The background of the entire page is a close-up, slightly blurred image of water ripples, showing various shades of blue and white highlights where the light reflects off the moving surface.

All The Same: Isoporous Membranes For Water Purification

Erik J. Vriezekolk

**ALL THE SAME:
ISOPOROUS MEMBRANES FOR WATER
PURIFICATION**

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1

Introduction

Water purification relies to a large extent on membrane technology¹. Although there are many technologies to purify water, e.g. adsorption, absorption or disinfection, the use of membranes is in general favored over other technologies since water purification by membranes is most cost-efficient². A membrane is a permselective barrier between two phases that allows some species to pass, while hindering or stopping others. For water purification, this means that water passes the membrane, while contaminants are rejected by the membrane. Most membranes for water purification are polymeric and are used in pressure-driven processes. These membranes are classified by their pore sizes (Table 1)³.

Ultrafiltration (UF) and microfiltration (MF) membranes are porous membranes. Water that needs to be purified is transported through the pores of the membrane by pressure-driven convective flow. Species are rejected by size-exclusion. For filtration membranes, a distinction is made between *screen filtration* and *depth filtration*⁴. In screen filtration, the pores at the surface of the membrane are smaller in size than the particles to be removed. As a result, particles are retained and accumulate at the surface. Screen filters often have an asymmetric morphology. A thin top layer that contains small pores determines the filtration properties of the membrane, while a much thicker and highly permeable underlying layer provides mechanical strength. In depth filtration, on the other hand, particles are rejected in the interior of the membrane by e.g. blockage at small constrictions or by adsorption. Pores of depth filters are often much larger than the size of the particles to be removed. The morphology of depth filters is often homogeneous through the entire thickness of the membrane. In general, most UF membranes can be seen as screen filters, while most MF membranes can be seen as depth filters.

There are many technologies to produce polymeric membranes. Examples are sintering, stretching and track-etching³. Sintering involves compressing a powder and subsequently sintering it at high temperatures, thereby fusing the particles together at their contact points. During stretching, mechanical stress is applied to a (semi) crystalline polymer film that leads to small ruptures (pores) in the film. Track-etching is a technique where a polymer film is exposed to high energy radiation, which causes damage on the film and creates tracks. The tracks can then be etched away to create pores. Most membranes, however, are fabricated through *phase separation* of polymer solutions³. In this process, an initial solution, containing at least a polymer and a solvent, is transformed into a (porous) polymer film by removing the solvent. This can be induced in many ways, though for UF and MF *liquid induced phase separation* is most common. Here, the polymer solution is immersed in a liquid that is miscible with the used solvent while it is a nonsolvent to the polymer. Due to solvent-nonsolvent exchange, the composition of the initially homogeneous solution changes. The solution splits into two phases that are thermodynamically in equilibrium: a polymer-rich phase, having a high polymer concentration, and a polymer-lean phase, having a low polymer concentration. The polymer-rich phase eventually solidifies and forms the polymer matrix of the membrane, while the polymer-lean phase leaves voids and forms the pores. Different morphologies of porous structures, e.g. interconnected pores or closed-cells, dense or open structures, can be obtained via phase inversion⁵. Also, symmetric and

Table 1. Classification of membrane processes for water purification³.

Membrane type (pore size)	Rejected species (dimensions)
Microfiltration (50-500 nm)	Yeasts (1000-10,000 nm) Bacteria (300-10,000 nm)
Ultrafiltration (2-50 nm)	Viruses (30-300 nm) Proteins (3-10 nm)
Nanofiltration (≤ 2 nm)	Smaller molecules (0.6-1.2 nm)
Reverse osmosis (0.3-0.6 nm)	Ions (0.2-0.4 nm)

asymmetric membranes can be fabricated. The obtained structure depends on both thermodynamics and kinetics of the phase inversion, which can be tuned by varying materials and process conditions⁶⁻⁷. This leads to the formation of membranes with a range of performances^{3,8}.

The complexity of the mentioned fabrication processes leads to membranes that are characterized by a high pore size distribution and/or a low porosity (Figure 1a and b). These characterizations lead in the extreme cases to either a quite permeable but not very selective membrane or a selective but not very permeable membrane⁹. The high pore size distribution leads to an imprecise rejection of molecules or particles with certain molecular weights or sizes. Therefore, the *selectivity* of UF membranes is determined by the largest pores, since these allow molecules or particles of most sizes to pass. The *permeability*, however, is determined by all pores, including the smaller pores that have a higher hydraulic resistance but do not contribute significantly to the selectivity of the membrane. Therefore, an ideal UF membrane has a selective top layer with pores that all have the same size, a characterization also known as *uniform pores*, *monodisperse pores* or *isoporous* (Figure 1c).

Since scarcity of clean water nowadays is a world-wide problem and also expected to increase, improvement of current membranes for water purification is of great importance¹⁰,

Figure 1. MF membrane (Durapore, 0.22 μm) with high porosity but high polydispersity (a), track-etch membrane (Nuclepore, 8 μm) with uniform pores but low porosity (b), polymeric microsieve with high porosity and uniform pores (c)¹¹.

and the creation of novel isoporous membranes, combined with a high porosity, is one clear way to do so.

The strategy in this work is to obtain UF membranes with a selective top layer containing ordered, straight-through and monodisperse pores. These membranes would have a sharp particle size cut-off or molecular weight cut-off combined with high permeabilities and, therefore, overcome the limitations of current commercial membranes. The selective layer of the membrane should be as thin as possible, as the thickness is inversely proportional to the membrane permeability. Three approaches to produce such highly porous, isoporous membranes are used in this thesis:

- The fabrication of polymeric microsieves by phase separation micromolding (PS μ M) and subsequent downscaling of the dimensions via solvent shrinkage.
- The fabrication of composite membranes with a thin selective top layer made of self-assembling diblock copolymers via spin coating.
- The fabrication of freestanding, isoporous, asymmetric membranes based on self-assembling diblock copolymers via phase inversion.

These three approaches are briefly discussed in the following paragraphs. At the end of this chapter, the scope and outline of this thesis is presented.

1.1 Polymer microsieves fabricated via PS μ M

Phase separation micromolding (PS μ M) is a technique that is used to produce polymer films with patterned surfaces¹². PS μ M combines the technique of phase inversion to fabricate membranes with the use of molds to fabricate negative replicates (Figure 2). The fabrication of microsieves is based on casting a polymer solution on a mold that contains uniform microstructures, for example pillars or cones¹³. Phase separation is initiated when the solvent is removed, and consequently the film solidifies. During phase separation, the film shrinks in both thickness and lateral directions¹⁴. Shrinkage of the polymer film in thickness allows the pillars to penetrate the entire film and leads to the formation of uniform pores¹⁵. Shrinkage in lateral directions leads to detachment of the film from the pillars, which makes it possible to (easily) peel off the film from the mold¹⁶. Virtually every polymer/solvent combination that is suitable for phase inversion can be used for PS μ M, with the only requirement that shrinkage in both thickness and lateral direction must take place.

The size of the pillars in microsieve molds is limited to about 1 μ m due to constraints regarding mechanical strength, and consequently the pores of microsieves are also limited to this size. As a result, the direct use of microsieves is limited to MF. In order to make microsieves applicable for UF, attempts were done to decrease the dimensions of polymer microsieves by means of shrinkage. Two approaches have been proposed: thermal

Figure 2. Principle of PSuM. A polymer solution is caste on a patterned surface (mold) (a). The polymer solidifies via phase separation (b) and a negative replica of the mold is obtained (c).

treatment¹³ and solvent-shrinkage¹⁷⁻¹⁸. In a thermal treatment, the microsieve is heated above its glass transition temperature (T_g). Using solvent-shrinkage, the T_g of the material of the microsieve is lowered by immersion in a solvent that swells the polymer. In both approaches, shrinking occurs due to densification of the polymer matrix of the microsieve. This makes the presence of voids (intrinsic pores) necessary for both approaches. Such a structure with intrinsic pores can be obtained using a suitable phase separation procedure. Although some preliminary research on the downscaling of microsieves has been done, it still lacks more systematic and extensive research to determine the application range of the approach.

1.2 Self-assembling block copolymers

The two other approaches described in this thesis make use of self-assembling block copolymers to fabricate nanoporous membranes or films. A block copolymer is a macromolecule that consists of two or more chemically different polymer blocks that are covalently linked together¹⁹. Various architectures are possible for block copolymers that contain two different monomers, A and B, e.g. linear chains such as diblock (AB) or triblock (ABA), and branched configurations such as star diblocks (AB)_n or other multiblock copolymers²⁰. A block copolymer of incompatible blocks has the ability to self-assemble into a variety of different nanostructures, depending on the composition and size of the block copolymer²¹. This self-assembly means that in order to minimize energy (interfacial area between the two block types) the block copolymer arranges itself in a morphology where the different block types form their own domains. Figure 3 shows the different morphologies obtained from a diblock copolymer (dBCP). The sizes of the nanodomains depend on the M_w of the blocks but are normally between 5-50 nm²². The strength of segregation between the polymer blocks A and B is determined by χN , which is the product of the interaction parameter χ and the degree of polymerization N ²³. The dimensionless interaction parameter χ (or χ_{AB}) represents the thermodynamic interaction between the blocks and has a positive value if the two blocks repel each other but has a negative value if the two blocks mix spontaneously²⁰. Different theoretical models have led to phase diagrams that predict the morphology for block copolymers²⁴. The obtained morphology depends on χN and the fraction of the block f_A ($= N_A/N$). However, the theoretical

Figure 3. Schematic overview of different thermodynamically stable morphologies of self-assembling diblock copolymers for increasing fraction of polymer A (f_A). The diblock copolymer is shown as a simple two-color chain for simplicity.

interaction parameter χ differs from experimentally obtained values, which leads to deviation of the real phase diagrams from theory²². As a result, the actual behavior of BCP systems has to be studied experimentally in order to get more insight in mechanisms and the versatility of the approach.

Block copolymers that form such periodic nanodomains have received significant attention, because the uniformity of these nanodomains has potential for applications such as templating²⁵⁻²⁸, high-density storage media²⁹, anti-reflection coatings³⁰, drug delivery³¹ and membranes². Two methods to produce BCP membranes are known and studied in this thesis. In the first method, a composite membrane is made by coating a BCP layer on top of a porous support membrane. In the second method, a freestanding, asymmetric BCP membrane is fabricated via phase inversion. Both methods will be explained in the following paragraphs. The molecular structures of the dBCPs used in this thesis are shown in Figure 4. These dBCPs are known to self-assemble well into ordered nanostructures because of the strong segregation between their individual blocks³²⁻³³.

Figure 4. Structures of the dBCPs used in this work.

Composite membranes with nanoporous BCP top layers

Asymmetric dBCPs that form a morphology of hexagonally packed cylinders perpendicular to the surface are interesting for use in membranes for water purification³⁴⁻³⁵, since removal of the cylindrical part results in a membrane with well-ordered, straight-through and monodisperse pores¹¹. Hence, a very selective and permeable membrane could potentially be produced based on this system⁴. The removal of the cylindrical part to create pores can be divided into two categories. In the first method, the minority part of the BCP that forms the cylinders is removed by e.g. etching³⁶⁻³⁹, UV radiation⁴⁰⁻⁴² or cleavage⁴³⁻⁴⁷. A second strategy is to add and subsequently remove a sacrificial component to the system and that resides in the core of the cylinder because of favorable interactions of that component with the minority part of the BCP^{30, 31, 35, 48-50}.

A promising method is to use a nanoporous BCP layer as the top layer of a composite membrane (Figure 5). The benefit of a composite membrane is that both layers (BCP layer and support membrane) can be optimized individually. The BCP film should be very selective and thin, whereas the purpose of the support membrane is to give the membrane mechanical strength while being very permeable. The BCP film can be coated directly on the support membrane^{38, 48} or coated on a model surface and transferred to the support membrane in a second step^{31, 34-35, 42, 51-52}. Different methods can be used for coating, e.g. spin coating, dip coating and spraying. In this thesis, spin coating has been used to fabricate composite membranes. Spin coating is an easy method to fabricate thin layers (thickness up to several hundred nanometers) on a laboratory scale. A polymer solution is deposited on a substrate that rotates at high speed. Due to centrifugal forces, the solution spreads evenly over the substrate. Evaporation of the solvent results in a thin, homogenous film. Several parameters, including solvent type⁵³, evaporation rate⁵⁴, rotation speed and polymer concentration⁵⁵, determine the thickness of the film. For BCP films, the evaporation rate also influences the orientation of the BCP nanodomains and is, therefore, an important parameter^{37, 56}.

Figure 5. Composite membrane with a thin isoporous BCP film on top of a porous support membrane.

Several working composite membranes with a selective BCP top layer have been fabricated. Li *et al.* fabricated a nanofiltration membrane with a top layer made of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) mixed with poly(acrylic acid) (PAA)⁴⁸. The PAA homopolymer resided in the core of the PEO cylinders and was selectively removed to create pores. The pore size could be controlled by varying the content of PAA. The different pore sizes led to different permeabilities (1 to 5 L·m⁻²·h⁻¹·bar⁻¹). However, these permeabilities were lower than expected. Interestingly, the different pore sizes did not change the selectivity of the membrane. The low permeabilities and constant selectivity suggested that the inner morphology of the film determined the permeability and selectivity of the membrane, probably because the orientation of the block copolymer domains changes deeper inside the film. Philip *et al.* fabricated a composite membrane with a selective top layer made of polystyrene-*block*-polylactide³⁷. Etching of polylactide and subsequent rinsing led to the formation of pores. The membrane showed rejection of solutes that was in agreement with theoretical predictions. However, also this membrane suffered from lower permeabilities than expected. When the inner morphology of the BCP layer was examined, it was found that indeed the structure of the BCP domains changed and that not all the pores span the thickness of the film. Also, it was noticed that the effective porosity of the composite membrane was very low since the support membrane already had a low surface porosity. Pores that span the thickness of the BCP film are blocked if they end on a region of the support that does not contain pores. A composite BCP membrane with a much higher permeability (400 L·m⁻²·h⁻¹·bar⁻¹) was fabricated by Yang *et al.*³⁵. They first coated a thin layer of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) mixed with PMMA homopolymers on a model surface. The substrate was then dissolved and the thin film was transferred to a highly porous MF support membrane. Subsequent removal of PMMA homopolymers led to the formation of pores. Although this method seems to overcome the problems of blocked pores, it has as major drawback that it cannot be upscaled, which makes this method practically unsuitable for industrial applications.

Freestanding BCP membranes via phase inversion

In a different approach, self-assembling BCPs were used to fabricate freestanding asymmetric porous membranes via *solvent evaporation* followed by liquid induced phase inversion⁵⁷⁻⁶⁰. This method, so called *dry-wet phase separation*, is used to fabricate asymmetric BCP membranes with a thin selective layer on top of a support layer⁶¹. The difference between phase inversion and the previous described method is that pores are formed during the solidification process of the polymer using phase inversion, while in the previously described method pores have to be created in a second step by removing parts of a dense film.

A polymer solution consisting of a BCP, a volatile solvent and a non-volatile solvent is used for the fabrication of the membrane. Commonly used BCPs for these processes are PS-*b*-P4VP and PS-*b*-PEO^{58, 62}. During the solvent evaporation step, the volatile solvent is allowed to evaporate, which causes the polymer concentration to increase locally at the top

Figure 6. HR-SEM image of an asymmetric BCP membrane made via dry-wet phase inversion, having a thin, selective, isoporous top layer⁶³.

of the cast film. The higher polymer concentration causes the BCP to self-assemble and form micelles. After immersion in a nonsolvent, the structure is quenched. The micelles in the top layer form a structure of ordered and monodisperse pores⁵⁹, while the rest of the film has a random, more open porous structure that acts as a support layer (Figure 6). The structure of the support layer is random because BCPs deeper inside the film do not get the possibility to self-assemble into ordered structures during phase inversion.

The permeabilities of these membranes are very high, in the range of $40\text{--}3000\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, and the membranes show good filtration properties^{57, 59, 64-65}. The high permeabilities are due to the highly porous support layer of the membrane, which has a structure that consists of a network of interconnected pores. Though very permeable, the support layer is also very costly since it is completely made of currently very expensive BCP.

The fabrication of asymmetric, ordered, isoporous BCP membranes is very challenging because of the many involved parameters that have to be optimized. Important parameters are the composition of the solvent mixture and the duration of the first evaporation step. This all makes it harder to upscale the process while still tuning the pore size and the morphology of the membrane^{60, 66}. BCP hollow fibers have been fabricated using dry-wet phase inversion, but only with the selective layer on the outside the fiber⁶⁷.

Scope of the thesis

The aim of the work presented in this thesis is to fabricate films and membranes that contain ordered and uniform pores with pore sizes in the range of 10-50 nm (UF membranes). Preferably the pores of the selective layer should be straight-through in order to maximize the permeability, hence, maximize the production of, for example, purified water. Special attention is given to tuning of pore sizes by varying simple parameters during the fabrication process. Different approaches are taken to meet these goals.

In **Chapter 2**, polymeric microsieves are fabricated using phase separation micromolding and subsequently downscaled in size by a solvent shrinkage treatment. The duration of this solvent shrinkage is used to tune the pore sizes of the microsieve. Special attention is given to *isotropic shrinkage*, which means that the microsieve shrinks in all dimensions at equal rates in order to retain its porosity. The effect of different types of microsieves (pore sizes and morphology of the polymer matrix) and different solvent mixtures on the shrinking behavior is investigated, but also the limitations of this versatile method are studied.

