diblock copolymer system in this connection is polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer, which has been studied in flat sheet[9−11] and hollow fiber[12] geometry

For membrane fabrication via SNIPS an amphiphilic block copolymer is dissolved homogeneously in a defined solvent system. Concentrated solutions are required in order to enable suitable conditions for the structure formation. The solution is cast on a support material or a glass plate using a doctor blade and the film is exposed to free air for a specified time. Then the film is transferred into a nonsolvent, usually water, leading to the so-called "phase inversion". The result is an integral-asymmetric membrane comprising an isoporous hexagonal[9] or square pore lattice[3] on top. The selective top layer consists of arranged cylinders aligned perpendicular to the surface with a length of typically in the range of 100 to 500 nm and this layer is merging into a spongelike substructure underneath with a thickness in the range typically between 40 and 60 μm.[2,10]

However, the high consumption of the expensive block copolymer limits the scalability and usability of the membranes even if the polymer concentration could be reduced by the inclusion of additives.[13−15] Recent work further pointed out that blending can be used to control the pore size when the synthesis of a desired block copolymer fails.[5] Moreover, current results of our group clearly point out that the substructures of PS-*b*-P4VP membranes play an important role with regard to their separation performance.[16] On the one hand it provides an additional resistance limiting the transport rate; on the other hand, it can act as an additional selective layer because of its density. Additionally, the thickness of the substructure also leads to higher adsorption rates and filtrate loss within the membrane. Therefore, the molecular weight cutoff (MWCO) does not depend only on the surface pore size; the substructure can also have a big influence.

Also without the phase inversion step, a hexagonally arranged microphase-separated open porous structure at the surface of block copolymer films can be achieved by solvent evaporation and etching. Phillip et al. discussed the thermodynamic and kinetic parameters influencing the structure formation of this well-ordered separation layer, which can reach thicknesses up to approximately 500 nm.[17] Together with the highly tortuous and

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not very porous substructure, such relatively thick separation layers will have a negative influence on the permeation flux.

To fully exploit the potential of the narrow pore size distribution and the high porosity of the surface layer of the block copolymer membranes, we should reduce the thickness and density of the substructure. Using blade casting, the thickness of the membranes up to now is limited to 11 μm. Additional attempts to further reduce the thickness by blade casting led to cracks or inhomogeneous membranes due to the sinking of the polymer solution into the porous support.[16]

Thin film coatings are widespread in various technologies, e.g., in packaging applications[18] or in organic transistor technology.[19] However, the manufacture of very thin layers requires extremely high precision capabilities. To ensure homogeneity and the desired properties, we established a range of techniques to apply thin film polymer coatings upon a support material. They can be classified in techniques such as chemical vapor deposition (CVD),[20] e.g., plasma polymerization,[21] atomic layer deposition (ALD) as a thin film deposition technique, and the chemical solution deposition (CSD), like spray, dip, or spin coating and brush casting.[22]

In the laboratory setting, the most common way to deposit a thin polymer film is the spin-coating. Unfortunately, the process operates discontinuously and it is impossible to deposit large areas.[23] In contrast, spray-coating is widely used to cover large areas or to coat 3D microstructures.[23,24] Both aforementioned methods are widely spread in the investigation of the self-assembly properties and the preparation of thin block copolymer films. Dimitriou et al. show that different surface compositions were achieved when using either spray- or spin-coating technique for the deposition of amphiphilic block copolymers. This is explained by differences in air−solvent interfacial area as well as the time frame available for surface organization during deposition. Using a spray-coating technique, they were able to produce a microphase-separated morphology.[23] Recent work of Hu et al. demonstrated that the electrospray deposition with dilute amphiphilic block copolymer solutions offers a way to well-ordered thin films and an opportunity to manipulate their microstructure.[25,26]

Large-area manufacturing of thin films is also possible using the dip-coating procedure. Its high potential is attributable to its low cost, simplicity, and good control in thickness. Furthermore, it is a waste-free process and easy to scale up.[27] Therefore, the dip-coating approach is widespread in membrane technology, in particular in the production of thin dense membrane layers for gas separation applications.[28,29] However, Mansouri et al. succeeded to combine a discontinuous dip-coating and the breath figure approach in order to produce very thin (300−400 nm) isoporous polysulfone membranes. In this way, they were able to produce membranes with pore sizes between 700 and 2000 nm.[30] Furthermore, dip coating in combination with controlled evaporation is a valuable tool in the production of highly ordered nanostructures because of block copolymer self-assembly.