In **Chapter 3**, nanoporous films are fabricated via spin coating using a system of block copolymers and homopolymers. The block copolymers self-assemble in a cylindrical structure, while the homopolymers reside in the core of the cylinders because of favorable interactions. After fabrication, the homopolymers are selectively washed away to create pores. The films are fabricated on a model surface (silica wafer) in order to easily investigate the effect of several parameters on the pore size and pore size distribution. For example, the molecular weight of the block copolymer and the content of homopolymer are important parameters that are varied.

The next step is to fabricate these nanoporous BCP films on top of a support to create a composite membrane. This is done in **Chapter 4**. The homopolymer content is again varied in order to create membranes with different pore sizes, and the concentration of the polymer solution is varied in order to vary the thickness of the top films. The effects of both the pore size and the thickness of the top film on the permeability of the membrane are investigated. Other important results are the different filtration performances of membranes that have different morphologies.

Chapter 5 focuses on the fabrication of freestanding asymmetric BCP membranes via dry-wet phase inversion with a minimum duration for the evaporation step. Different parameters in the fabrication process are varied, such as the composition of the solvent mixture and the polymer concentration. It is shown under which circumstances ordered, isoporous membranes are formed. The different morphologies of the support layer that come with the different recipes are examined, and their effects on the permeability are evaluated as well. Filtration experiments are performed to see the difference in filtration behavior between isoporous and non-isoporous membranes.

Chapter 6 summarizes and discusses the results of the different chapters and provides an outlook for future research and challenges.

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2

Downscaling of polymeric microsieves by solvent- shrinkage

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A solvent-shrinkage method for producing polymeric microsieves with sub-micron size pores

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Abstract

This chapter presents a thorough investigation of a simple method to decrease the dimensions of polymeric microsieves. Pore sizes of microsieves are usually in the micrometer scale, but need to be reduced to below $1\text{ }\mu\text{m}$ to make the microsieves attractive for aqueous filtration applications. In this work polyethersulfone/polyvinylpyrrolidone microsieves were prepared with pores with diameters in the range of $2\text{--}8\text{ }\mu\text{m}$ (perforated pores) and a very open internal structure containing many voids. Subsequently, size reduction in terms of pore size and periodicity of the perforated pores was performed by immersing microsieves in mixtures of acetone and N-methylpyrrolidone. Microsieves shrunk because of swelling and weakening of the polymers, and subsequently collapse of the open internal structure. Shrinking typically occurred in two stages: first, a stage where both the perforated pores and periodicity shrink, and second, a stage where the perforated pores continue to shrink while the periodicity remains constant. Microsieves with initial pore diameters of $2.6\text{ }\mu\text{m}$ were reduced down to only $0.2\text{ }\mu\text{m}$. The maximum isotropic shrinkage was $\sim 35\%$, which was determined by the amount of voids in the polymer matrix. We propose that to come to higher (nearly) isotropic shrinkage, the amount of voids should be further increased.

2.1 Introduction

Microsieves are membranes that are characterized by straight-through, uniform and well-ordered pores between 0.5 μm and 10 μm in diameter¹. These characteristics lead to a high flux and excellent separation behavior²⁻³. The first microsieves were made of silicon-based materials. Although these microsieves are resistant to extreme chemical conditions and high temperatures, the use of cleanroom facilities for their fabrication process causes high manufacturing costs¹. The use of polymers as basic material makes it possible to fabricate microsieves at lower costs and with the choice for a large variety of polymers with different material properties and as such also tune e.g. hydrophobicity/ hydrophilicity of the surface. Several techniques have been developed to fabricate polymeric microsieves. One method is to create pores in an existing polymer film, for example with interference holography⁴ or track etching⁵. Other methods to fabricate isoporous films include *particle-assisted wetting*⁶⁻⁷. With this technique, a monolayer of a polymer solution with embedded colloidal particles is prepared. After solidification, the colloidal particles are etched away to create pores.

A very versatile and promising technique to create polymeric microsieves is *Phase Separation Micromolding* (PS μ M). PS μ M combines the technique of *polymer phase inversion* to fabricate membranes with the use of molds to fabricate replicates⁸⁻¹¹. In the case of fabricating microsieves, a polymer solution is cast on an inorganic structured substrate that contains a field of uniform pillars or cones. Phase separation is initiated when the solvent is removed, and the film solidifies. Shrinking of the polymer solution in thickness allows for the pillars to perforate the film, thereby creating straight-through pores. At the same time shrinking in lateral direction causes separation of the polymer and mold, which makes it possible to peel off the obtained microsieve relatively easy from the mold¹². Recently, the techniques of particle-assisted wetting and PS μ M have been combined to fabricate a well-ordered microporous structure¹³. Instead of a silicon-based mold, dissolvable polymer molds have also been used to fabricate microsieves¹⁴. Here, the mold is dissolved in order to obtain the microsieve. The advantage of this process is that the microsieve does not have to be peeled off from the mold. However, it is a destructive process since the mold has to be dissolved and consequently cannot be reused.

The size of pillars in microsieve molds is limited to about 1 μm due to constraints regarding mechanical strength and consequently also the pores of microsieves are limited to this size. Recently, some preliminary research was done on a very new approach to achieve smaller microsieve pores using the PS μ M technique: the downscaling of pore sizes and pore periodicity by shrinking of the membrane^{9,15}. Such a shrinkage approach has huge advantages. Firstly, it allows the manufacturing of membranes with a variety of pore sizes using just one single microsieve mold. Secondly, it circumvents the ordinary lower size limit of microsieves and would possibly result in microsieves with pore sizes small enough to be attractive for e.g. sterile filtration.

Different approaches to decrease the pore sizes of polymer microsieves have been proposed, like a thermal treatment^{9,16} and solvent-shrinkage¹⁵. In a thermal treatment, the microsieve is heated above its glass transition temperature (T_g). This causes the polymer matrix to densify and, as a result, the microsieve shrinks. Using solvent-shrinkage, the microsieve is immersed in a solvent that swells the polymer, thereby making the polymer chains mobile (swelling effectively lowers the T_g of the material). Also here, densification of the polymer matrix leads to shrinkage of the microsieves. Since in both approaches shrinking occurs due to densification, the presence of intrinsic pores in the polymer matrix is required for both approaches.

Although some preliminary research on the downscaling of microsieves has been done, it still lacks more extensive research. This chapter presents the first full investigation into downscaling of microsieves by shrinkage and looks at both the strengths and limitations of this technique. We focus on downscaling of PSuM fabricated polyethersulfone (PES)/polyvinylpyrrolidone (PVP) microsieves by solvent-shrinkage, since it is a versatile technique where (as we will show) kinetics can be controlled by adjusting experimental parameters. PES is a widely used material for membranes and support materials, because of its good chemical and thermal stability properties⁵. PVP is used in membranes as polymer additive in order to tune pore sizes in ultrafiltration membranes¹⁷, to suppress the formation of macrovoids¹⁶ and/or to increase hydrophilicity¹⁹. Fabricated microsieves are immersed in an acetone/*N*-methylpyrrolidone (NMP) mixture for downscaling. NMP is a good solvent for both PES and PVP, while acetone can swell PVP¹⁵. We study the shrinkage as a function of time for various acetone/NMP mixtures, a number of molds and for different internal membrane structures. The porous morphology in the polymer matrix required for downscaling is obtained by using two steps of phase inversion: vapor induced phase separation (VIPS) and liquid induced phase separation (LIPS). VIPS uses water vapor for phase inversion, which creates macrovoid-free symmetric films with closed-cell intrinsic pores^{11,20-22}. The relative humidity (RH) during VIPS is varied in order to investigate the influence on the polymer morphology. LIPS is done to remove the remaining solvent and completely solidify the film.

2.2 Experimental

Materials

Polyethersulfone (PES, BASF, Ultrason E6020P) was used as polymer for the membrane. Polyvinylpyrrolidone PVP K30, (Fluka, $M_w = 40,000 \text{ g}\cdot\text{mol}^{-1}$, polyvinylpyrrolidone PVP K90 (Fluka, $M_w=360,000 \text{ g}\cdot\text{mol}^{-1}$) and polyethyleneglycol (PEG400, Merck) were used as polymer membrane additive. Acetone (Atlas & Assink Chemie) was used as a volatile component. *N*-methylpyrrolidone (NMP, Acros Organics, 99% purity) was used as a solvent. Milli-Q pure water (deionized water purified by a Synergy water purification system of Millipore) was used as water vapor during VIPS. All components were used as received.

Table 1. SEM pictures ($\times 1500$, tilt= 26°) and dimensions (pillar base diameter ϕ_p , periodicity p_c , height h and shape) of the molds used for PSuM.

	Mold A	Mold B	Mold C
ϕ_p (μm)	3.1	2.6	8.0
p_c (μm)	9	20	19
h (μm)	18	34	42
shape	cone	needle	pyramid

Molds

Three different structured silicon substrates were used as molds (Table 1). All molds had pillars that were arranged in a square grid. Mold A had uniform cone-shaped pillars with a base-diameter of $\sim 3.1 \mu\text{m}$ and a height of $\sim 18 \mu\text{m}$ with a periodicity (distance center-center) of $9 \mu\text{m}$. Mold B had needle-shaped pillars with a base-diameter of $\sim 2.6 \mu\text{m}$ and a height of $\sim 34 \mu\text{m}$ with a periodicity of $\sim 20 \mu\text{m}$. Mold C had uniform pyramid-shaped pillars with a base-diameter of $\sim 8 \mu\text{m}$ and a height of $\sim 42 \mu\text{m}$ with a periodicity of $\sim 19 \mu\text{m}$. Molds A and C were chosen to create microsieves with different pore sizes and surface porosity. In this work, surface porosity is defined as the fraction of the surface covered by pores created by pillars. Mold B replaced Mold A in a later stage of the work when the latter broke. Photolithographic techniques and cryogenic deep reactive ion etching were used to fabricate the molds⁹.

Polymer solution preparation

The standard composition of the polymer solution for microsieving fabrication consisted of 10.0 wt% PES, 49.0 wt% NMP, 39.0 wt% acetone, 1.0 wt% PVP K30 and 1.0 wt% PVP K90 and was based on literature⁹. All components were put together and stirred overnight at room temperature. The solution was then allowed to degas for several hours to ensure that all air bubbles were removed from the solution.

In addition, a polymer solution more rich in PVP (9.9 wt% PES, 48.5 wt% NMP, 38.6 wt% acetone, 1.5 wt% PVP K30 and 1.5 wt% PVP K90) was used to investigate the effect of PVP on shrinking. A 6.5 wt% PES, 40.7 wt% NMP, 39.5 wt% acetone, 2.0 wt% PVP K30, 2.0 wt% PVP K90 and 9.4 wt% PEG400 solution was used to fabricate microsieves with a different polymer matrix morphology. This solution was prepared at 50°C in order to speed up dissolution of the polymer.

Microsieve fabrication

Before use, the mold was cleaned by immersion in NMP for 15 minutes, rinsed with acetone and finally dried with nitrogen. Then the mold was treated with oxygen plasma at 500 Watt for 10 minutes using a Plasma Fab 508 (Electrotech).

Figure 1 shows a schematic overview of the PSuM process that was used in this project. A polymer solution was cast on the structured mold (Figure 1a) using a custom made casting-machine with an adjustable casting knife (accuracy of 1 μm). The polymer solution consisted of a polymer (PES), a volatile component (acetone), a non-volatile solvent (NMP) and polymer additives. Casting was done 5 μm above the pillars. Acetone was allowed to evaporate for 2 minutes (Figure 1b) in an environment of nitrogen, which caused the film to shrink in thickness and resulted in perforation of the film by the pillars. Then the film was placed in a water vapor bath for 3 minutes, in order to get a microsieve with a morphology of small voids (intrinsic pores) that is necessary for shrinking. The vapor bath was continuously refreshed by a mixture of a stream of dry nitrogen and a stream of nitrogen saturated with water at a temperature of 30 °C. By adjusting the flow rate of the two streams, the relative humidity (RH) inside the box was regulated (between 20-95%). Initial phase separation started because of the presence of water vapor (VIPS, Figure 1c) and the film became turbid. The remaining NMP was removed by immersing the film in a coagulation bath (LIPS, Figure 1d) for 5 minutes at room temperature, which completely solidified the film. The standard coagulation bath consisted of 1 L Milli-Q pure water. A different coagulation bath of 70 wt% NMP/30 wt% Milli-Q-pure water was used to fabricate a morphology with smaller intrinsic pores. For this coagulation step, the microsieve was immersed for four hours since the presence of NMP in the coagulation bath led to slower demixing. After this second phase separation stage a polymer replica was obtained and peeled off from the mold (Figure 1e). The microsieve was rinsed in Milli-Q pure water and was left overnight in air to dry.

Different types of polymer microsieves were fabricated by adjusting process conditions during fabrication. An overview of the process conditions of all fabricated microsieves is shown in Table 2.

Microsieve shrinkage

After preparation of the native polymer microsieves, they were further used to investigate the effect of membrane structure and morphology on their shrinkage to reduce pore size. Microsieve shrinkage was done by immersing the polymer microsieves in a covered 500 mL Petri dish filled with pure acetone, a 5 wt% NMP in acetone mixture or a 10 wt% NMP in acetone mixture. A nonwoven was placed on the bottom of the dish in order to prevent the microsieves from sticking to the glass. Immersion was done for different durations (0-150 minutes). The microsieves were immersed in 1 L of Milli-Q pure water for one hour after shrinking to remove remaining solvents used for shrinking.

Figure 1. Schematic overview of the PS μ M process. A polymer solution is cast on a structured mold (a). The volatile solvent (acetone) is allowed to evaporate (b) which causes the film to shrink in thickness and allows for the pillars to perforate the film. Phase separation occurs in two steps: with water vapor in humidified nitrogen (VIPS) (c) and subsequently with water in a coagulation bath (LIPS) (d). After solidification, the film is peeled off from the mold (e).

Table 2. Process parameters for the fabrication of microsieves.

Name	Mold	Polymer solution composition (wt%)					RH VIPS (%) ^a	LIPS ^b
		PES	PVP ^c	NMP	Acetone	PEG		
M1	A	10.0	2.0	49.0	39.0	0	<20	H ₂ O
M2	A	10.0	2.0	49.0	39.0	0	83±6	H ₂ O
M3	B	10.0	2.0	49.0	39.0	0	<20	H ₂ O
M4	B	10.0	2.0	49.0	39.0	0	33±7	H ₂ O
M5	B	10.0	2.0	49.0	39.0	0	59±1	H ₂ O
M6	B	10.0	2.0	49.0	39.0	0	83±4	H ₂ O
M7	B	10.0	2.0	49.0	39.0	0	94±1	H ₂ O
M8	B	10.0	2.0	49.0	39.0	0	77±7	H ₂ O
M9	B	10.0	2.0	49.0	39.0	0	83±2	NMP/H ₂ O
M10	B	6.5	4.0	40.7	39.5	9.4	83±2	NMP/H ₂ O
M11	B	9.9	3.0	48.5	38.6	0	77±6	H ₂ O
M12	C	10.0	2.0	49.0	39.0	0	84±6	H ₂ O

^a) VIPS: 3 minutes in all cases.

^b) LIPS: H₂O = Milli-Q pure water coagulation bath for 5 minutes. NMP/H₂O LIPS = 70 wt% NMP/30 wt% H₂O coagulation bath for 5 hours.

^c) Total wt% PVP = 50/50 wt% PVP K30/PVP K90.

Characterization

Scanning electron microscopy (SEM, Jeol JSM 5600 LV, at 5 kV) was used to visualize and characterize the microsieves and molds. For preparation of the cross-section samples, the microsieves were immersed in ethanol and then broken in liquid nitrogen. All SEM samples were dried under vacuum at 30 °C for 24 hours and then coated with a thin layer of gold using a Balzer Union SCD 040 sputter device. SemAfore (Jeol) software was used to measure the perforated pore diameter and periodicity of the microsieves.

The shrinkage of both pore diameter and periodicity was defined as:

$$\text{Shrinkage} = \frac{x_{\text{initial}} - x_{\text{final}}}{x_{\text{initial}}}$$

Where x is the size of the perforated pore diameter (d_p) or periodicity (p). The diameter of the perforated pores was determined from the surface of the microsieve that was formed by the base-diameter of the pillars. Pore diameters and periodicities were determined by taking the average diameter of 24 perforation pores and average size of 12 periodicities. Standard deviations were typically 8-14% for pore diameters and 2-7% for periodicities. When the pore diameter shrinkage was >70%, standard deviations in pore diameters rose to 20-30%. The error in shrinkage was calculated using standard rules for error propagation.

2.3 Results and discussion

For clarification, the straight-through pores made by perforation are called perforated pores and the pores in the polymer matrix formed by phase inversion are called intrinsic pores.

The dimensions of the fabricated microsieves are shown in Table 3. Microsieves M1 and M2 were both fabricated with Mold A and have similar dimensions: a perforated pore size of $\sim 3.1 \mu\text{m}$ and a periodicity of $\sim 9.4 \mu\text{m}$. The perforated pore diameters of the microsieves fabricated with Mold B deviate, from $\sim 2.5 \mu\text{m}$ for M10 till $\sim 5.0 \mu\text{m}$ for M9. These differences are probably caused by different shrinking rates of the microsieves during solidification. Literature reports that process parameters, for example the composition of the polymer solution, influence the shrinking rate during solidification¹¹. Since different polymer solutions and different process conditions were used during phase separation, this may explain the different dimensions of the polymer microsieves. When Mold C was used a microsieve with a perforated pore diameter of $8 \mu\text{m}$ (M12) was obtained.

Table 3. Perforated pore diameter (d_p) and periodicity (p_c) of fabricated microsieves.