To the best of our knowledge, this is the first time that either spray- or dip-coating could be implemented successfully in the SNIPS process allowing the fast production of thin isoporous block copolymer membranes. In this paper, we present first results mainly on PS-*b*-P4VP diblock copolymer membranes prepared by dipcoating and two spraying techniques. We also demonstrate the pH responsivity of such a novel membrane, which is significantly thinner compared to membranes obtained by blade casting.

RESULTS AND DISCUSSION

Membrane Preparation. Three different application techniques, namely spray coating using a TLC-fine-spray system or an airbrush system and a dip coating approach using a homemade coating machine, were incorporated in the SNIPS process in order to apply thin polymer films to a defined substrate and substitute the blade coating (Figure 1). Using blade casting for preparation of isoporous integral asymmetric membranes requires rather highly concentrated block copolymer solutions (approx. 20−30 wt %) and solvent mixtures inducing varying degrees of swelling of both blocks.[2] Such concentrated solutions are difficult to spray or dipcoat because of their higher viscosities. Therefore, highly diluted systems are essential in order to ensure a uniform application using the spray or dip coating. In comparison to blade coating, the polymer consumption is much lower.

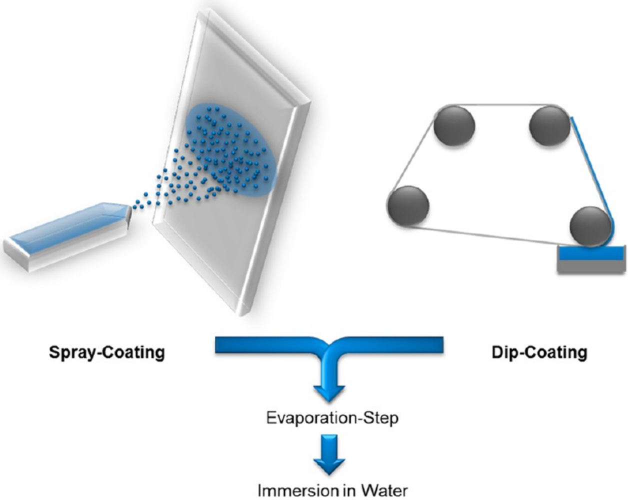

Figure 1. Schematic presentation of the membrane production process involving either spray (upper left) or dip coating (upper right), adapting the SNIPS.

One weight percent solutions of $PS_{17}P4VP_{83}^{88}$ (the subscript numbers indicate the weight percentages of the respective blocks and the superscript number the total molecular weight in kg/mol) in dioxane could be successfully utilized for the membrane fabrication using either of the aforementioned thin film preparation methods.

The surface structures of the resulting membranes are depicted in Figure 2.

Each of these membranes has a regular hexagonal pore pattern with a narrow pore size distribution confirming the potential of the self-assembly process from dilute solutions for the preparation of thin block copolymer membranes via phase inversion. However, each application technique has advantages and drawbacks, which should be described briefly with regard to our development.

To validate the concept on laboratory scale and to figure out the process drivers and the limitations of the system, we should keep the consumption of the expensive block copolymer as small as possible. The TLC-fine spray system and airbrush gun are our devices that are most suitable to enable small scale production and therefore a low consumption of polymer solution. However, the reproducibility using the TLC-fine spray system is critical, because the pressure in the device used in this

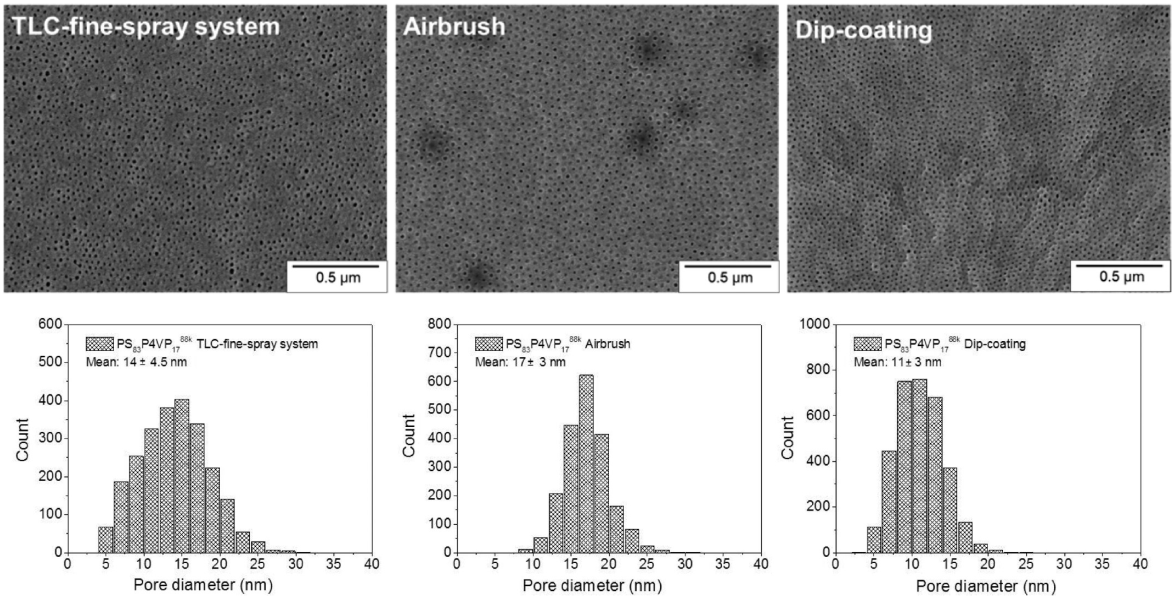

Figure 2. SEM images of the surface of membranes made from 1 wt % solutions of $PS_{83}P4VP_{17}{}^{88}$ in dioxane using a TLC-fine-spray system (left) and an airbrush gun (middle) as spray coating and the dip-coating technique (right). Pore statistics were obtained by the software "analySIS".