Name	Mold	d_p (μm)	p_c (μm)
M1	A	3.1 ± 0.3	9.2 ± 0.3
M2	A	3.1 ± 0.2	9.6 ± 0.1
M3	B	3.1 ± 0.3	18.8 ± 0.5
M4	B	3.1 ± 0.1	19.2 ± 0.3
M5	B	2.8 ± 0.3	19.3 ± 0.2
M6	B	3.0 ± 0.3	19.4 ± 0.3
M7	B	2.9 ± 0.2	18.9 ± 0.2
M8	B	2.6 ± 0.5	19.4 ± 0.6
M9	B	5.0 ± 0.4	18.7 ± 0.3
M10	B	2.5 ± 0.3	18.5 ± 0.2
M11	B	2.6 ± 0.3	19.0 ± 0.6
M12	C	8.0 ± 0.2	18.3 ± 0.1

Effect of relative humidity

Microsieves were fabricated with relative humidities (RH) between $<20\%$ and 83% (M1-M7) during VIPS (and equal conditions during LIPS). Figure 2 shows that the surface of the microsieve that was exposed to the water vapor during fabrication dramatically changes when the RH is varied. When a low RH of $<20\%$ is used, the surface of the fabricated microsieve looks smooth (Figure 2a), but crater-like defects started to appear when the RH was increased (Figure 2b-f). The amount of craters is the highest when high RH's of 83% (d) and 94% (e) are used. Large areas containing these craters occupied the back-surface of the microsieve (Figure 2f). Condensation of water during solidification of the microsieve is probably causing the formation of these craters, since it only occurs at high RH's and only at

Figure 2. SEM images (magnification 1000x) of back surface of microsieves (M3-M7) fabricated with a RH during VIPS of <20% (a), $33 \pm 7\%$ (b), $59 \pm 1\%$ (c), $83 \pm 4\%$ (d) and $94 \pm 1\%$ (e) (all other conditions equal). (f) SEM image of the microsieve fabricated with RH= $94 \pm 1\%$ at a lower magnification (250x).

the surface that is exposed to water vapor. The craters only appear at the surface and do not go deep into the polymer matrix.

Figure 3 shows that also the cross sectional structure of the polymer matrix dramatically changes when the RH during VIPS is varied. A polymer matrix with a dense structure and large macrovoids is formed when the RH is low (<20%), while a structure with closed-cell intrinsic pores is formed when the RH is 83%. The dense structure with macrovoids is likely caused by fast demixing. Below 20% RH VIPS was not observed. As a result, the film solidified only by LIPS, which is a process that takes place rapidly.

Figure 3. SEM images of microsieves fabricated with a RH of $\leq 20\%$ (left, magnification 2500 $\times$) and 83% (right, magnification 3500 $\times$).

At higher RH's phase separation takes place with both VIPS and LIPS, which results in a microsieve with a different polymer matrix structure of closed-cell pores with sizes between 0.5 μm and 2.0 μm . VIPS is visually observed since the polymer solution/film became turbid.

The images in Figure 3 show that VIPS is required to create intrinsic pores or internal porosity (Figure 3, right). VIPS creates small pores at the surface as well, while on the contrary the microsieve has a smooth surface when phase separation only takes place by LIPS. As the presence of intrinsic pores is required for downscaling microsieves by solvent-shrinkage, this type of microsieves is used in further experiments.

Downscaling microsieves by solvent-shrinkage

Microsieves (M8) were immersed in pure acetone (0 wt% NMP), a 5 wt% NMP in acetone mixture or a 10 wt% NMP in acetone mixture. These microsieves had an initial perforated pore diameter of 2.6 μm and a periodicity of 19.4 μm . Figure 4 shows SEM images of cross-sections and surface views of the microsieve that was immersed in a 5 wt% NMP in acetone mixture for different durations. The pore diameter, periodicity and thickness decrease in time. The SEM images of the cross-sections (Figure 4d, e and f) also show that the intrinsic pores in the polymer matrix get smaller and finally disappear. This shrinkage can be explained by the presence of NMP. Since NMP is a good solvent for both PES and PVP, it can penetrate the polymer matrix of the microsieve and thereby swell and mobilize the polymers¹⁵ by lowering the T_g of the material. As a result, the intrinsic pores get smaller and finally collapse. Since the polymer matrix densifies, perforated pores, periodicity and thickness decrease in size as well.

Measuring the mass of the microsieve before and after the solvent shrinkage (120 minutes) showed that $\sim 5\%$ of the microsieve was dissolved in 5 wt% NMP in acetone, which indicates that the densification of the microsieve can be linked for the most part to swelling of the polymer matrix, but that some dissolution also occurs. After $\sim 70\%$ of shrinkage, the perforated pores start to shrink inhomogeneously, i.e. pores lose their circular shape and the

Figure 4. Surfaces (left, magnification 2000 $\times$) and cross-sections (right, magnification 3500 $\times$) of microsieves after immersion in a 5 wt% NMP in acetone mixture for 0 minutes (a and b), 20 minutes (c and d) and 70 minutes (e and f).

pore size distribution increases (Figure 5). The effect of solvent-shrinkage on the pore size distribution will be discussed further on in this chapter.

Figure 6 shows the shrinkage of the pore diameter and periodicity as function of time for microsieves that were immersed in mixtures of pure acetone (a), 5 wt% NMP in acetone (b) and 10 wt% NMP in acetone (c). Immersion of microsieves in pure acetone leads to a decrease in size of both the perforated pore diameter and periodicity. After 30 minutes, the shrinkage is about 20%, and the microsieve continues to shrink to 30% in 150 minutes. The shrinkage of PES/PVP microsieves in acetone has previously been explained by swelling of

Figure 5. SEM surface image (magnification 4500 $\times$) of microsieve M11 after immersion in 5 wt% NMP in acetone for 120 minutes.

PVP, partially dissolution of PVP, and the removal of PVP-bound water by acetone¹⁴. PES and PVP are insoluble in acetone, but our experiments showed that PVP swells when it is immersed in acetone. We propose that acetone does not dissolve, but is able to swell and weaken the polymer matrix and makes the polymer chains mobile, leading to a collapse of intrinsic pores and subsequent shrinkage.

Immersing microsieves in an NMP/acetone mixture leads to more and faster shrinkage. Using a 5 wt% NMP/acetone mixture, the perforated pores and periodicity shrink $\sim 55\%$ and $\sim 40\%$, respectively, in the first 30 minutes. After that, the perforated pores continue to shrink, while the periodicity remains constant. Perforated pores shrink to 80% after two hours, which results in pore sizes of approximately $0.6\ \mu\text{m}$. During the whole solvent treatment, the shrinking rate of the perforated pores is higher than the shrinking rate of the periodicity. As a result, the surface porosity decreases as soon as the solvent treatment starts and decreases more rapidly when the periodicity stops shrinking. A similar shrinking experiment in 5 wt% NMP/acetone was done with microsieve M11, that was fabricated with a more PVP rich polymer solution. The results of this experiment are similar to the results obtained with microsieve M8, which is expected since NMP is a good solvent for both PES and PVP. Figure 6b also shows the shrinkage of the thickness of the microsieve as function of time. Since measuring the thickness of shrunken microsieves was difficult, these kind of measurements were only done using a solvent mixture of 5 wt% NMP in acetone. The shrinkage in thickness is less than the periodicity in the first hour and becomes more after 100 minutes. It was expected that both periodicity and thickness would shrink with similar rates, since in both cases shrinking occurs with the same mechanism (collapsing of intrinsic pores). The small difference in shrinking rate can be explained by the presence of perforated pores, which induces shrinking in lateral direction because of their curvatures⁹.

Using a 10 wt% NMP/acetone mixture leads to a higher shrinking rate for both the perforated pores and periodicity (Figure 6c). As this mixture is a better solvent for PES and PVP, intrinsic pores collapse more rapidly. However, also in this case the shrinking rate of the perforated pores is higher than the shrinking rate of the periodicity. The perforated

Figure 6. Shrinkage of pore diameter (■), periodicity (▼) and (in b) thickness (●) as function of time for microsieves immersed in pure acetone (a), 5 wt% NMP in acetone (b) and 10 wt% NMP in acetone (c).

pores shrink $>90\%$ in 30 minutes, which results in a pore size of $0.2\ \mu\text{m}$. When the immersion of the microsieve is continued, the perforated pores finally collapse and a dense film is obtained. What is also striking in Figure 6 are the large error bars for the shrinkage of perforated pores when the shrinkage exceeds $\sim 70\%$. The reason for this is that the standard method for error propagation does not seem to be appropriate for high shrinkage values, where the relative error is high (size of the pore diameter is close to the value of the standard deviation). Although the error bars are large, the authors are convinced the data points are reliable. SEM images (like Figure 4) clearly show that microsieves shrink to high percentages and support the data.

Since the periodicity stops shrinking after a certain time, the shrinkage-behavior can be divided into two stages. First, a stage where both the perforated pores and periodicity shrink. Second, a stage where the perforated pores continue to shrink while the periodicity does not change and remains constant. Stage one is likely dominated by the collapse of intrinsic pores that induces shrinkage of periodicity and perforated pore size. In the second stage, the perforated pore size still decreases, likely because the weakened polymer matrix slowly flows to fill the perforated pore. In an ideal case, in the first stage the perforated pores and periodicity shrink in equal rates, i.e. isotropic shrinkage, and thus the surface

Figure 7. SEM images of cross-sections of PES microsieves with intrinsic pores of 1.5-3.5 μm (a, M8, magnification 2500 $\times$), intrinsic pores of 0.5-1.5 μm (b, M9, magnification 2500 $\times$) and interconnected intrinsic pores (c, M10, magnification 4500 $\times$).

porosity does not decrease. However, microsieve M8 does not show this perfect isotropic shrinkage-behavior. Nearly isotropic shrinkage is observed only until 35-40% when shrinkage is carried out in higher NMP concentrations where shrinking occurs more and faster.

The structure of the intrinsic pores might influence the shrinking behavior of the microsieves. In order to investigate the influence of the morphology of these intrinsic pores on the shrinkage-behavior, three more solvent-shrinking experiments were performed with microsieves that have different polymer matrix morphologies. Microsieve M8, which was used in the previous experiments, has closed-cell intrinsic pores of 1.5-3.5 μm (Figure 7a). Microsieve M9 has smaller closed-cell intrinsic pores of 0.5-1.5 μm (Figure 7b). Microsieve M10 has interconnected intrinsic pores (Figure 7c) to allow for better and quicker access of the solvents to the polymer matrix, and hence, a faster shrinkage of the periodicity is expected.

Figure 8 shows the shrinkage of the perforated pore diameter and periodicity of these microsieves in a 5 wt% NMP in acetone mixture as function of time (compare with Figure 6b). The microsieve with smaller intrinsic pores (M9, Figure 8a) shows a perforation diameter shrinking rate that is similar to the shrinking-rate of the microsieve with larger

Figure 8. Shrinkage in 5 wt% NMP in acetone of pore diameter and periodicity as function of time for microsieve M9 with small intrinsic pores (a) and microsieve M10 with interconnected intrinsic pores (b) (compare with Figure 6b).

intrinsic pores (M8, Figure 6b). However, the shrinking rate of the periodicity and the maximum shrinkage in periodicity are lower, which leads to a significant decrease in surface porosity. Although it was expected that smaller intrinsic pores would collapse faster, the denser structure of the smaller intrinsic pores restricts the shrinkage in periodicity.

The observed behavior supports the idea that initially shrinkage is dominated by collapse of intrinsic pores. When a polymer matrix morphology of interconnected pores is used (M10, Figure 8b) the shrinkage is again clearly divided in two stages: an initial stage where both pore diameter and periodicity shrink at similar rates until $\sim 35\%$, and a second stage where the periodicity remains unchanged while the perforated pores continue to shrink. Due to the isotropic shrinkage in the initial stage of the shrinking process the microsieve is first downscaled without losing surface porosity, but loses porosity rapidly as soon as the periodicity stops decreasing. The fast and constant shrinking rate of the periodicity can be explained by the interconnected intrinsic pores in the polymer matrix, which make it possible for the solvent to penetrate into the entire microsieve, thereby enhancing the shrinking rate. Also, the shrinking rate of the perforated pore is lower compared to the previous experiments, which also contributes to the isotropic shrinkage in this case. The lower shrinking rate of the perforated pore can be explained by the larger diameter of these pores, since in this case more movement of polymers has to take place to obtain a certain amount of shrinkage.

A similar shrinkage-experiment in 5 wt% NMP in acetone was done with microsieve M12 (Figure 9), which had a larger perforated pore ($\sim 8.0 \mu\text{m}$) compared to the other microsieves. In the first stage of the shrinkage-experiment the shrinkage in periodicity seems to be higher than the shrinkage of the perforated pore, which means that the surface porosity in this part increases. This is mainly attributed to a slower shrinking-rate of the perforated pore. The shrinkage in periodicity is similar to the previous shrinkage-experiments in 5 wt% NMP in

Figure 9. Left: Shrinkage of perforated pore and periodicity as function of time in 5 wt% NMP in acetone for microsieve M12 (pore size: $\sim 8 \mu\text{m}$). Right: SEM surface image of microsieve M12 (magnification 2000 $\times$).

acetone during the first ~ 20 minutes (see Figure 6b and Figure 8), but the shrinking-rate of the perforated pore is significantly lower. Also here, the shrinking rate is lower most likely due to a larger perforated pore diameter which requires a higher mobility of the polymer in order to shrink.

The correlation of the shrinkage in periodicity and perforated pore size is shown in Figure 10. All data points of the shrinking experiments with microsieves M8, M9, M10, M11 and M12 are displayed in this figure together with a diagonal line that represents ideal isotropic shrinkage. Independent of shrinking solvent composition or microsieve morphology, a trend in shrinkage is observed. The microsieve shrinks close to isotropically until 30-40%, but deviates from this ideal case when the perforated pores continue to shrink while the periodicity remains constant. Pore sizes shrink further up to 80-90%, while the shrinkage in periodicity is limited to 50%. Similar trends have been found when microsieves were given a thermal treatment⁹ or when microsieves with relatively large closed-cell intrinsic pores were given solvent shrinkage treatment¹⁴.

The highest perfectly isotropic shrinkage of $\sim 35\%$ was obtained for a microsieve with interconnected intrinsic pores. Only in two cases the periodicity shrunk more than the perforated pore: when microsieve M12 (with larger pores) was immersed in 5 wt% NMP in acetone, and when microsieve M8 was immersed in pure acetone. In both cases this happened in the first stage of shrinkage, and happened because the perforated pores shrunk significantly slower than during experiments with other microsieves or solvent mixtures.

The morphology of the microsieve determines the maximum isotropic shrinkage. Shrinkage in periodicity is limited by the amounts of voids in the polymer matrix. Shrinking occurs because of pore collapse, which means that the voids in the polymer matrix disappear and the structure densifies. When all intrinsic pores have collapsed, no voids are present anymore and further densification of the structure is not further possible. Consequently, the shrinking in periodicity stops. Perforated pores can shrink until they also finally collapse. Together both processes finally lead to the dense structure presented in Figure 11. We thus

Figure 10. Top: Shrinking of periodicity as function of shrinkage of pore diameter. The dotted diagonal line represents ideal isotropic shrinkage. Bottom: Relative error of the size of the perforated pore (standard deviation σ /absolute pore diameter d_p) as function of the shrinkage of the perforated pore.

Figure 11. SEM cross-section image (magnification 10,000 $\times$) of microsieve M10 after immersion in 5 wt% NMP in acetone for 170 minutes.

propose that to reach higher (nearly) isotropic shrinkage rates, the volume of voids, or intrinsic pores, in the membrane should be increased even further. Figure 10 (bottom) shows the relative error of the size of the perforated pore (standard deviation/absolute pore diameter d_p) as function of the shrinkage of the perforated pore, as a measure of the pore size distribution of the perforated pores. Again all data points of the shrinking experiments are displayed.

Figure 10 (bottom) shows in terms of pore size distribution that during solvent-shrinkage the polydispersity of the pores stays low till a shrinkage of 70%, with the exception of two measurements of microsieve M12 (with larger pores). The relative error is constant up to a shrinkage of $\sim 70\%$, but starts to increase when shrinking is continued. The absolute value of the standard deviation of the pore size was constant during the whole shrinking experiments, but the relative error increases since the pore size d_p decreases. The high relative error of 0.86 at 95% shrinkage was caused because some of the perforated already collapsed while others did not.

2.4 Conclusions

PES/PVP microsieves were prepared using Phase Separation Micromolding (PS μ M). The obtained microsieves had very uniform perforated pores and a polymer matrix structure that consisted of small intrinsic pores. The size of these intrinsic pores was tuned by changing the composition of the coagulation bath. Changing the composition of the polymer solution changed the morphology of the intrinsic pores from closed-cell to interconnected pores. When only LIPS was used during fabrication, the polymer matrix structure consisted of a dense structure with large macrovoids.

Immersion of microsieves with intrinsic pores in pure acetone and NMP/acetone mixtures led to shrinkage of the microsieve. More and faster shrinkage occurred when a higher concentration of NMP was used. In a 10 wt% NMP in acetone solution the perforated pore diameter was decreased from 2.6 μm to 0.2 μm in 30 minutes. Shrinking typically occurred

in two stages: first, a stage where both the perforated pores and periodicity shrink, and second, a stage where the perforated pores continue to shrink while the periodicity remains constant. In the first stage the shrinkage in both periodicity and perforated pore size is likely dominated by collapse of intrinsic pores. In the second stage the perforated pore size continues to decrease likely because the weakened polymer matrix slowly flows to fill the perforated pore. The microsieves retain their low pore size distribution, until high levels of shrinkage ($>70\%$) are reached.

In an ideal case the microsieve shrinks isotropically until this maximum isotropic shrinkage is reached. However, an undesired decrease in surface porosity was observed when the shrinking rate of the perforated pores is higher than the shrinking rate of the periodicity. In two cases this does not occur. Firstly, when microsieves with a polymer matrix structure of interconnected intrinsic pores are used, and secondly, when microsieves with larger perforated pores and a higher surface porosity are shrunk.