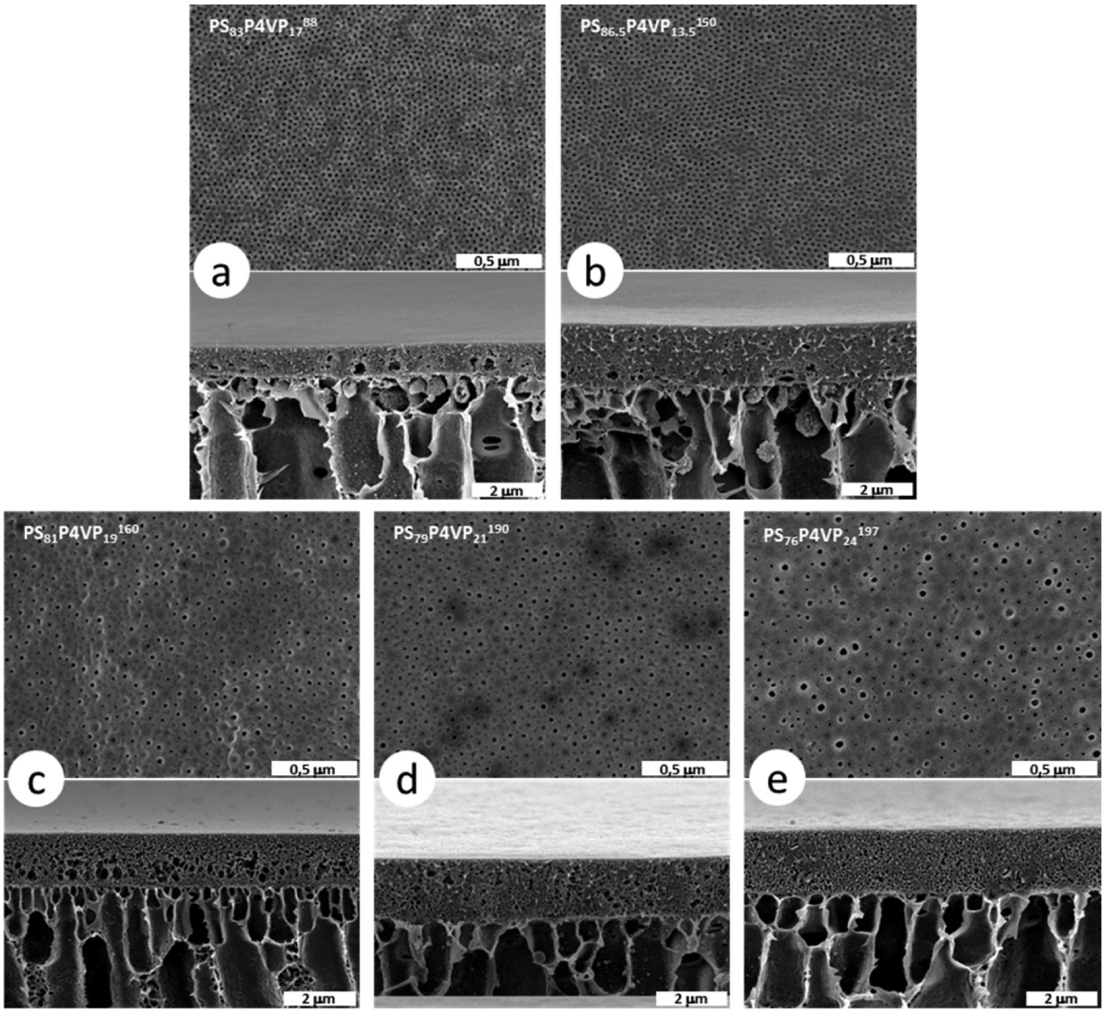

Figure 3. SEM images of self-assembled membranes made from PS-*b*-P4VP with different molecular weights and P4VP contents. For each block copolymer, the resulting membrane surface structure is depicted and the corresponding cross-sectional view is shown underneath. All membranes were prepared by using the airbrush technique on PVDF membranes, followed by immersion in water.

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study is built up manually and is therefore dependent on the operator. This has a considerable impact on the coating thickness. Moreover, the distribution of the droplets is not well-defined. In contrast, the airbrush technique allows working with defined pressures and the distribution of the droplets is controlled by the nozzle diameter. The dip-coating approach is highly promising for upscaling, since it provides a good control over the thickness and prevents the formation of explosive gas mixtures. In comparison to the spraying techniques, higher amounts of polymer solutions are consumed. Because the pore size distribution of the membrane prepared by the airbrush technique was narrower compared to the membranes obtained by the two other techniques, the airbrush technique was mainly used in the following studies.

Recent results of our group clearly point out that the pore size of self-assembled block copolymer membranes obtained by blade casting can be tailored by adjusting the molecular weight and the composition of the PS-*b*-P4VP diblock copolymer or diblock copolymer blends used in the SNIPS process.[9,5] Therefore, selected PS-*b*-P4VP diblock copolymers varying in molecular weight and P4VP content were used in the membrane fabrication process on polyvinylidene fluoride (PVDF) support membranes using the airbrush spraying technique.

Figure 3 shows the SEM-images of the resulting membrane surfaces and cross sections, whereas Table 1 summarizes the diblock copolymers used and the statistical analysis of the surface morphology.

Table 1. PS-*b*-P4VP Diblock Copolymers Used for the Membrane Formation by Airbrush Technique on PVDF, Resulting Pore Diameter, and Average Membrane Thickness

sample[a]	PS-*b*-P4VP[b]	pore diameter (nm)[c]	no. of open pores (%)[d]	average PS-*b*-P4VP thickness (μm)[e]
a	$PS_{83}P4VP_{17}{}^{88}$	16 ± 4.5	70–75	1
b	$PS_{86.5}P4VP_{13.5}{}^{150}$	21 ± 4.5	50–60	2
c	$PS_{81}P4VP_{19}{}^{160}$	16 ± 5.5	45–50	3
d	$PS_{79}P4VP_{21}{}^{190}$	15 ± 5	65–70	2
e	$PS_{76}P4VP_{24}{}^{197}$	20 ± 7.5	75–80	2

[a] Connecting the given information to Figure 3. [b] The subscript numbers indicate the weight percentages of the respective blocks and the superscript numbers the total molecular weight in kg/mol. [c] Pore diameters were measured from SEM images using the software "analySIS". [d] The number of pores was obtained by the software "analySIS" and depends on the gray scale borderline, above which a pore is considered open. [e] The thickness of the PS-*b*-P4VP layer was measured from SEM images of the cross-section.

Hexagonal pore patterns on the surface can be found consistently for all membranes. However, the pore structures are not completely developed for membranes made of polymers with higher molecular weight and higher P4VP content (Figure 3c–e) indicating that some of the pores are still closed. The pore size seems to increase with growing molecular weight and P4VP content. However, different from the blade cast membranes discussed before,[9] a clear relationship between these parameters and the pore diameter cannot be stated here. The cross-sectional views of these membranes reveal an integral-asymmetric substructure in the thin block copolymer layer with quite varying thicknesses (1–3 μm), which is supported by a PVDF membrane containing huge caverns. The huge thickness variations in the different block copolymer layers are most likely due to the manual operation of the airbrush spraying and this may also be a reason for the pore sizes found in these membranes.

pH Responsive Behavior. PS-*b*-P4VP membranes in contrast to the support membranes used here are known to be pH sensitive providing a tool to adjust their separation performance.[15] Decreasing the pH value of the permeate induces the swelling of the P4VP-block and thereby a reduction of the effective pore size leading to a flux decline. At low pH values (pH approximately 3) the pores are nearly closed. In order to verify whether thin block copolymer membranes prepared by the airbrush attempt show pH dependent water flux behavior and ensure that defect free block copolymer films were prepared, water fluxes were measured at six different pH values (Figure 4, left). The process is reversible.[16] Stepwise decreasing the pH value leads to a reduction in flux to a minimum of ~30 L m^{-2} h^{-1} bar^{-1} at pH ~ 3.2. Subsequent increase of the pH value induces a gradual increase of the flux until at pH ~ 5.1 the initial flux is almost recovered. Therefore, our results confirm the pH responsive behavior of thin block copolymer membranes of PS-*b*-P4VP. Four pH cycles were applied in order to test the stability of the membrane (Figure 4 right). In each cycle, the initial flux could be recovered and the switching could be confirmed. Since the flux decline at pH 3 is quite high (around 80% compared to the flux at pH 5) the PS-*b*-P4VP layer will be homogeneously distributed on the support membrane without huge defects.

Furthermore, the membrane with a pore size of ~16 nm has a pure water flux (pH ~ 5.1) of about 400 L m^{-2} h^{-1} bar^{-1} at the beginning. This corresponds to a more than 6-fold increase in water flux compared to conventional PS-*b*-P4VP membranes with similar pore sizes prepared by blade casting.[31] The primarily rather high water flux value decreases after storing the membrane for a longer time in water, as can be seen from the lower values of about 250 L m^{-2} h^{-1} bar^{-1} in the pH cycling experiments (Figure 4b). The initial water flux value compares reasonably well with a theoretical value of approximately 630 L m^{-2} h^{-1} bar^{-1} obtained by applying Hagen–Poisseuille's law and a fraction of 70% open pores as indicated in Table 1. If only the top layer (approximately 50 nm) is considered as a flow resistant layer, the expected water flux value would be approximately 12700 L m^{-2} h^{-1} bar^{-1}. This indicates that there are no large defects in the membrane and the relatively dense structure under the top layer also contributes to the membrane resistivity. It will be also a future challenge to increase the porosity of the membrane's substructure.

Versatility of the Process. Different support materials were tested in the airbrush spray coating approach in order to verify the versatility of the process. To ensure a successful coating, the support material should fulfill several important requirements, such as a suitable wettability and a flat and homogeneous surface. Figure 5 depicts SEM figures of the resulting thin film membranes on top of three different support membranes, namely polyacrylonitrile (PAN), polycarbonate (PC), and PVDF

Either PAN, PVDF, and PC membranes could be successfully used for the production of isoporous thin film block copolymer membranes by the combination of the spray coating attempt and the SNIPS process. However, the SEM figure of the cross-section reveals that the PC track etched membrane is not stable under the chosen conditions clarifying the limits of the method. Because dioxane is a solvent for PC, the support material is partially dissolved in the short time of

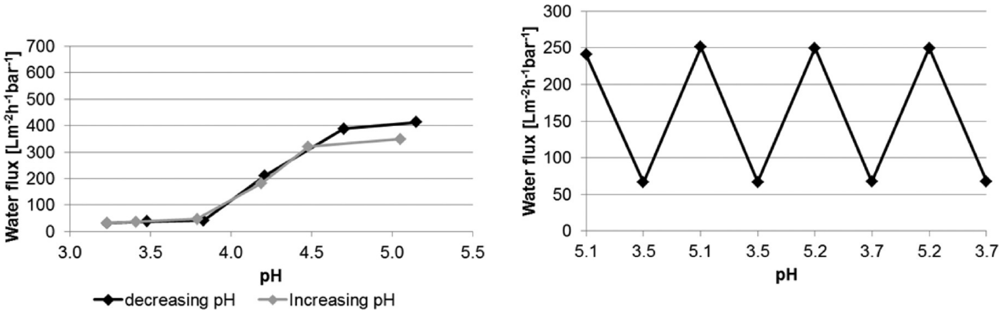

Figure 4. pH-dependent water flux of a thin block copolymer membrane consisting of $PS_{83}P4VP_{17}^{88}$ supported by a PVDF membrane (left) and pH responsive behavior of this block copolymer membrane after storage in water overnight for 4 test cycles (right). Measurements were performed at transmembrane pressures of 2.0−2.1 bar at room temperature.