Since shrinking in periodicity occurs due to pore collapse of intrinsic pores, the polymer matrix became denser with increased shrinkage. Therefore the amount of voids in the matrix determined the maximum shrinkage in periodicity, and hence, the maximum isotropic shrinkage, which was 35-40% in most cases. We propose that to come to higher (nearly) isotropic shrinkage, the amount of voids in the polymer matrix should be further increased.

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3

Control of pore size and pore uniformity in films based on self-assembling block copolymers

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Control of pore size and pore uniformity in films based on self-assembling block copolymers

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Abstract

Blends of self-assembling polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) diblock-copolymers and poly(4-vinyl pyridine) (P4VP) homopolymers were used to fabricate isoporous and nanoporous films. Block-copolymers (BCP) self-assembled into a structure where the minority component forms very uniform cylinders, while homopolymers resided in the core of the cylinders. Selective removal of the homopolymers by ethanol immersion led to the formation of well-ordered pores. In films without added homopolymer, just immersion in ethanol and subsequent swelling of the P4VP blocks was found to be sufficient to create pores. Pore sizes were tuned between 10 nm and 50 nm by simply varying the homopolymer content and the molecular weight of the block-copolymer. Uniformity was lost when the average pore size exceeded 30 nm because of macrophase separation. However, preparation of films from low M_w diblock-copolymers showed that it is possible to have excellent pore size control and a high porosity while retaining a low pore size distribution.

3.1 Introduction

Spontaneous self-assembly of block copolymers (BCPs) has gained a lot of interest, since these polymers have the ability to form periodically well-ordered structures with sizes in the nanometer-range¹. Depending on their nature, composition and size, block copolymers can self-assemble into various types of nanostructures, e.g. spherical, lamellar and cylindrical²⁻⁴. Thin films made of block copolymers having a morphology of hexagonally packed cylinders perpendicular to the film surface are promising for use in several applications, e.g. ultrafiltration (UF) membranes⁵⁻⁷, anti-reflection coatings and drug delivery⁸, since removal of the minority component that forms the cylinders leads to a film with a very narrow pore size distribution. Ordered structures of block copolymers can also be used as a template for preparing nanoarrays⁹⁻¹⁰ or as a mask for nanopatterning¹¹ after selectively removing one of the domains. In addition, it can be used as a template for porous inorganic materials by mixing block copolymers and inorganic species and subsequently removing the BCPs by calcination¹²⁻¹⁴.

Fabrication of block copolymer-based nanoporous structures can be divided into three strategies. In the first approach, a film is made where block copolymers self-assemble into a nanostructure. Subsequently, a minority component is selectively removed by e.g. etching¹⁵⁻²¹. Because the formation of the nanostructure is based on equilibrium, very ordered structures can be obtained after a thermal or solvent annealing step²²⁻²⁹. However, the pore size is determined only by the size of the minority component and is typically only in the range of 5-55 nm²⁰, depending on the nature of the copolymers³⁰, which reduces the range of applicability for separations. A second strategy is the direct formation of pores by *phase inversion*³¹⁻³⁴. Here, a polymer which is initially dissolved in a solvent, rapidly solidifies due to a fast exchange between the solvent and a nonsolvent³⁵. This results in a structure where the block copolymers are kinetically frozen in a nanoporous matrix. Although this technique does not require a subsequent step in order to create pores, it has some drawbacks: first, a large amount of block copolymers is required to fabricate films, since most of the block copolymer is used to fabricate a thick support layer. Second, it is difficult to tune the pore sizes. A third strategy to create nanoporous films is to add a sacrificial component to the system that is later removed by rinsing, thereby creating pores^{8, 36-39}. The idea is that this additional component, i.e. a homopolymer (HP), will reside in the nanodomain of one of the copolymer blocks because of preferential interactions between this polymer block and the additional component. With this technique, pore sizes can be tuned by simply adjusting the content of the homopolymer for films with perpendicularly orientated cylinders³⁶, and pore sizes can be obtained that are smaller than achievable with pure block copolymer films⁴⁰. However, while adding a small fraction of homopolymers can enhance the ordering of cylinders⁴¹⁻⁴², larger additive fractions that are required to create pores come at a cost of pore size distribution, since the desired structure of uniformly distributed homopolymers will not be an equilibrium structure but a kinetically trapped structure³⁶. For the combination of BCPs and HPs, much research has focused on the orientation of the BCP nanodomains or the involved phase separation mechanisms⁴³⁻⁵³. Furthermore, the removal

Figure 1. Schematic overview of the fabrication of nanoporous layers. (a) A PS-*b*-P4VP block copolymer/P4VP_{HP} homopolymer film is made by spin coating a PS-*b*-P4VP/P4VP_{HP} solution on a silicon substrate. The block copolymers self-assemble in a hexagonal cylindrical structure perpendicular to the surface, where the homopolymers reside in the cylinders. Subsequent removal of the homopolymer with a solvent rinse (b) leads to a film with uniform and straight-through nanopores (c).

of HPs by UV-radiation rather than by selective solvents has been carefully investigated⁵⁴. However, the precise control of pore sizes and porosities, using the selective solvent approach, has not been investigated thoroughly. This is somewhat surprising, as understanding and control over this final step, where the nanoporous, straight-through films are fabricated, is key for various applications, e.g. membrane technology.

This chapter presents a very detailed investigation into the fabrication of nanoporous, isoporous films using a block copolymer/homopolymer system by removing the HP with a selective solvent. We show that a combination of HP removal by solvent and swelling of BCP determines the pore size and porosity, especially at smaller pore sizes. While pore formation by UV radiation does not change the nanodomain-periodicity of the film⁵⁵, HP removal by a solvent does change the nanodomain sizes and periodicities by swelling.

We focus on understanding strategies to tune the pore size and porosity, while keeping the pore size distribution low, by varying process parameters during the fabrication of films. The thin films under investigation are based on asymmetric polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) block copolymers and poly(4-vinyl pyridine) (P4VP_{HP}) homopolymers. PS-*b*-P4VP is a block copolymer that is commonly used and studied because of its excellent self-assembly properties^{36, 56, 57}. In our work, the block copolymers self-assemble into a hexagonal cylindrical nanostructure, where the P4VP blocks form cylinders and the P4VP homopolymers are situated inside these cylinders (Figure 1a). Subsequent selective removal of P4VP_{HP} leads to the formation of uniform and straight-through nanopores (Figure 1b). The molecular weight of the block copolymer, the content and molecular weight of the homopolymers and the procedure for selective removal of the

homopolymer are varied in order to investigate their effects on the formed morphology. Additionally, the effect of solvent vapor exposure of the fabricated films is investigated as a method to enhance the ordering and uniformity of the pores.

3.2 Experimental

Materials

Polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) block copolymers P5546P-S4VP ($M_w = 160\text{-}b\text{-}21 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.07), P3910A-S4VP ($M_w = 109\text{-}b\text{-}30 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.15) and P4829P-S4VP ($M_w = 50\text{-}b\text{-}13 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.05) and poly(4-vinyl pyridine) homopolymers P8285-4VP ($M_w = 22 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.16), P8284-4VP ($M_w = 11 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.15) and P3414-4VP ($M_w = 5.2 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.20) were all purchased from Polymer Source, Inc., Canada. All polymers were used without further purification. Chloroform, acetone and ethanol (all of analytical grade) were purchased from Sigma Aldrich.

Preparation of nanoporous films

PS-*b*-P4VP block copolymers and P4VP homopolymers were dissolved in chloroform and stirred for several hours at room temperature. The total polymer concentration (block copolymer + homopolymer) was kept constant at 2 wt%, while the total polymer weight fraction of the homopolymers was varied between 0-0.35. Thin films were prepared by spin coating a polymer solution on a 2x2 cm silicon wafer with a native oxide layer of several nanometers, which was cleaned with acetone before use. The coverage of solution on the wafer prior to spin coating was $\sim 0.1 \text{ ml}/\text{cm}^2$. Spin coating was performed at 2000 rpm for 1 minute in nitrogen environment at room temperature. To obtain nanopores, the films were subsequently immersed in ethanol for different durations (10 sec–2.5 hrs) in order to dissolve and rinse away the homopolymers.

Chloroform was chosen as a solvent because it dissolves both polystyrene and poly(4-vinyl pyridine). Interaction parameters of chloroform and the polymer blocks are $\chi_{\text{chloroform-PS}} = 0.10$ and $\chi_{\text{chloroform-P4VP}} = 0.15^{58}$, which indicates a good solvent quality of chloroform towards both blocks. Ethanol is chosen because it dissolves poly(4-vinyl pyridine) but not polystyrene, which makes it possible to selectively remove the homopolymers without significantly modifying the block copolymer film.

Different types of nanoporous films were fabricated by adjusting materials and/or process conditions during fabrication. An overview of these parameters of all fabricated nanoporous films is presented in Table 1.

Some films (PS(160)-*b*-P4VP(21)/P4VP_{HP}(22), $f_{\text{P4VP-HP}} = 0.21$) were also given a chloroform vapor annealing treatment, which took place prior to or after immersion in

Table 1. Film fabrication process parameters that were varied during experiments. Names and values in bold show the range in which the parameter is varied.

BCP (kg·mol ⁻¹)	HP (kg·mol ⁻¹)	$f_{\text{P4VP-HP}}^a$ (-)	$f_{\text{P4VP-total}}^b$ (-)	Ethanol immersion time
160-<i>b</i>-21	22	0-0.31	0.12-0.39	2.5 hrs
109-<i>b</i>-30	22	0.10	0.29	2.5 hrs
50-<i>b</i>-13	22	0.04-0.35	0.23-0.48	2.5 hrs
160- <i>b</i> -21	5; 11; 22	0.16	0.26	2.5 hrs
160- <i>b</i> -21	22	0.21	0.30	10 sec-2.5 hrs

^a Weight fraction of P4VP homopolymers of the total polymer content.

^b Weight fraction of BCP P4VP chains and P4VP homopolymers of the total polymer content.

ethanol. Films were placed in a closed Petri dish that was saturated with chloroform vapor at room temperature for different durations (0.5-4 hours).

Characterization

Atomic Force Microscopy (AFM, Digital Instruments) was used to visualize and characterize the surface of the films. A Nanosensors SSS-NCH probe with supersharp tip (tip radius < 2 nm) was used as AFM probe. Ellipsometry (Spectroscopic Ellipsometer M-2000X, J.A. Woolam Co. Inc., light reflection at 70°, spot size of 2 mm in diameter, wavelength range of 600–1000 nm) was used to determine the thickness of the films. The average pore diameter, surface porosity and domains per μm^2 were determined from three or four $1 \times 1 \mu\text{m}$ AFM images from a minimum of two samples. The error in pore diameter was calculated using standard rules for error propagation.

3.3 Results and discussion

For clarity, block copolymers are denoted as PS(*x*)-*b*-P4VP(*y*), where *x* and *y* are the molecular masses (in kg·mol⁻¹) of the PS block and P4VP block, respectively. P4VP homopolymers are denoted as P4VP_{HP}(*z*), where *z* is the molecular mass of the homopolymer (in kg·mol⁻¹). The term *surface porosity* is defined as the fraction of the film surface covered by pores. All fabricated films had a thickness of 282 ± 34 nm.

Tuning pore sizes

Initially, films were fabricated without the addition of homopolymers. It is known that a nanoporous structure can be obtained by immersing a film of PS-*b*-P4VP micelles in ethanol⁵⁹. Ethanol selectively swells the P4VP micellar core, which in turn pushes the PS corona's together to form a continuous film. Upon drying, the P4VP deswells and pores are formed of about 30-50 nm and with a high polydispersity⁵⁹. We investigated if ethanol immersion would also create pores in a dense PS-P4VP film. Figure 2 shows AFM height images of a PS(160)-*b*-P4VP(21) film before and after immersion in ethanol. Before

immersion in ethanol the film shows small dots. The dots are the cylindrical P4VP nanodomains seen from above, which are elevated several nanometers with respect to the flat surface. After immersion in ethanol, small pores can be seen instead with an average diameter of 10.2 ± 2.6 nm. This indicates that just immersion in ethanol indeed creates nanopores within the pure block copolymer film. In contrast to the micellar approach mentioned earlier, the film remains well ordered and has a very low pore size distribution.

Figure 2. AFM height images of a PS(160)-*b*-P4VP(21) film before (left) and after (right) immersion in ethanol for 2.5 hours.

Figure 3 shows AFM pictures of PS(160)-*b*-P4VP(21) films made from 2 wt% polymer/chloroform solutions with different weight fractions of P4VP_{HP}(22). The dark dots seen on the AFM images are the pores. Comparing Figure 3a, b and c shows that larger pores are obtained when a higher P4VP_{HP} content is used, which implies that the pore size can be tuned by simply varying the amount of P4VP_{HP}. Apparently, when a higher P4VP_{HP} content is used, larger HP domains are formed and after the homopolymer is rinsed away, this leads to larger pores. As was demonstrated earlier, also swelling of the BCP P4VP chains in ethanol can create pores, which could contribute significantly to the formation of pores when low amounts of homopolymers (=smaller pores) are used. However, it is also possible that the voids that are created by the removed homopolymers provide enough space for the BCP P4VP chains to swell. In this case, swelling of the BCP P4VP chains would not contribute to pore formation anymore. Further on in this paper we will come back to this, when we discuss the porosity of the formed layers.

Figure 3a-c also shows that a higher P4VP_{HP} content also leads to less uniform pore sizes, i.e. a higher pore size distribution. A P4VP_{HP} fraction of 0.31 (Figure 3c) leads to a structure with several large pores of >100 nm and smaller pores in the range of tens of nanometers. When the P4VP_{HP} content is decreased, also the pore size distribution decreases (Figure 3). The formation of the cheese-like structure of the film made with P4VP_{HP} = 0.31 (Figure 3c) has been defined as *macrophase separation*, while the formation of more isoporous and ordered structures seen using lower P4VP_{HP} values has been defined as *microphase separation*⁵⁵. To explain this, we consider two competing mechanisms to occur during solidification of the

Figure 3. AFM height images and relative pore diameter frequencies of films made of PS(160)-*b*-P4VP(21)/P4VP_{HP}(22) blends using P4VP_{HP} weight fractions of (a) 0.08, (b) 0.16 and (c) 0.31.

polymers and structure formation. First, the thermodynamically driven self-assembly of the block copolymers that forms the well-ordered equilibrium nanostructure, and second, the solidification of the P4VP_{HP} that tends to form larger domains in order to minimize the surface area. At low P4VP_{HP} fractions, the effect of the self-assembly of BCP's dominates, and since P4VP_{HP} has a favorable interaction with the P4VP blocks of the block copolymer they will distribute along the cylindrical nanodomains. However, at higher P4VP_{HP} fractions the influence of the self-assembly of the block copolymers becomes less and the formation

Figure 4. AFM height image of a film made with a PS(160)-*b*-P4VP(21)/P4VP_{HP}(22) blend using a P4VP_{HP} weight fraction of 0.20. The arrows show gutters on the surface that connect several pores. This phenomenon was observed in films when a P4VP_{HP} fraction higher than 0.15 was used together with this block copolymer.

of larger sized P4VP_{HP} domains occurs, which results in a larger pore size distribution and eventually macrophase separation. When the fraction of P4VP_{HP} exceeded 0.15, also small gutters that connect two or more pores can be seen on the surface, as shown in Figure 4. These gutters are most likely also formed by P4VP_{HP} segregated from the block copolymer nanodomains as a result of macrophase separation.

Although the pore uniformity is high using low homopolymer fractions, the pores are less ordered than the ordering of cylindrical domains usually seen in films made from pure block copolymers. It seems that the pore size distribution caused by the distribution of homopolymer over the block copolymer domains, although small, still leads to a less ordered arrangement of the pores.

Similar studies of fabricating films with PS-*b*-P4VP/P4VP_{HP} blends and subsequently removing the P4VP_{HP} to create pores were performed with the lower M_w PS(109)-*b*-P4VP(30) and PS(50)-*b*-P4VP(13) block copolymers. Figure 5 shows that films with significantly smaller pore sizes are obtained with PS(109)-*b*-P4VP(30) and PS(50)-*b*-P4VP(13) than with PS(160)-*b*-P4VP(21) using the same homopolymer content. Also, the pores of the lower M_w block copolymers seem more ordered and monodisperse. This demonstrates that the average pore size and pore size distribution are not only dependent on the fraction of P4VP_{HP}, but also on the molecular weight of the block copolymer. Smaller block copolymers self-assemble into smaller nanodomains, and since the amount of nanodomains per μm^2 is higher for smaller nanodomains, homopolymers can distribute themselves along more cylindrical nanodomains. When the homopolymers are then rinsed away, the result is smaller pores. A very promising feature is that no macrophase separation was observed in the $f_{\text{P4VP-HP}}$ range of 0.04–0.35 using the lower M_w PS(50)-*b*-P4VP(13), while it did occur for the higher M_w PS(160)-*b*-P4VP(21) block copolymer using homopolymer fractions larger than 0.16. This implies that the transition from microphase separation to macrophase separation not only depends on the molecular weight and fraction

Figure 5. AFM height images and relative pore diameter frequencies of films made of PS-*b*-P4VP/P4VP_{HP} blends using the same P4VP(22) content ($f_{\text{P4VP-HP}} = 0.1$) but different BCPs: (a) PS(50)-*b*-P4VP(13), (b) PS(109)-*b*-P4VP(30) and (c) PS(160)-*b*-P4VP(21).

of the homopolymer (as demonstrated previously⁵⁵), but also on the size of the block copolymer. It is likely that the effect of the block copolymers to form well-ordered nanodomains remains dominant over a larger range of $f_{\text{P4VP-HP}}$ values for smaller block copolymers, since smaller block copolymers produce smaller pores. Thus, with these smaller diblock-copolymers, it is possible to create films with a very controlled pore size, a low pore size distribution and a high porosity.