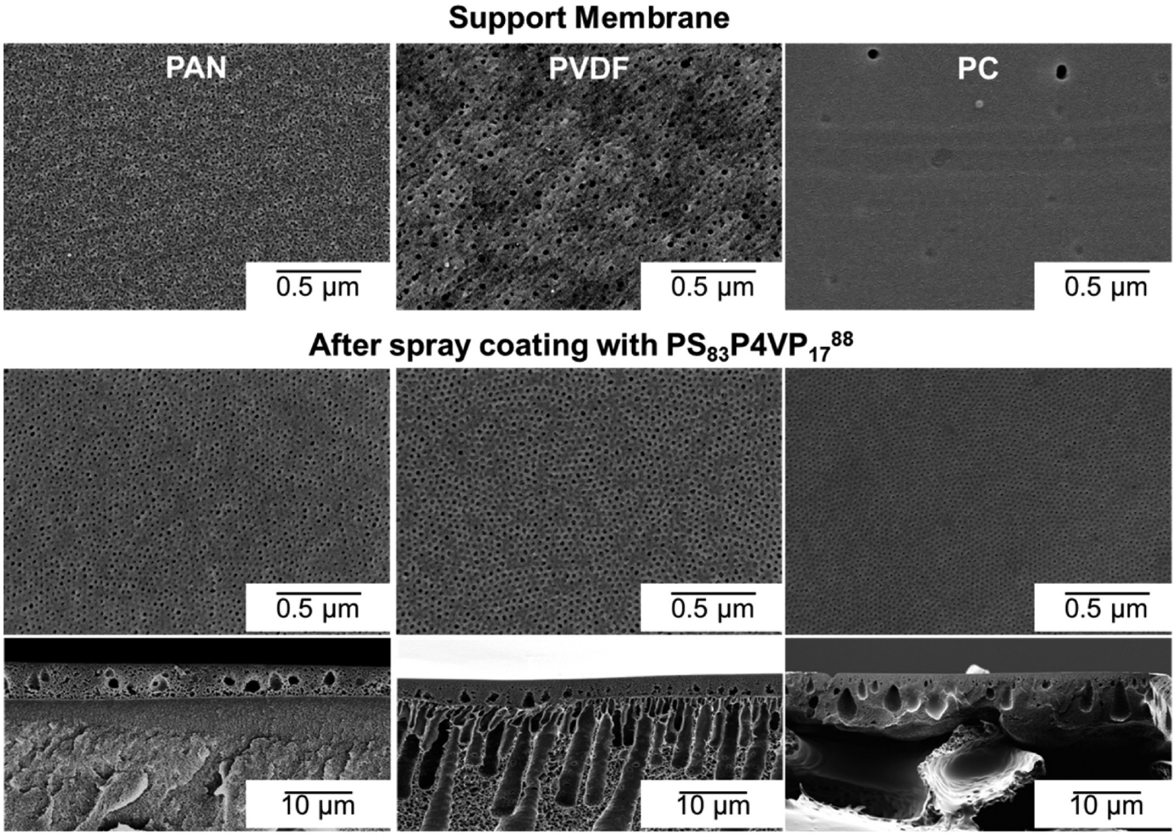

Figure 5. SEM images of the surface and the cross-section of self-assembled diblock copolymer spray membranes. First the surface structure of the pure support membrane is depicted followed by the coated membranes of the PAN membrane (column left), PVDF membrane (column middle), and on PC track etched membrane (column right).

exposure to dioxane resulting in the deformation of this support material. However, a track etched membrane will not be a finally useful support membrane for application, because of its low porosity.

Certainly, the spray and the dip coating approaches have a huge potential for the coating of materials of different geometries, e.g., flat and hollow fiber membranes. Our results depicted in Figure 6 demonstrate that the spray coating approach using $PS_{83}P4VP_{17}^{88}$ provides a promising route to dual-layer hollow fiber membranes using only small amounts of block copolymer. However, delamination is a problem when spraying on poly(ether imide) (PEI) as done here. To overcome this problem, we have to modify the support material in order to enable a better adhesion of the coating layer.

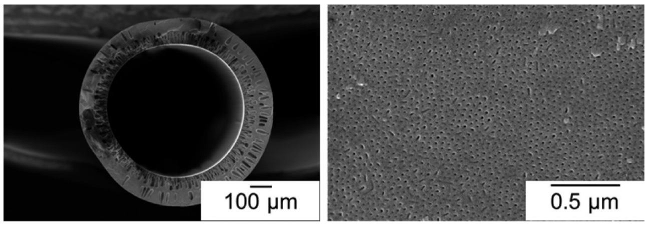

Figure 6. SEM images of the cross-section of a pure PEI hollow fiber (left) and the resulting surface structure after spray coating with $PS_{83}P4VP_{17}^{88}$.

In recent years, the SNIPS process could be successfully expanded on various diblock copolymer[32−34] or triblock terpolymer[3,35] systems. Figure 7 illustrates the flexibility of

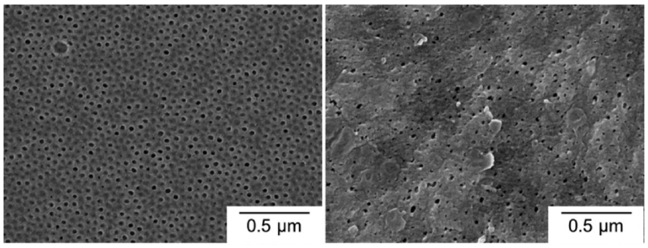

Figure 7. SEM images of the surface structure of a PαmS$_{78.1}$P4VP$_{21.9}$^{81}(left) and PS$_{72}$PIPGMA$_{28}$^{88} (right) membranes that were prepared via airbrush spraying on PVDF support membrane.

the spray coating SNIPS methods. The membrane fabrication using poly(α-methylstyrene)-*block*-poly(4-vinylpyridene) (PαmS-*b*-P4VP) and polystyrene-*block*-poly(*iso*-propyl glycidyl methacrylate) (PS-*b*-PIPGMA) shows very promising results. Especially in the case of PαmS-*b*-P4VP, we were able to produce membranes with a regular hexagonal open pore pattern. As the glass transition temperature (T_g) of PαmS (170 °C) is significantly higher than the T_g of PS (100 °C) the resulting block copolymer membranes show an enhanced thermal stability, i.e., they resist boiling water. Even for PS-*b*-PIPGMA a porous block copolymer layer could be obtained. The pore forming block of this diblock copolymer offers the possibility to introduce hydroxyl groups by a post modification reaction. However, further optimization of parameters like the evaporation time or the solvent system are required in order to obtain a really isoporous self-assembled pore structure on the surface of this membrane.

CONCLUSION

The combination of the spray or dip coating approach with the block copolymer self-assembly and the nonsolvent induced phase inversion process provides a versatile and flexible way to thin film isoporous block copolymer membranes.

A successful coating could be achieved either by airbrush gun, TLC fine spray system, or a homemade dip coating machine using highly diluted diblock copolymer solutions in dioxane. Consequently, block copolymer thin film membranes with a thickness of about 1−4 μm could be prepared. Therefore, the process has a huge potential for large scale manufacturing, because the consumption of the expensive block copolymer is exceptionally low compared to the conventional SNIPS process using blade casting. The pore size of the membranes can be influenced by varying the molecular weight and the P4VP content of the block copolymer. Furthermore, varied support materials and diblock copolymer systems were used for the membrane fabrication. Thin film PS-*b*-P4VP membranes supported by a porous PVDF support show huge water flux and show a reversible pH responsive behavior. Our future work will focus on the upgrade of the equipment for membrane production to improve the potential and versatility of the process. The increase of the porosity of the substructure will be an important task. Also the support material will be considered, in particular, the porosity of its surface layer. Moreover, the blending approach[5] will be tested providing an additional way to adjust the pore size.