Figure 6. Average pore diameter (a), surface porosity (b) and amount of pores per μm^2 normalized by the amount of block copolymer domains per μm^2 without P4VP_{HP} addition (c) for PS(160)-*b*-P4VP(21) (■) and PS(50)-*b*-P4VP(13) (▼) films as function of the polymer weight fraction of P4VP_{HP}. Note that the error bars in (a) show the standard deviation, a measure for the pore size distribution, the error in the average pore size (standard deviation in the average) is always smaller than the used symbol).

The correlation between the fraction of P4VP_{HP} and the pore diameter for the systems with the large and small BCP is displayed in Figure 6a. Both systems show a clear trend and a higher P4VP_{HP} content leads to larger pores and a higher pore size distribution (larger error bars). Pores with average diameters between 10.2 ± 2.6 nm and 47.6 ± 24.6 nm were formed using the high M_w PS(160)-*b*-P4VP(21) BCP with P4VP_{HP} fractions in the range of 0-0.31. Pores between 11.4 ± 4.7 nm and 21.5 ± 5.5 nm were formed using the low M_w PS(50)-*b*-P4VP(13) BCP with P4VP_{HP} fractions in the range of 0.04-0.35. This implies that pore sizes can be tuned by varying the homopolymer content and/or the M_w of the block copolymer. However, since macrophase separation at higher P4VP_{HP} content leads to a higher pore size distribution, uniformity of the pore sizes that can be obtained is limited for the bigger block-copolymer.

Another important characteristic is the porosity of the films (Figure 6b). A higher P4VP_{HP} content leads to a higher porosity, since more polymer is washed away to create voids. The correlation between porosity and $f_{\text{P4VP-HP}}$ are very similar for the large BCP and small BCP system, which implies that the porosity is indeed only a function of the amount homopolymers added. However, there is no linear 1 to 1 correlation between the fraction of

P4VP_{HP} and the porosity, as one would expect. In the first region with $f_{\text{P4VP-HP}}$ values between 0.03 and 0.1 the porosity is similar to $f_{\text{P4VP-HP}}$ or even higher, but the trend deviates from this ideal case when larger amounts of P4VP_{HP} are used and lower porosities are obtained. The lower than expected porosities are most likely due to aggregation of homopolymers (macrophase separation) that form large regions on top, below or even inside the film (not visible on the surface). The “gutters” as shown in Figure 4 are an example of this. The higher porosities in the first region can be explained by swelling of the BCP P4VP chains. As mentioned before, swelling of BCP P4VP chains by ethanol creates pores of ~ 10.2 nm in a pure PS(160)-*b*-P4VP(21) film, which already leads to a porosity of 0.03. Therefore, the contribution of the swelling of BCP P4VP chains to the pore formation can be significant when a low P4VP_{HP} content is used to create pores. Taking this contribution into account, it is likely that the surface porosity created by washing away homopolymers (and not solvent swelling) is always lower than the used fraction of homopolymers.

Figure 6c shows the normalized amount of pores per μm^2 as function of the polymer weight fraction of P4VP_{HP} using PS(160)-*b*-P4VP(21) and PS(50)-*b*-P4VP(13). Here, the amount of pores per μm^2 is normalized by the amount of domains per μm^2 for a film of pure block copolymers (without P4VP_{HP} addition) to take into account the effect of the pore formation ability of the pure polymer, which differs with the M_w of the polymer. For both block copolymers the amount of pores $\cdot \mu\text{m}^{-2}$ decreases with increasing P4VP_{HP} fraction with reference to the initial amount of domains $\cdot \mu\text{m}^{-2}$ of the pure block copolymer film. P4VP_{HP} polymers that reside in the core of the block copolymer cylinders force the block copolymer domain to expand, which results in a larger domain area (block copolymer + homopolymer) and hence, a lower amount of pores (domains) per μm^2 . PS(160)-*b*-P4VP(21) has an initial amount of domains $\cdot \mu\text{m}^{-2}$ of 360. With the addition and subsequent removal of P4VP_{HP}, the amount of pores $\cdot \mu\text{m}^{-2}$ decreases rapidly and almost linear to 155 (0.43 normalized) at a $f_{\text{P4VP-HP}}$ of 0.16. Using larger P4VP_{HP} content leads to a lower value of $86 \cdot \mu\text{m}^{-2}$ (0.24 normalized) for $f_{\text{P4VP-HP}} = 0.31$, but the rate of decrease of the amount of pores $\cdot \mu\text{m}^{-2}$ is lower. This is likely coupled to the small increase in porosity at these homopolymer ratio's (Figure 6b) which was explained by part of the homopolymer (macro)phase separating on top, at the bottom or inside the polymer film. PS(50)-*b*-P4VP(13) has an initial amount of domains $\cdot \mu\text{m}^{-2}$ of 1410, but this amount is more than halved to 570 (0.40 normalized) when a small of P4VP_{HP} ($f_{\text{P4VP-HP}} = 0.035$) is added and subsequently removed. When more P4VP_{HP} is used the amount of pores keeps decreasing very slowly to $456 \cdot \mu\text{m}^{-2}$ for $f_{\text{P4VP-HP}} = 0.35$. The rapid decrease in domains $\cdot \mu\text{m}^{-2}$ in the first region of the graphs with small amounts of P4VP_{HP} for both block copolymers is most likely due to the swelling of P4VP_{block}, which creates pores even without the addition of P4VP_{HP}. Especially in the case of the smaller PS(50)-*b*-P4VP(13) block copolymer this phenomenon dominates the pore formation at low P4VP_{HP} amounts (however, we were not able to measure the pore sizes and amount of pores of the $f_{\text{P4VP-HP}} = 0$ film accurately due to the small pore size). At P4VP_{HP} contents > 0.15 , the relatively low amount of pores $\cdot \mu\text{m}^{-2}$ also suggests that the

homopolymers do not distribute equally along the block copolymer domains, although macrophase separation starts to occur at much higher $P4VP_{HP}$ fractions. This suggests that it is likely that cylindrical nanostructures without homopolymers are present in the films.

The results in this paragraph show that isoporous nanoporous films can be made by selectively removing homopolymers from ordered block copolymer/homopolymer films, or even by simply immersing a block copolymer film in ethanol. The pore sizes and porosity can be tuned by simply varying the amount of homopolymer, which makes this approach a promising method to fabricate very selective ultrafiltration membranes. However, only a range of homopolymer content can be used before the homopolymers start to macrophase separate, which dramatically increases the pore size distribution. Since also the M_w of the block copolymer influences the pore size and the range in which homopolymers microphase separate, selection of both homopolymer content and block copolymer M_w is crucial for fabricating a film with a desired pore size and porosity. We demonstrated that by using a low M_w block-copolymer, it is possible to create films with the desired controlled pore size, low pore size distribution and high porosity.

Fabrication optimization

In this paragraph several process parameters that influence the formation of the nanoporous films are discussed: M_w of used homopolymer, ethanol immersion duration and the solidification rate during the film fabrication. Also results of a solvent annealing treatment are presented and discussed.

Effect of M_w homopolymer

PS(160)-*b*-P4VP(21) films were made from solutions with different molecular weights of homopolymers (5, 11 and 21 $\text{kg}\cdot\text{mol}^{-1}$), but with a fixed composition ($f_{P4VP-HP}=0.16$). Our main interest was to investigate the effect of the M_w of the homopolymer on the pore size distribution. Figure 7 shows that the average pore diameter slightly increases when the M_w

Figure 7. Average pore diameter of films made with PS(160)-*b*-P4VP(21)/P4VP_{HP} blends using P4VP_{HP} with different molecular weights. Error bars show the standard deviation, a measure for the pore size distribution.

of the homopolymer is increased, but the differences fall within the experimental error (± 2 nm). This effect was also observed for a system with polystyrene-*b*-poly(methyl methacrylate) block copolymers and poly(methyl methacrylate) homopolymers⁵⁵. With increasing homopolymer size, one would expect an increase in pore size, as for longer chains the driving force for phase separation is stronger. However, when the pore size becomes independent of homopolymer chain length, it demonstrates that, for this range of homopolymer sizes, phase separation is complete: no P4VP homopolymer remains within the PS matrix, in line with the strong incompatibility between PS and P4VP. For PS and PMMA, which have a weaker incompatibility, stable pore sizes as a function of M_w were only found at much higher molecular weights. Additionally, the standard deviations in Figure 7 do not show a trend and stay in the same order of magnitude, which indicates that the M_w of the homopolymer does not have a significant effect on the pore size distribution as well.

Effect of rinsing time

PS(160)-*b*-P4VP(21)/P4VP_{HP}(22) films ($f_{\text{P4VP-HP}} = 0.16$) were immersed in ethanol for different durations, in order to investigate the effect of the immersion on the pore size and film morphology.

Figure 8a shows that the average pore size and pore size distribution is constant and independent on the immersion treatment. After 10 seconds (first data-point) the average pore size is already 31 ± 9 nm and does not change during the following 2.5 hours. This indicates that P4VP_{HP} dissolves rapidly and immersion in ethanol almost instantly creates pores. However, since surface images do not indicate the depth of the pores, it may take longer before all P4VP is washed away and straight-through pores are formed along the whole thickness of the film.

Figure 8b shows that the surface porosity increases when the film is immersed in ethanol for a longer time. The porosity is $\sim 9\%$ after 10 seconds and increases to $\sim 14\%$ in 2.5 hours. This is the result of an increase in the number of pores per μm^2 (Figure 8c), which increases from 108 after 10 seconds to 149 in 2.5 hours. Since it is shown that P4VP_{HP} dissolves very rapidly in ethanol, it is not likely that more pores are formed in time because more P4VP_{HP} is washed away. The formation of more pores in time is probably due to situations where BCP P4VP chains swell in time but where rearrangement of the PS matrix is also necessary to create voids.

Figure 8. Pore size (a), porosity (b) and number of domains per μm^2 (c) as function of the ethanol immersion time using a film made of a PS(160)-*b*-P4VP(21)/P4VP_{HP}(22) blend with a P4VP_{HP} weight fraction of 0.21.

Effect of chloroform vapor annealing

In order to investigate the effect of a chloroform annealing step on the pore size distribution and film morphology prepared films received a chloroform annealing treatment. Chloroform was chosen as solvent because it is a solvent for both PS and P4VP and can therefore mobilize the complete polymer chain. Two routes were evaluated: Solvent vapor annealing prior to pore formation (route 1) and solvent vapor annealing after pore formation (route 2). Figure 9 shows AFM height images of films subjected to vapor annealing for the two routes.

When both routes are compared, no significant change is seen for the first two hours of the annealing treatment. However, after four hours, the morphologies of the films are dramatically different. In the case of solvent vapor annealing prior to pore formation, large circular domains appear on the surface where initially pores were present (Figure 9d). These dots are no longer pores but instead hollows of several nanometers deep with diameters that are significantly larger than the diameters of the initial pores. In the case of solvent vapor annealing after pore formation, the film is still porous. However, the edges of the pores have become more smooth and in some cases the pores seem to be clogged.

Figure 9. AFM height images of films exposed to chloroform vapor for different durations. Vapor annealing was performed following two routes: Prior to or after immersion of the films in ethanol. Films were prepared from a PS(160)-*b*-P4VP(21)/P4VP_{HP}(22) blend with a homopolymer weight fraction of 0.21.

Films have a different structure after four hours of solvent vapor annealing for both routes compared to films that are not exposed to solvent annealing. This indicates that chloroform mobilizes the polymer chains and rearranges the morphology of the films. While thermal or solvent annealing is often used to improve the ordering of equilibrium nanostructures (pure block copolymer films)²²⁻²⁸, we demonstrate that chloroform solvent annealing is not beneficial for improving the structure of our block copolymer/homopolymer films with non-equilibrium structures.

3.4 Conclusions

Selective removal of a homopolymer from a self-assembling polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) diblock copolymer and poly(4-vinyl pyridine) (P4VP_{HP}) homopolymer film is an easy method to produce isoporous nanoporous films. Nanoporous films were made by spin coating a block copolymer/homopolymer solution and subsequently immersing the fabricated film in ethanol. Both dissolution of the P4VP homopolymers and swelling of the P4VP block copolymer chain contributed to pore formation. We demonstrate for the first time that even without the addition of homopolymer, immersion in ethanol can still lead to a nanoporous block-copolymer film due to swelling of the P4VP chains. Swelling influences pore formation significantly when relatively small pores are formed. Therefore, pore formation not only depends on the content of homopolymers, but also on the solvent and block copolymer type and composition.

Pore sizes can be tuned between 10 nm and 50 nm by simply varying the homopolymer content and the molecular weight of the block copolymer. Porosities of the films can be tuned between 0.03 and 0.2, and their values depend on the homopolymer content and the duration of immersion in ethanol.

When the average pore size exceeded 30 nm the pore size uniformity is lost as a result of macrophase separation, which limits the range of uniform pore sizes that can be obtained for large BCPs. However, we demonstrate that by using low M_w BCPs, we can obtain excellent pore size control, reach high porosities, while retaining a relatively even pore size distribution. The transition from microphase separation to macrophase separation occurs at lower P4VP_{HP} fractions for larger block copolymers, since larger pores are formed using larger block copolymers.

Varying the molecular weight of homopolymers in a low range (5–22 kg·mol⁻¹) does not influence the obtained morphology significantly, demonstrating full phase separation of P4VP homopolymers from the PS matrix.

Solvent vapor annealing rearranges the polymers and thereby changes the structure of the films. However, exposing the films to chloroform vapor does not enhance the ordering nor

uniformity of the pores. Chloroform vapor annealing prior to immersion in ethanol leads to a non-porous film with only cylindrical domains, while chloroform vapor annealing after immersion in ethanol leads to a film with a smoother surface and pores with smoother edges.

Because of the presented film characteristics the authors believe that the nanoporous films fabricated in this work are promising for use in ultrafiltration membranes applications. Therefore the next step (Chapter 4) will be to fabricate a composite membrane, consisting of a permeable support membrane that provides mechanical strength and our thin BCP layer that provides a high filtering selectivity on top. In this challenging case, our BCP layer will be transferred to, or directly coated onto the support membrane.

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4

Composite membranes based on a self-assembling block copolymer/ homopolymer system

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Composite ultrafiltration membranes with tunable properties based on a self-assembling block copolymer/ homopolymer system

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Abstract

Composite ultrafiltration membranes were fabricated by coating a thin film of self-assembling polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) block copolymers and poly(acrylic acid) (PAA) homopolymers on top of a support membrane. Block copolymers self-assembled into a nanostructure where the minority component forms cylinders, while homopolymers resided in the core of the cylinders. Selective removal of the homopolymers led to the formation of pores. The morphology of the polymer layer was controlled by varying the content of homopolymers or polymer concentration of the coating solution, which led to membranes with different molecular weight cut-offs (MWCO) and permeabilities. Uniform pores were obtained using low homopolymer contents, while high homopolymer contents caused macrophase separation and resulted in large polydisperse pores or craters at the surface. The thickness of the block copolymer film also influenced the structure and performance of the membranes, where a thicker film results in a strong decrease in permeability but a lower MWCO.

4.1 Introduction

Scarcity of clean water is a world-wide problem, which demands for improvement of current techniques to produce clean water, e.g. water filtration by membranes¹. Current ultrafiltration membranes are characterized by a wide pore size distribution and/or a low porosity, which leads to either a quite permeable but not very selective membrane or a selective but not very permeable membrane². Block copolymers that self-assemble into a nanostructure of hexagonally and vertically aligned cylinders have the potential to overcome these limitations. Nanoporous membranes derived from self-assembling block copolymers have a narrow pore size distribution and a high porosity, which would improve both selectivity and permeability³.

A block copolymer is a macromolecule that consists of segments (blocks) of two or more repeating units. Some block copolymers have the ability to self-assemble into different nanostructures, depending on the composition and molecular weight of the block copolymer⁴⁻⁵. A morphology of hexagonally packed cylinders perpendicular to the surface is interesting for use in membranes applications, e.g. ultrafiltration⁶⁻⁷ or drug delivery⁸, since removal of the cylindrical part results in a membrane with well-ordered and monodisperse pores. Hence, a very selective and permeable membrane could be produced based on this system.

Fabrication of selective block copolymer based membranes can be divided into three categories. In the first method, an asymmetric porous membrane is directly formed by rapid solidification of a polymer during fast exchange between a solvent and a nonsolvent⁹, a technique called *phase inversion*¹⁰. Although with this approach pore sizes can be tuned by varying the block copolymer molecular weight¹¹ or gold deposition inside the pores to decrease the pore diameter¹², it has as major drawback that it requires a large amount of (expensive) block copolymers as the whole membrane (including support) is made of the block copolymer.

A second strategy is to fabricate a composite membrane consisting of a thin, selective block copolymer film on top of a membrane support. This block copolymer film can be coated directly on the support membrane by spin or dip coating¹³⁻¹⁴ or transferred to the support membrane in a second step^{6-8, 15-17}. Initially the block copolymer film is a dense film where the blocks form an equilibrium based self-assembled nanostructure. Subsequent removal of the minority component that forms the cylinders, e.g. by etching or UV radiation, results in a porous structure¹⁸⁻²⁰. Although well-ordered and monodisperse films can be produced with this technique, the pore size is determined by the size of the minority component of the block copolymer and cannot easily be tuned independently²¹.