EXPERIMENTAL SECTION

Materials and Methods. *The Block Copolymers.* Tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were ordered from Th. Geyer. Styrene, α-methylstyrene (αmS), 4-vinylpyridine (4VP), ethylaluminum dichloride (1 M in hexane), and *sec*-butyllithium (*sec*-BuLi) were purchased from Sigma-Aldrich, *iso*-propylglycidyl methacrylate (IPGMA) was received from BASF SE. THF was purified by successive distillation from potassium under argon atmosphere. Styrene and αmS were treated with dibutylmagnesium (MgBu$_2$) and freshly distilled prior to use. 4VP and iso-propylglycidyl methacrylate were distilled under reduced pressure and stored over calcium hydride (CaH$_2$) and distilled again after treating twice with ethylaluminum dichloride. PS-*b*-P4VP, PαmS-*b*-P4VP, and PS-*b*-PIPGMA were synthesized via sequential anionic polymerization at −70 °C in THF. The polymerization of styrene or αmS, respectively, was initiated by *sec*-BuLi. After 2 or 6 h, respectively, 4VP was added via a syringe and the solution was stirred overnight. In case of PS-*b*-PIPGMA, 1,1-diphenylethylene was added prior the addition of IPGMA and the mixture was stirred for 2 h. The polymerization was quenched with degassed methanol/HCl. After partial removal of THF under reduced pressure, the polymer was precipitated by immersion in water. The polymer precipitated quantitatively and was filtered and dried in vacuum until constant weight.

The fractional compositions of the block copolymers were determined by ^{1}H NMR (300 MHz, CDCl$_3$) using a Bruker advance 300 NMR spectrometer. Molecular weights of the precursors and polydispersities were measured by gel permeation chromatography (GPC) (Waters 2410 refractive-index detector or Rhowdex RI-101 refractive-index detector).

Membrane Preparation. The different block copolymers were dissolved with 1 wt % in dioxane while stirring until a homogeneous solution was obtained.

Spray-Coating. The different block copolymer solutions were spray-coated on various support materials, namely polyacrylonitrile (PAN, HZG), polyvinylidene difluoride (PVDF, HZG), polycarbonate track-etched membrane (PC, Pieper) or poly(ether imide) hollow fiber (PEI,HZG) membranes, using either a TLC fine-spray system or an airbrush gun type Sogolee AB-430 with a nozzle diameter of 0.3 mm. The support material was fixed on a glass plate and the spray system was either configured for vertical or horizontal application. In airbrush application the spraying pressure was set to 0.3 or 1 bar, respectively. Spray duration and distance between the gun and the support material were varied between 2 to 10 s and 5 to 10 cm, respectively. The films were left for a certain time on air before immersing them in water. The membranes were dried for 2 days under vacuum at 60 °C to remove all residual solvents.

Dip Coating. The different block copolymer solutions were dip-coated on a PVDF membrane using a homemade casting machine. The films were left for a certain time on air before immersing them in water. The membranes were dried 2 days under vacuum at 60 °C to remove all residual solvents.

Characterization. Scanning electron microscopy (SEM) was carried out on a LEO Gemini 1550 VP or a Zeiss Merlin at a voltage of 3−5 kV. Samples were sputtered with 2 nm Pt. Cross sections were prepared under cryogenic conditions.

pH dependent water flux was measured in dead-end mode using a homemade Millipore testing device. Measurements were performed at transmembrane pressures of 2.1 bar. These studies were conducted employing demineralized water with an electrical conductivity of ~0.055 μS cm^{-1}. The effective membrane area was 1.77 cm^2. HCl was used to set the desired pH stepwise between pH 5 and pH 3. For each pH value the membranes were rinsed for 20 min at 2.1 bar transmembrane pressure to reach equilibrium. Subsequently, the water flux was measured manually.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

SNIPS, self-assembly combined with the nonsolvent induced phase-separation
CVD, chemical vapor deposition
CSD, chemical solution deposition
TLC, thin layer chromatography
THF, tetrahydrofuran
DMF, *N,N*-dimethylformamide
αmS, *alpha*-methylstyrene
PS-*b*-P4VP, polystyrene-*block*-poly(4-vinylpyridine)
sec-Buli, *secondary*-butyllithium
^{1}H NMR, ^{1}H nuclear magnetic resonance
GPC, gel permeation chromatography
SEM, scanning electron microscopy
PAN, polyacrylonitrile
PVDF, polyvinylidene difluoride
PC, polycarbonate
PEI, poly(ether imide)
IPGMA, *iso*-propylglycidyl methacrylate
αMS, α-methylstyrene

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