A third strategy to create pores is to add a homopolymer to the system and selectively remove it after a thin film or membrane is casted. Because of favorable interactions of the homopolymer with the block copolymer minority component, the homopolymer resides in

the core of the block copolymer cylinders²²⁻²³ and is subsequently rinsed away to create well-ordered pores²⁴. By varying the content of homopolymers, the pore size and the porosity can be tuned²⁵⁻²⁷, which leads to membranes with different performances¹³. While addition of a small homopolymer fraction can enhance the ordering of the cylindrical block copolymer nanodomains²³, larger homopolymer fractions tend to lead to a wider pore size distribution²⁵⁻²⁶. Finally, this approach provides interesting opportunities for membrane modification, as the minority chain remains inside the pore.

A major challenge for the fabrication of block copolymer based membranes in the latter two approaches is to control the orientation of the cylinders. This orientation can be either parallel or perpendicular to the surface, but only the latter is suitable for fabricating membranes. However, in order to minimize the interfacial and surface energy, thermodynamically one of the blocks tends to *wet* the substrate-surface and the solution-air interface because of its more favorable interactions with the surrounding media. This leads to formation of the cylindrical nanodomains that are oriented parallel to the surface²⁸⁻²⁹. The orientation of the nanodomains can be changed to vertical by adding salt that forms complexes with the block copolymer minority chain³⁰⁻³¹, by modifying the surface in order to change its interaction with the different copolymer blocks³²⁻³⁵ or by inducing a gradient field over the thickness of the film that directs the orientation of the nanodomains³⁶⁻⁴⁰. For thin films (<60 nm) also their thickness influences the orientation⁴¹. For films that are casted, a simple method to enhance perpendicular orientation is by fast solidification that causes vertical alignment of the cylindrical nanodomains⁴²⁻⁴⁷. However, the vertical orientation only occurs in the upper part of the film⁴⁸. Due to the challenge of controlling the orientation of BCP cylinders, the gyroid morphology has also been used to fabricate nanoporous membranes⁴⁹. Although the gyroid morphology has a continuous structure that does not require orientation in order to have interconnected pores, it has as drawback that the tortuosity is higher, thereby decreasing the maximum obtainable permeability.

This chapter presents a method to produce well-ordered and monodisperse composite ultrafiltration membranes with tunable pore sizes, and thus filtration properties, using a block copolymer/homopolymer system. While this approach has been used to fabricate nanofiltration membranes¹³, this is the first time that this method is applied to ultrafiltration membranes. As we will show, the system behaves quite different for the fabrication of ultrafiltration membranes in terms of how the homopolymers distribute. A composite membrane is fabricated by spin coating a block copolymer/homopolymer film directly on top of a support membrane and subsequently removing the homopolymer with a selective solvent. The block copolymer/homopolymer system under investigation is based on an asymmetric polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) block copolymer and a poly(acrylic acid) (PAA) homopolymer. In our work, the block copolymers self-assemble into a hexagonal cylindrical structure, where the PEO blocks form the cylindrical nanodomains. PAA co-assembles into the core of the cylinders (Figure 1a) because of favorable hydrogen bonding interactions between acrylic acid and ethylene glycol⁵⁰.

Figure 1. Schematic overview of the fabrication of nanoporous composite membranes. (a) A PS-*b*-PEO block copolymer/PAA homopolymer film is coated on top of a support membrane by spin coating. The block copolymer self-assembles into a hexagonally packed cylindrical structure perpendicular to the surface, where the homopolymer resides in the cylinders. Subsequent removal of the homopolymer with a solvent rinse (b) leads to a nanoporous selective top film (c).

Subsequent removal of PAA by a selective solvent (Figure 1b) leads to the formation of nanopores (Figure 1c). The pore sizes were tuned by varying the content of homopolymer, and the thickness of the block copolymer film was varied by changing the polymer concentration of the coating solution. The composite membranes were challenged to filtration experiments using aqueous poly(ethylene glycol) (PEG) solutions. We show that by simply varying the content of homopolymers, membranes with different pore sizes and different filtration performances (molecular weight cut-off, MWCO) can be made using just one type and size of block copolymer. The thickness of the block copolymer film was varied, which influences both the permeability and the MWCO. The influence of the composition of the filtration feed solution on the PEG rejection was studied also. Finally, a careful comparison is made of the pros and cons of this approach, compared to the other approaches to produce block copolymer membranes.

4.2 Experimental

Materials

Polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) block copolymers P4377-SEO ($M_w = 62\text{-}b\text{-}16\text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.08) and poly(acrylic acid) (PAA) homopolymer P11381-AA ($M_w = 5.8\text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.13) were purchased from Polymer Source, Inc., Canada. All polymers were used without further purification. Tetrahydrofuran (THF, analytical grade) was purchased from Sigma Aldrich and was used as solvent.

Poly(ethylene glycol) (PEG) with mean molecular weights of 200, 2000, 6000, 10,000, 20,000, 35,000 and 100,000 $\text{g}\cdot\text{mol}^{-1}$ were purchased from Merck (Germany) and were used for filtration experiments. Although PEG and PEO are chemically identical (PEG is normally used for low M_w chains), for clarity, the name *PEG* is used for filtration solutes and *PEO* for the block copolymer segment. Ether glycol (EG), sodium nitrate (NaNO_3) and sodium azide (NaN_3) (all of analytical grade) were purchased from Merck (Germany) and were used for GPC analysis. Milli-Q pure water (deionized water purified by a Synergy water purification system of Millipore) was used to make PEG solutions and to dissolve and rinse PAA.

Nadir UV-150 ultrafiltration membranes were kindly provided by Nadir and were used as support membranes. These membranes have pore sizes varying from 50 nm up to > 300 nm and a surface porosity of $7.6 \pm 1.8\%$ (Figure 2).

Figure 2. SEM surface image (magnification 10,000x) of the Nadir UV-150 support membrane.

Preparation of composite membranes

PS-*b*-PEO block copolymers and PAA homopolymers were dissolved in THF and stirred for several hours at room temperature. The total polymer concentration (block copolymer + homopolymer) was kept constant at 1.0, 1.5, 2.0 or 4.8 wt%, of which the homopolymer weight fraction was varied between 0.05-0.40. THF was chosen as a solvent because it dissolves both PS-*b*-PEO and PAA, and was found in preliminary experiments to be a good solvent for preparing defect-free films. Interaction parameters of THF and the block copolymer and homopolymer components are $\chi_{\text{THF-PS}} = 0.32$, $\chi_{\text{THF-PEO}} = 0.27$ and $\chi_{\text{THF-PAA}} = 0.42^{51}$, which indicates a good solvent quality of THF towards all polymers.

Composite membranes were prepared by spin coating a polymer solution on a support membrane (3x3 cm). The coverage of solution on the support prior to spin coating was $\sim 0.1 \text{ mL}\cdot\text{cm}^{-2}$. Spin coating was performed at 1500 rpm for 2 minutes in nitrogen environment at room temperature. To obtain nanopores, the composite membranes were immersed in Milli-Q pure water for 12 hours in order to dissolve and rinse away the homopolymers. Water was chosen because it dissolves PAA but not PS, which makes it possible to selectively remove the homopolymers without significantly modifying the block

Table 1. Overview of compositions of polymer solutions used to fabricate composite membranes. All solutions consisted of PS-*b*-PEO, PAA and THF.

Solution	C _{polymer} ^a (wt%)	f _{PAA} (-)
1	1.0	0.05
2	1.5	0.05
3	1.0	0.15
4	1.5	0.15
5	2.0	0.15
6	4.8	0.15
7	1.5	0.30
8	1.5	0.40

^a Total polymer concentration (PS-*b*-PEO + PAA)

copolymer film. The same procedure was used to fabricate films on a silicon wafer in order to determine the thickness of the block copolymer films and for AFM and High-Resolution SEM analysis.

To differentiate the polymer solutions with different homopolymer contents, the following notation is used through the whole chapter:

$$f_{\text{PAA}} = \frac{m_{\text{PAA}}}{m_{\text{PAA}} + m_{\text{PS-}b\text{-PEO}}}$$

where m_x is the mass of component x used to make the solution.

Different types of nanoporous block copolymer films were fabricated by using different polymer solutions. An overview of the compositions of all used polymer solutions is presented in Table 1.

Characterization

The block copolymer films were imaged by atomic force microscopy (AFM, Nanoscope 3, Veeco, US) in tapping-mode under ambient conditions using silicon cantilevers (Nanosensors) with resonance frequencies between 204 – 497 kHz and spring constants between 10–130 Nm⁻¹. Scanning electron microscopy (SEM) (Jeol JSM 6010 LA, at 5 kV for magnifications up to 10,000x, and High Resolution SEM, Zeiss Merlin, at 0.5 kV for higher magnifications) was used to visualize and characterize the membranes. Low magnification SEM samples were dried under vacuum at 30 °C for 24 h and then coated with a thin layer of gold using a Balzer Union SCD 040 sputter device. Ellipsometry (Spectroscopic Ellipsometer M-2000V, J.A. Woolam) was used to determine the thickness of the films that were spin coated on silicon wafers.

The average pore diameter and surface porosity were determined from three or four AFM (block copolymer films) or SEM (support membrane) images from a minimum of two samples. The error in pore diameter was calculated using standard rules for error propagation.

Permeation experiments

The permeability of the membranes was determined by measuring the flux of Milli-Q pure water at different pressures (0.5-2.5 bar) using a dead-end filtration set-up. A membrane (circular, 2.5 cm in diameter) was placed in a filter holder cell with a volume of 400 mL. The cell was connected to a vessel filled with Milli-Q pure water that was pressurized by compressed nitrogen.

The permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) was calculated as the ratio of the flux over the applied pressure:

$$\text{Permeability} = \frac{V}{A \cdot t \cdot \Delta P} = \frac{J}{\Delta P}$$

where V is the permeate volume (L), A is the membrane area (m^2), t is the time (h), J is the permeate flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) and P is the pressure (bar).

All measurements were performed using at least two different membranes to ensure reproducibility.

PEG filtration

The membranes were challenged to PEG filtrations performed at 1.50 ± 0.04 bar using the dead-end filtration set-up described before. Aqueous solutions were made containing a mixture of PEG components with mean molar masses of 200, 2000, 6000, 10,000, 20,000, 35,000 and 100,000 $\text{g} \cdot \text{mol}^{-1}$ in MilliQ pure water. Each PEG fraction had a concentration of $\sim 0.04 \text{ g} \cdot \text{L}^{-1}$, with a total PEG concentration of $\sim 0.28 \text{ g} \cdot \text{L}^{-1}$. Besides using a PEG mixture, also single M_w PEG filtration was performed using PEG with a mean molar mass of only 10,000 $\text{g} \cdot \text{mol}^{-1}$ or 100,000 $\text{g} \cdot \text{mol}^{-1}$ with a concentration of $\sim 0.04 \text{ g} \cdot \text{L}^{-1}$. Table 2 shows an overview of the used PEG molecules and some relevant properties.

Table 2. Mean molecular weight (M_w), diffusion constant (D_∞) and hydraulic diameter (d_h) of the PEG molecules used in filtration experiments.

	PEG ₂₀₀	PEG _{2k}	PEG _{6k}	PEG _{10k}	PEG _{20k}	PEG _{35k}	PEG _{100k}
M_w ($\text{g} \cdot \text{mol}^{-1}$)	200	2000	6000	10,000	20,000	35,000	100,000
D_∞ ($\text{m}^2 \cdot \text{s}^{-1}$) ^a	$8.4 \cdot 10^{-10}$	$2.1 \cdot 10^{-10}$	$1.1 \cdot 10^{-10}$	$8.1 \cdot 10^{-11}$	$5.4 \cdot 10^{-11}$	$3.9 \cdot 10^{-11}$	$2.1 \cdot 10^{-11}$
d_h (nm) ^b	0.6	2.3	4.4	6.0	9.1	12.7	23.8

^a Diffusion constant of PEG in water determined at 25 °C⁵²

^b Hydraulic diameter determined using Einstein-Stokes equation⁵³

The composition of the feed, permeate and retentate was analyzed by gel permeation chromatography (GPC). The GPC setup consisted of two SUPREMA 100 Å columns from PSS Polymer Standards Service GmbH (Germany), a HPLC pump from Waters (Millipore B.V., The Netherlands) and a Shodex RI-Detector from Showa Denko GmbH (Germany). The columns were calibrated using 16 different PEG standards (M_w : 62–42,000 g·mol⁻¹, PSS Polymer Standards Service GmbH, Germany).

Prior to GPC analysis, NaNO₃ was added to the samples to achieve a GPC eluent concentration of 0.05 M. NaN₃ was added (0.05 g·L⁻¹) to prevent bacteria growth, and EG was added (4 μL·mL⁻¹) as a flow marker (internal standard). For each GPC analysis, 100 μL of a sample was injected into the GPC, which ran at 1 mL·min⁻¹. Every GPC measurement was performed at least two times to ensure reproducibility.

The rejection R was determined via:

$$R = \frac{C_{\text{Cell}} - C_{\text{permeate}}}{C_{\text{Cell}}}$$

where C_{permeate} is the permeate concentration and C_{cell} the concentration inside the test cell. Since the setup ran in dead-end mode, accumulation of the retained PEG molecules caused the concentration in the membrane cell to rise in time. Since it was not possible to monitor the concentration inside the cell in time, the average of the original feed concentration and the final retentate concentration was used as C_{cell} .

4.3 Results and discussion

The results section is divided into four parts. First, the effects of the homopolymer content on the pore size, pore size distribution and porosity of the block copolymer films are investigated. In the second part, the permeabilities of the composite membranes are determined, where both the homopolymer content and the polymer concentration of the solution are varied in order to understand their effects. In the third part, aqueous PEG solutions with a wide range of PEG molecular weights are filtered using the composite membranes in order to determine the separation properties of the membranes. From these experiments it will become clear that changing the homopolymer content and the polymer concentration leads to different composite membranes with different permeability and separation properties. In the final part the advantages and disadvantages of this method to fabricate composite membranes based on self-assembling block copolymers are discussed.

Tuning the pore size

Figure 3 shows AFM height images of PS-*b*-PEO films made from 1.5 wt% polymer/THF solutions with different weight fractions of PAA homopolymer (0.05; 0.15; 0.30), and their corresponding relative and cumulative pore size frequencies. The dark dots and regions seen

Figure 3. AFM height images and relative and cumulative frequencies of pore diameters of films made of PS-*b*-PEO/PAA blends using f_{PAA} values of (a) 0.05, (b) 0.15 and (c) 0.30.

on the images correspond to lower altitudes, i.e. these dots and regions are pores and craters. In preliminary experiments also films were fabricated without using PAA, but in these films no pores were detected. In the images, two types of pores can be distinguished. First, small pores in the range of 5 to 40 nm, which seem to be ordered and uniform, and second, larger randomly distributed pores up to several hundreds of nanometers. The small pores are formed by microphase separation, where homopolymers reside in the center of

the packed block copolymer cylinders. The larger pores are however formed by macrophase separation, where the homopolymers form their own separated regions outside the block copolymer nanodomains. These phenomena have been well described by Jeong *et al.*²². Comparing Figure 3 (a-c) shows that the small pores formed by microphase separation become slightly larger when f_{PAA} is increased from 0.05 to 0.15, where average pore sizes are obtained of 21 nm and 26 nm respectively, taking only pores in the range of 0-100 nm into account. When the PAA fraction is further increased to 0.30, the size of the smaller pores drops to 16 nm. This is surprising, since if all homopolymers reside in the block copolymer cylinders, the average pore size should increase with increasing homopolymer content²⁵⁻²⁶. The reason for this population of the pores to become smaller is the relative depletion of the amount of homopolymer available for their formation by microphase separation due to the parallel formation of the larger domains by macrophase separation. For $f_{\text{PAA}} = 0.05$, all pores seem ordered and uniform, but for $f_{\text{PAA}} = 0.15$, some random larger pores start to appear because of a small degree of macrophase separation. When an even higher f_{PAA} of 0.30 is used, very large dark areas can be seen with diameters up to several hundreds of nanometers, which are either big pores or craters. Since more homopolymers form larger regions outside the block copolymers, less homopolymers reside inside the block copolymer cylinders. This causes the smaller pores (formed by microphase separation) to decrease in size.

Figure 4 shows High-Resolution SEM surface and cross-section images of the same films discussed before. The surface images confirm the pore sizes and pore size distribution determined by AFM. Interestingly, the larger pores (> 100 nm) in Figure 4b seem to be craters that have smaller pores at the bottom. The entire morphology of the films becomes clear in the cross-section images. For $f_{\text{PAA}} = 0.05$ (a) and 0.15 (b), the cross-section SEM images show that most pores penetrate the entire thickness of the film, which is ~ 90 nm. However, not all pores seem to penetrate the entire thickness of the film as a single channel, but instead are also interconnected with other channels to form an interconnected network of pores beneath the surface. Apparently the orientation of the block copolymer domains changes already directly underneath the surface, which creates this type of morphology. For $f_{\text{PAA}} = 0.30$, the big pores also seem to be craters that do not span the entire thickness of the film. The bottom of the craters consists of a dense layer that contains the small microphase separation pores that are also seen on the surface of the film. At relatively high homopolymer contents ($f_{\text{PAA}} = 0.40$) microphase separation no longer occurs and small pores are not formed (Figure 5). Instead, a dense structure is obtained with large craters of 1 to 3 μm in diameter, which seem to appear at the surface and not completely span the entire thickness of the block copolymer film.

The effect of the increasing homopolymer content on the morphology of the films formed differs from the previous reports on the PS-*b*-PEO/PAA mixtures^{13,50}, where instead of the macrophase separation a transition to lamellar morphology was observed at larger homopolymer contents. The difference between both studies is that the PS-*b*-PEO in our

Figure 4. HR-SEM surface (left) and cross-section (right) images of films made of PS-*b*-PEO/PAA blends using f_{PAA} values of 0.05 (a,b), 0.15 (c,d) and 0.30 (e,f). Magnifications are 200,000 $\times$ (a-c), 314,000 $\times$ (d), 350,000 $\times$ (e) and 310,000 $\times$ (f).

system has a relatively high M_w , which is required for obtaining larger pores in the ultrafiltration range. In block copolymer/homopolymer systems macrophase separation starts occurring at lower homopolymer contents when a higher M_w block copolymer is used²⁵. As already indicated by our results, this effect makes it more challenging to fabricate ultrafiltration membranes using a block copolymer/homopolymer system.

Although the number fraction of small pores is high for all block copolymer films (Figure 3), the effect of the larger pores on the total pore area is more significant. Figure 6 shows the cumulative pore area fraction for increasing pore diameter of films made with different homopolymer contents. A steep curve is obtained for $f_{PAA} = 0.05$, which indicates that all

Figure 5. SEM surface image (magnification 10,000 $\times$) of a film made of a PS-b-PEO/PAA blend with a f_{PAA} value of 0.40.

small pores contribute significantly to the total pore area. For $f_{PAA} = 0.15$, the curve is less steep because the pores become less monodisperse. After ~ 100 nm, the graph levels off due to the larger pores formed by macrophase separation that contribute to $\sim 20\%$ of the total pore area. For $f_{PAA} = 0.30$, an undefined graph is obtained where $\sim 80\%$ of the total pore area is obtained from pores larger than 100 nm.

Since larger pores give rise to a higher permeability¹⁰, one would expect that the larger pores formed by macrophase separation will determine the properties of the fabricated membrane. However, the AFM and SEM images (Figure 3 and Figure 4) show that the large pores are not necessarily straight-through pores. Some large dark spots have a more funnel-like shape and show smaller pores at the bottom, indicating that some or all pores are more like craters rather than pores that span the thickness of the film. In that case, the craters could potentially influence the performance of the membrane, rather than determining. In the next paragraph, we will discuss the influence of the film thickness and homopolymer content on the permeability.

Figure 6. Cumulative pore area fraction for increasing pore diameter of block copolymer top films made with 1.5 wt% polymer solutions with $f_{PAA} = 0.05$, 0.15 and 0.30.

Permeability

Effect of film thickness

Figure 7 shows the pure water permeability of prepared composite membranes as a function of the total polymer concentration (block copolymer + homopolymer) of the coating solution. For the fabrication of all membranes, f_{PAA} was kept constant at 0.15. The highest permeability is obtained using a 1.0 wt% polymer solution, that results in a membrane with a permeability of $19.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. When a higher polymer concentration is used, the permeability decreases. Permeabilities of 10.6 and $2.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ are obtained using a polymer concentration of 1.5 and 2.0 wt%, respectively. The lowest measurable permeability is obtained when a polymer concentration of 4.8 wt% is used, which leads to a permeability of $0.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ only. It was not possible to go beyond $19 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ by using a lower polymer concentration, since this caused defects in the top film (as observed by SEM).

The influence of the polymer concentration on the permeability can be explained by the obtained thickness of the block copolymer top films. A thicker film is obtained when the polymer concentration in the solution during spin coating is increased⁵⁴. It was found that the thickness of thin films spin coated on silica wafers increases linearly from 70 to 430 nm using polymer concentrations in the range of 1.0 to 4.5 wt%, which is a good indication for the block copolymer film thicknesses of our composite membranes. A thicker film increases the hydraulic resistance of the membrane and thereby decreases its permeability. Still, our observed decrease in permeability is much larger than expected on the basis of just a change in thickness.

Films made from block copolymers often have perpendicular orientated block copolymers at the top, initiated by fast evaporation, but still have cylinders with a different orientation deeper inside the film^{28, 29, 48}. Thus, a thicker film fabricated by using a higher polymer

Figure 7. Pure water permeability of composite membranes (■) as function of the total polymer concentration (block copolymer + homopolymer) of the solution used for spin coating. f_{PAA} was kept constant at 0.15. Line is plotted to guide the eye. Theoretical values (---) based on the assumption that the flux is inversely proportional to the thickness of the film, with 1.0 wt% polymer concentration ($19.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) as reference.

Figure 8. HR-SEM cross-section image (magnification 340,000 $\times$) of a film made using a 4.8 wt% PS-*b*-PEO/PAA/THF solution with a f_{PAA} value of 0.15.

concentration will lead to a thicker film of block copolymers having a different and undesired orientation. When in our case PAA homopolymers *microphase-separate* inside these block copolymer domains, not all pores will go straight-through, but will also have different orientations and be less interconnected. Figure 8 shows a HR-SEM cross-section of a 380 nm thick film made with a 4.8 wt% polymer solution with an f_{PAA} value of 0.15. The orientation of the polymer matrix changes deeper inside the film to a more horizontal orientation. However, most part of the film seems highly permeable and also the horizontal morphology still seems permeable. It seems plausible that a thicker film increases the change of having dead-end pores, which will lead to a lower permeability.

The theoretical permeability values are also shown in Figure 7, which are based on the assumption that the flux is inversely proportional to the thickness of the film and have the 1.0 wt% polymer concentration ($19.4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) as reference point. The decline of the experimentally obtained permeabilities is much faster than the expected decline, which implies that the resistance of the block copolymer film exponentially increases with the thickness of the block copolymer film.

Effect of homopolymer content

Figure 9 shows the water permeability as a function of the homopolymer content of the solution used to fabricate the top film of the composite membrane. The total polymer concentration for all solutions was kept constant at 1.5 wt%. In preliminary experiments, no water permeation was detected when a membrane was fabricated without addition of PAA. A permeability of $2.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ is obtained for $f_{PAA} = 0.05$. When a higher fraction of 0.15 is used, a higher permeability ($10.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) is obtained also. Surprisingly, using a higher f_{PAA} value of 0.30 does not increase the permeability, and using an even higher fraction of 0.40 leads to a lower permeability again. Intuitively one would expect a higher permeability for increasing homopolymer content, since at higher homopolymer content more voids are created when the homopolymers are rinsed away, leading to a higher permeability. However, Figure 9 shows that there is a maximum permeability for f_{PAA} in the range of 0.15-0.30. This is caused by the transition from microphase-separation to

Figure 9. Water permeability ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) as function of f_{PAA} using 1.5 wt% polymer/THF solutions during film formation.

macrophase-separation (Figure 3-6), which leads to a structure that has more voids but is less permeable. For $f_{PAA} = 0.30$, the reproducibility of the membranes is also less. Probably in some membranes more large macrophase-separated areas perforate the entire thickness of the BCP film than others, thereby increasing the permeability. This phenomenon also gives rise to a high standard deviation of the permeability (Figure 9).

The high resistance of the block copolymer film becomes clear when the experimentally obtained permeabilities are compared with theoretical approaches. According to the Hagen-Poiseuille equation for laminar flow through a tube, the lowest possible permeability of our film should be $\sim 1600 L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ (diameter pores = 24 nm, porosity = 0.1, tortuosity = 1, thickness film = 400 nm)¹⁰. Taking into account the porosity of the support membrane (7.6%), the maximum possible permeability is lowered to $115 L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, which is slightly lower than the permeability of the support membrane ($\sim 180 L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, as determined experimentally). Since the experimentally obtained permeabilities are at least an order of magnitude lower, and the thickness of the top film influences the permeability of the composite membrane, it is clear that the block copolymer film determines the hydraulic resistance of the composite membrane.

Besides a low effective porosity (product of the porosities of the support membrane and block copolymer film) and less interconnected pores, some other issues may decrease the permeability as well. First, it is known that during rinsing away of homopolymers by a selective solvent not all the homopolymers might be removed⁵⁵. When homopolymers are removed in a relatively thick film (≥ 70 nm), not all homopolymers situated deeper into the film have the possibility to diffuse out of the film, which results in funnel-like pores where the pore diameter becomes smaller deeper into the film. It is likely that this phenomenon initially plays a role in our relatively thick top films, and is enhanced even more when the orientation of the block copolymers changes. However, since our homopolymer is soluble in water, all accessible homopolymers should be rinsed away when water permeates the pores. Another phenomenon that is expected to lower the permeability is swelling of the

Figure 10. Schematic illustration of PS-*b*-PEO domains in dry and wet state. In dry state the PEO chains (in red) are solidified and form the wall of the pore. In wet state the PEO chains are swollen, by (or even dissolved in) water, thereby decreasing the hydraulic diameter of the pore.

PEO chains of the block copolymers that cover the surface of the walls of the pores. Figure 10 shows schematically how the pore size changes from the dry to the wet state. In the dry state the PEO chains form the walls of the pores, as seen in the AFM and SEM images. However, since PEO is soluble in water, the PEO blocks will swell when the pores are filled with water, thereby increasing the hydraulic resistance of the pores. This means that the permeability of the pores will be lower than what is expected based on the pore size as determined by AFM and SEM. While the PEO layer lowers the permeability, the presence of PEO is certainly not unfavorable. PEO layers are well established to act to prevent fouling, especially by protein molecules^{56, 57}. Still this specific effect is beyond the current investigation.

Our experimentally obtained permeabilities (of $19 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) are much higher compared to the permeabilities of other block copolymer based composite membranes found in literature, which varied from $1.2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for a composite block copolymer membrane made by etching away the cylindrical domains⁴⁸ to 1 to $5 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for a composite block copolymer membrane fabricated by removing homopolymers to create pores¹³. We showed that the permeability of the block copolymer composite membranes is determined by the polymer concentration of the coating solution. Our use of low polymer concentrations to fabricate composite membranes explains why some composite membranes fabricated in this work have much higher permeabilities than block copolymer based composite membranes found in literature.

Filtration

The composite membranes were challenged to dead-end filtration of an aqueous poly(ethylene glycol) (PEG) solution with a variety of molecular masses. Figure 11a shows the rejection of different PEG mean molar masses using composite membranes with a block copolymer top film made from 1.5 wt% polymer solutions with homopolymer weight

Figure 11. Rejection of PEG mean molar masses using different composite membranes. a) Block copolymer top film made from 1.5 wt% polymer solutions with homopolymer weight fractions of 0.05, 0.15, 0.30 and 0.40. b) Block copolymer top film made from 1.0 and 1.5 wt% polymer solutions with homopolymer weight fractions of 0.15 and 0.30. Dotted lines are shown to guide the eye.

fractions of 0.05, 0.15, 0.30 and 0.40. The PEG rejection by the native Nadir UV-150 support membrane is much lower than the PEG rejections of our fabricated composite membranes, which implies that the block copolymer film is the selective layer of the composite membrane. The rejection curve starts after $\sim 2000 \text{ g}\cdot\text{mol}^{-1}$ for all composite membranes, indicating that PEG particles with a hydraulic diameter smaller than 2.3 nm are not rejected. The filtration curves become less steep when a larger amount of homopolymers is used. The smallest pores are obtained for $f_{\text{PAA}} = 0.05$, resulting in the highest rejection of PEG molecules. When a higher homopolymer content is used, larger pores are obtained that are accessible for larger PEG molecules, which results in a lower rejection. PEG molecules of $\sim 75,000 \text{ g}\cdot\text{mol}^{-1}$ and $\sim 130,000 \text{ g}\cdot\text{mol}^{-1}$ are for 90% rejected using $f_{\text{PAA}} = 0.05$ and 0.15, respectively. These values correspond to hydraulic diameters of 20 and 28 nm, which are similar to the average size of the microphase separation pores of the membranes (see Figure 3). The rejection curves of membranes made using $f_{\text{PAA}} = 0.30$ and 0.40 are significantly lower than the rejection curves for f_{PAA} values of 0.05 and 0.15. This happens because the larger pores formed by macrophase separation that span through the entire block copolymer film thickness do not have any rejection in the range of the molecular weights used in these filtration experiments. Although many macrophase separation regions appear as craters on top the block copolymer film, there are still regions that span the entire thickness of the film, thereby significantly influencing the selectivity of the membrane. Still, this experiment demonstrates clearly that the separation behavior can be tuned by simply varying the amount of homopolymers.

Figure 11b shows the effect of the polymer concentration on the filtration performance. The rejection of the different PEG mean molar masses is displayed using composite membranes with a block copolymer top film made from 1.0 and 1.5 wt% polymer solutions. When f_{PAA} is kept constant (0.05 or 0.15), a higher total polymer concentration leads to higher rejections. This implies that when the top film is thicker, it influences the separation

behavior of the membrane. A different morphology of the block copolymer domains deeper in the film may explain this behavior⁴⁸, as well as different process conditions such as permeabilities.

The trends found in our experiments are different than the trends that Li *et al.* found for their PS-*b*-PEO/PAA based composite nanofiltration membranes¹³. They found that increasing the homopolymer content always leads to higher permeabilities but not to different separation behaviors. In contrast, we find that changing the homopolymer content leads to different separation behaviors for our ultrafiltration membranes. Also a maximum permeability is obtained when the homopolymer content is varied. The main difference between the two approaches is the used molecular weight of the block copolymer, which determines the maximum homopolymer content before macrophase separation occurs²⁵. The much smaller block copolymer used by Li *et al.* did not come to macrophase separation when f_{PAA} was increased to 0.30 but instead led to a change of domain orientation (from cylindrical to lamellae). In our case, where we use larger block copolymers, increasing the homopolymer weight fraction leads to the formation of macrophase-separated areas of homopolymers that influence the performance of the composite membrane in a very different way.

Effect of feed solution

The previous section showed how the composition of the coating solutions determines the separation behavior of the formed composite membrane. However, the composition of the feed solution can also influence filtration results, which is often neglected in other studies on composite block copolymer based membranes. In order to investigate the effect of the feed solution on the PEG rejection, additional filtration tests were performed using just one M_w of PEG in the feed solution. Single M_w filtrations were performed with low and high M_w PEG (10k and 100k) using a membrane made from a 1.5 wt% polymer solution with $f_{\text{PAA}} = 0.15$. The concentration of the single M_w PEG used was the same as the concentration of the corresponding PEG in the PEG mixture filtration experiments ($0.04 \text{ g}\cdot\text{L}^{-1}$).

Figure 12a shows the rejection of the individual PEG M_w 's for both types of filtration experiments. The rejection of PEG_{10k} is ~ 0.57 during the PEG mixture filtration, but is more than halved in the single M_w filtration (~ 0.22). Also the rejection of the higher M_w PEGs is lower during single M_w filtration, but the decrease is less dramatic.

Figure 12b shows the pure water normalized flux as function of the permeate volume during the different filtration experiments. A fast flux decline is observed during the PEG mixture filtration in the initial stage of the experiment, where the flux rapidly decreases to $\sim 20\%$ of its initial flux. After that the flux is stagnant, indicating the formation of a cake layer⁵⁸. A similar trend is observed during the PEG_{100k} single M_w filtration where the flux rapidly drops to $\sim 35\%$ of its initial value. During the PEG_{10k} single M_w filtration a flux decline is also observed, however, this is far less. The flux slowly decreases from $\sim 80\%$ to $\sim 75\%$ and does not stabilize in the first 30 mL of permeate volume. The graphs indicate

Figure 12. a) Rejection of PEG_{10k} and PEG_{100k} using single M_w PEG and a mixture of different M_w PEG for filtration. b) Normalized flux, normalized on the pure water flux. Membrane used made from a 1.5 wt% polymer solution with $f_{PAA} = 0.15$.

that most of the flux decline during the PEG mixture filtration is caused by the larger PEG molecules. The larger PEG molecules have a stronger rejection than the smaller PEG molecules and will be more abundant at the surface of the membrane. Because of their low diffusion constants, larger PEG molecules will enhance concentration polarization even more, which causes an additional resistance. This can also influence the separation behavior of the membrane⁵⁹⁻⁶⁰. To conclude this paragraph, the MWCO is a function of conditions chosen, so absolute rejection values may change depending on specific experiments. However, the observed trends are correct.

Pros and cons of the method

Coating a thin block copolymer based film on top of a composite membrane is a promising method to fabricate very selective and highly permeable membranes for liquid filtrations. Membranes with different separation properties can be made using just one type of block copolymer by simply varying the amount of homopolymers. When a selective layer of ~100 nm is coated on a support membrane, only ~0.1 g·m⁻² polymer is needed and this is a huge advantage in terms of the cost-effectiveness and durability. However, this method also has some problems that need to be overcome. First, spin coating is a powerful tool for fabricating composite membranes on lab scale, but it cannot easily be scaled up to industrial sizes. Fortunately, dip coating is a good alternative to spin coating. This can be used to coat membranes with a larger area and with different geometries. If the solvent evaporation rate can be controlled, the solidification process is similar to spin coating. The drawback of this method is that more solution is needed, making spin coating more practical for lab scale experiments than for scale up. A second problem is intrusion of the polymer solution into the pores of the support membrane during coating. This can lead to blockage of the pores and thereby decreasing the permeability or to unsuccessful covering of the support membrane. Filling the pores with a fluid that is either miscible or immiscible with the polymer solvent could potentially solve this problem, however, in initial experiments we found that this can also create large defects in our block copolymer film. The way to deal

with this problem seems to be to find an optimum between the pore size of the support membrane and the polymer concentration of the block copolymer coating solution. Smaller pores of the support membrane cause less intrusion and make it possible to use a lower polymer concentration of the coating solution, but comes at the cost of the permeability of the support membrane. This is not a problem when the block copolymer film has the dominating hydraulic resistance, but when the block copolymer film becomes thinner, the support membrane can contribute the most to the hydraulic resistance. Also, the pores of the support membrane can become so small that they start to reject particles in the same range of sizes as the block copolymer film, thereby making the latter obsolete. Finally, it can be concluded that the thickness of the block copolymer film should be minimized in order to obtain a high permeability, and the occurrence of macrophase separation (at higher homopolymer content) limits the range of pore sizes that can be obtained.

4.4 Conclusions

Coating a thin film made from self-assembling PS-*b*-PEO block copolymer and PAA homopolymer on top a support membrane and subsequent removal of the PAA homopolymer is a straightforward method to rationally design and fabricate composite ultrafiltration membranes with tunable pore sizes. We demonstrate for the first time that varying the PAA content or polymer concentration of the coating solution leads to membranes with different separation properties and permeabilities in the ultrafiltration range.

Two different types of pores are formed: Small pores in the range of 10–40 nm by microphase separation, and larger pores up to several hundreds of nanometers by macrophase separation. Using low homopolymer fractions leads to small ordered and monodisperse pores. Increasing the homopolymer content first increases the size of the microphase separation pores, but also enhances the formation of macrophase separation pores. At higher homopolymer contents ($f_{\text{PAA}} > 0.15$), the pores formed by microphase separation become smaller and at some point even disappear, because more homopolymers end up in large areas formed by macrophase separation that appear as craters at the surface. This implies that the use of the method described in this chapter is limited to a certain homopolymer content, and hence pore size, for fabricating monodisperse pores.

The permeability of the composite membranes increases when a lower polymer concentration is used for the coating solution. A lower polymer concentration leads to a thinner top film, hence shorter pores with a lower resistance. Also, the change of vertical to other orientations of the block copolymer nanodomains deeper into the film causes a higher hydraulic resistance. This effect is enhanced when the top block copolymer film becomes thicker.

The simple method based on a block copolymer/homopolymer system reported in this chapter is a promising method to fabricate ultrafiltration membranes. Properties of membranes can simply be tuned by varying the homopolymer content.

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5

Block copolymer membranes fabricated via dry-wet phase inversion with a minimum evaporation step

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Dry-wet phase inversion block copolymer membranes with a minimum evaporation step from NMP/THF mixtures

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Abstract

Block copolymer (BCP) membranes are a very promising new type of membranes, but often have a difficult fabrication method that involves a long evaporation step prior to phase inversion. In this work, we study new novel BCP phase inversion recipes for the fabrication of asymmetric membranes with a thin, ordered isoporous selective layer on top of a highly interconnected porous support layer. A key aim is to shorten the processing time while simultaneously allowing the formation of even thinner selective top layers. Asymmetric membranes were fabricated via the combination of polystyrene-*block*-poly(4-vinyl pyridine) self-assembly, solvent evaporation and liquid induced phase separation. Using a solvent mixture of THF and NMP, a selective top layer of just 60 nm thick was formed with an ordered honeycomb-like pore structure. The formed structure depended on several parameters, such as THF/NMP ratio, polymer concentration of the polymer solution and the duration of solvent evaporation. When a high THF/NMP ratio was used (more THF than NMP) the solvent evaporation step could be reduced to only 1 second, which is a huge benefit from a processing point of view. The THF/NMP ratio also influenced the morphology of the support layer, which translated into a variety of permeabilities ($270\text{--}1320\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$). Filtration experiments showed that the different top layer structures result in different filtration performance, with more ordered pores resulting in more selective filtration.

5.1 Introduction

Self-assembling block copolymers (BCPs) are considered to be very promising for the production of nanoporous membranes, since their ability to self-assemble can lead to membranes with very ordered and uniform pores in the range of 10–40 nm¹. These characteristics can overcome the drawbacks of commercial ultrafiltration membranes², which are either very permeable but not selective (polydisperse pores) or selective but not that permeable (low porosity)³. Self-assembling BCPs are macromolecules that consist of blocks of two or more distinct monomers that can self-assemble into a variety of different nanostructures⁴. This self-assembling process is a thermodynamically driven process. The formed morphology depends on the composition and molecular weight of the BCP⁵.

Diblock copolymers that form a morphology of hexagonally packed cylinders are interesting to use for membrane fabrication, since these cylinders can easily lead to isoporous nanochannels⁶. Fabrication of selective membranes based on BCPs can be divided into several categories. In the first category, a thin dense BCP film (thickness of ~100 to several hundred nanometers) is fabricated by spin coating or dip-coating, where the hexagonally packed cylinders are orientated perpendicular to the surface. Pores are formed by removing the cylinders by etching or cleaving^{7–8}, by removing an additional component that resides in the core of the cylinders^{9–12}, or by an annealing step^{6, 13}. The thin nanoporous film acts as the selective top layer of the composite membrane¹⁴. Although selective membranes have been successfully fabricated, the permeabilities of these membranes are significantly lower than commercial membranes^{15–16}. The main reason for these low permeabilities is that the orientation of the cylinders changes deeper inside the film and that the pores are not highly interconnected¹⁴.

Much higher permeabilities have been obtained by fabricating freestanding asymmetric BCP membranes via a combination of a solvent evaporation step prior to phase inversion in a coagulation bath^{17–22}. This method, *dry-wet phase separation*, is a common method that is used to fabricate asymmetric ultrafiltration and gas separation membranes that contain a thin selective layer on top of a highly interconnected support layer²³. For the fabrication of the membrane, a polymer solution is used that consists of a polymer, a volatile solvent and a non-volatile solvent²⁴. Often, the non-volatile solvent has a higher affinity with the nonsolvent than the volatile solvent. After casting a film, the volatile solvent is allowed to evaporate for a certain time, which results in an increase of polymer concentration at the top of the film. In the case of BCPs, this leads to the formation of cylindrical or threadlike micelles, because of their self-assembling properties. The film is then solidified very rapidly by immersing the still liquid film in the coagulation bath. The increased polymer concentration at the top of the films results in a thin top film with a structure of ordered hollow channels on top of a more open porous support layer with highly interconnected pores²⁵.

Unfortunately, a solvent evaporation duration of tens of seconds is required for the ordering of the BCPs^{21, 26-27}. The downside of the longer solvent evaporation is that the selective top layer will become thicker, which increases its hydraulic resistance and therefore reduces its permeability. It also makes it harder to upscale the process. Hollow fiber BCP membranes have been fabricated, but only with the selective layer on the outside of the fiber²⁸. The different additional parameters involved during the spinning process make it more challenging to tune the morphology of the membrane²⁹⁻³⁰.

In this chapter, we study novel BCP phase inversion recipes that have a much shorter evaporation step (and thus processing time) for the fabrication of asymmetric membranes with a thin, ordered isoporous selective layer on top of a highly interconnected porous support layer. Asymmetric polystyrene-*block*-poly(4-vinyl pyridine) is used as a polymer, which has the ability to self-assemble into a cylindrical morphology. The membranes are fabricated by dry-wet phase separation that involves a very short solvent evaporation step followed by fast liquid induced phase separation. A solvent mixture of volatile tetrahydrofuran (THF) and non-volatile N-methylpyrrolidone (NMP) is used to prepare polymer solutions. This is a common combination for the preparation of asymmetric gas separation and ultrafiltration membranes³¹⁻³³, but has not been used for the preparation of highly-ordered BCP membranes. We study the effect of NMP/THF ratio, the polymer concentration and the solvent evaporation duration on the formed structure. Contrary to previous isoporous BCP membranes fabricated with dry-wet phase inversion, we demonstrate that highly ordered isoporous membranes with thin top layers can be fabricated with a very short (~1 second) solvent evaporation step, which makes it more easy to upscale this method to e.g. hollow fiber spinning. The fabricated membranes are characterized by permeability measurements and several filtrations. Finally, because the P4VP chains are pH responsive³⁴, the permeability of our membranes is tested at different pH values.

5.2 Experimental

Materials

Polystyrene-*b*-poly(4-vinyl pyridine) (PS-*b*-P4VP) block copolymer P3910A-S4VP ($M_w = 109\text{-}b\text{-}30\text{ kg}\cdot\text{mol}^{-1}$, PDI = 1.15) was purchased from Polymer Source, Inc., Canada and was used without further purification. Tetrahydrofuran (THF, Sigma Aldrich, analytical grade) and N-methylpyrrolidone (NMP, AcrosOrganics, 99% purity) were used as solvents. Milli-Q pure water (deionized water purified by a Synergy water purification system of Millipore) was used as nonsolvent for phase inversion and for preparing aqueous filtration solutions. Silver nanoparticles (diameter of 10 and 30 nm) in a 2 mM sodium citrate solution were purchased from NanoComposix, Czech Republic and were used for filtration experiments. Sodium citrate (tribasic dehydrate, $\geq 99.0\%$ purity, Sigma Aldrich) was used for preparing silver nanoparticle buffer solutions. Bovine serum albumin (BSA, $\geq 98\%$ purity, Sigma

Table 1: Overview of compositions of polymer solutions used to fabricate composite membranes.

Solution	Polymer concentration (wt%)	THF/NMP ratio (wt/wt)
1	15	60/40
2	18	0/100
3	18	50/50
4	18	60/40
5	18	70/30
6	21	60/40

Aldrich) was also used for filtration experiments. Hydrochloric acid (HCl, fuming 38 wt%, Sigma Aldrich) was used to prepare water solutions with different pH values.

Preparation of composite membranes

PS-*b*-P4VP block copolymers were dissolved in THF and NMP and stirred for several hours at room temperature. The solutions had a polymer concentration of 15, 18 or 21 wt% and a THF/NMP ratio of 0/100, 50/50, 60/40 or 70/30 (wt/wt). Different types of nanoporous BCP films were fabricated by using different polymer solutions. An overview of the compositions of all used polymer solutions is presented in Table 1.

The interaction parameters of the BCP and THF are $\chi_{\text{THF-PS}} = 0.35$ and $\chi_{\text{THF-P4VP}} = 0.60^{35}$, which indicates that THF is a better solvent for PS than for P4VP. The interaction parameters of the BCP and NMP are $\chi_{\text{NMP-PS}} = 0.41$ and $\chi_{\text{NMP-P4VP}} = 0.01^{36}$, which indicates that NMP is a better solvent for P4VP than for PS.

The polymer solution was cast on a glass plate using a custom made casting-machine with an adjustable casting knife (accuracy of 1 μm). The casting height was set to 200 μm . The film was immersed in a MilliQ-pure water coagulation bath at room temperature, ~ 1 second after casting (amount of times elapsed checked using a timekeeper). During this immersion step (~ 1 hour) the film solidified and could be subsequently detached from the glass plate.

Characterization

Scanning electron microscopy (SEM) (Jeol JSM 6010 LA, at 5 kV for magnifications up to $\times 10,000$, and High Resolution SEM, Zeiss Merlin, at 0.5 kV for higher magnifications) was used to visualize and characterize the membranes. Low magnification SEM samples were dried under vacuum at 30 $^{\circ}\text{C}$ for 24 h and then coated with a thin layer of gold using a Balzer Union SCD 040 sputter device.

UV-Visible spectroscopy (Cary 300 Scan Varian spectrophotometer) was used to determine the concentration of the silver nanoparticles (wavelength of ~ 410 nm for 30 nm particles, ~ 393 nm for 10 nm particles) and BSA (wavelength of ~ 278 nm) in the retention measurements.

Permeation experiments

The permeability of the membranes was determined by measuring the flux of Milli-Q pure water at different pressures (0.4–1.2 bar) using a dead-end filtration set-up. A membrane (circular, 2.5 cm in diameter) was placed in a filter holder cell with a volume of 4 cL. The cell was connected to a vessel filled with Milli-Q pure water, which was pressurized by compressed nitrogen.

The permeability ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) was calculated as the ratio of the flux over the applied pressure:

$$\text{Permeability} = \frac{V}{A \cdot t \cdot \Delta P} = \frac{J}{\Delta P}$$

where V is the permeate volume (L), A is the membrane area (m^2), t is the time (h), J is the permeate flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) and P is the pressure (bar).

All measurements were performed using at least six different membranes to ensure reproducibility. The average permeability and the standard deviation are reported.

Filtration

The membranes were challenged to 30 nm and 10 nm (diameter) silver nanoparticles and BSA (diameter of roughly 7 nm³⁷) filtrations performed at 1.00 ± 0.04 bar using the dead-end filtration set-up described before to determine the corresponding retention. Each component was filtrated individually. Aqueous feed solutions were prepared containing 2 $\text{mg} \cdot \text{L}^{-1}$ nanoparticles in 0.02 M sodium citrate ($\text{pH} = 7.6$) or 1 g/L BSA ($\text{pH} = 6.8$).

The rejection R was determined via:

$$R = \frac{C_{\text{cell}} - C_{\text{permeate}}}{C_{\text{cell}}}$$

where C_{permeate} is the permeate concentration ($\text{g} \cdot \text{L}^{-1}$) and C_{cell} the concentration inside the test cell ($\text{g} \cdot \text{L}^{-1}$). Since the setup ran in dead-end mode, accumulation of the retained solutes caused the concentration in the membrane cell to rise in time. Since it was not possible to monitor the concentration inside the cell in time, the average of the original feed concentration and the final retentate concentration was used as C_{cell} . During every filtration experiment, 10–20 ml permeate was collected, of which the first 5 ml was discarded in order to prevent influence of remaining water in the dead volume under the membrane.

5.3 Results and discussion

Fabrication and characterization of membranes

We started with fabricating a membrane from a simple 18 wt% polymer in NMP solution. NMP is a solvent that is frequently used to fabricate membranes via phase inversion with water as nonsolvent. After casting, the film was immediately immersed in the coagulation bath, which resulted in a minimized evaporation step of approximately 1 second. This resulted in a very porous membrane with pores of 10-30 nm at the surface (Figure 1a). The structure of the membrane changed when THF was added to the polymer solution, while keeping the polymer concentration constant. The BCP polymers started to form a more cylindrical threadlike structure when a THF/NMP ratio of 50/50 was used as solvent (Figure 1b). When the THF/NMP ratio was increased even further to 60/40, the cylindrical threads started to form an ordered structure with more monodisperse pores (Figure 1c). Using a solvent mixture of 70/30 THF/NMP, a well-ordered honeycomb-like structure was obtained with pores of sizes of 38 ± 7 nm and a surface porosity of 0.39 (Figure 1d). The improved structure of the 70/30 membrane seems mainly caused by a smoother surface. While the honeycomb-structure seems flat, the surface of the 60/40 membrane shows elevations where some cylindrical threads are situated higher than others. All membranes, however, showed a defect-free surface.

Figure 1. SEM surface images (magnification 100,000 $\times$) of PS-*b*-P4VP membranes made of 18 wt% polymer solutions with different THF/NMP ratios. a) 0/100, b) 50/50, c) 60/40 and d) 70/30.

Figure 2. SEM surface image (magnification 50,000 $\times$) of a PS-*b*-P4VP membranes made of 18 wt% polymer solutions with a THF/NMP ratio of 60/40 (*w/w*), and 10 seconds of solvent evaporation prior to liquid phase inversion.

Even higher THF concentrations (80/20) were also investigated, but resulted in gels unsuitable for casting membranes.

Ordered nanoporous structures from BCPs have been fabricated before via dry-wet phase inversion, using different combinations of solvent composition, polymer concentration and the duration of solvent evaporation^{26, 38}. However, in our case, the presence of THF seems vital for the formation of the ordered honeycomb-like porous structure. THF is known as a good solvent for the formation of thermodynamic driven PS-*b*-P4VP nanostructures^{9, 39-40}. It has been used as a co-solvent to fabricate PS-*b*-P4VP membranes with similar well-ordered surfaces via dry-wet phase inversion, but at significantly lower concentrations¹⁷.

The formation of the ordered pores is attributed to the evaporation step prior to liquid induced phase inversion. Evaporation of the more volatile THF leads to a higher polymer concentration at the top of the casted film where the BCPs start to form micelles. This thermodynamically driven formation of micelles leads to the formation of the ordered honeycomb-like pores. The formation of the BCP micelles can take place within 4 seconds of solvent evaporation⁴¹, however, can apparently take place even faster since our membranes were fabricated using only 1 second of solvent evaporation, much shorter than previous reported values^{21, 26-27}. The polymer solutions in this work that lead to honeycomb-like structures contain significantly higher contents of THF, which is known for the formation of PS-*b*-P4VP micelles⁴². It is therefore possible that micelles are already present before the start of phase inversion.

The duration of solvent evaporation also influences the morphology of the top of the film. When the evaporation step was prolonged to 10 seconds, a structure was obtained with worm-like cylinders that are orientated parallel to the surface and having small pores in between (Figure 2). Worm-like cylindrical structures made from polymer solutions that were also used to fabricate ordered porous structures have been observed before²⁰. The duration

Figure 3. SEM images of PS-*b*-P4VP membranes made of 18 wt% polymer and a THF/NMP ratio of 60/40. a) cross-section, magnification 45,000 $\times$; b) cross-section, magnification 100,000 $\times$; c) bottom, magnification 10,000 $\times$.

of the evaporation step influences the structure of the top layer^{21, 26} and in many cases there is an optimum evaporation duration for a given polymer solution^{20, 38}. In our case, using a 18 wt% polymer solution with a THF/NMP ratio of 70/30, the ideal evaporation duration is very short: only 1 second.

Figure 3 shows the cross-section and the bottom side of a PS-*b*-P4VP membrane made from an 18 wt% polymer solution with a THF/NMP ratio of 70/30. On the cross-section images, the porous ordered honeycomb-like structure can be seen on top of a more open sponge-like network of interconnected pores. This asymmetric structure is the result of the combination of the very short solvent evaporation prior to liquid induced phase inversion²³⁻²⁴. The thickness of the top-film is just 40-60 nm and of the same order of magnitude as the domain length of the honeycombs. This is thin compared to the thicknesses of BCP top layers found in other asymmetric BCP membranes, which are typically in the range of 100-300 nm^{17, 19-21, 27, 38}. For dry-wet phase separation, the thickness of the top layer is determined by the duration of the solvent evaporation step and the ratio of volatile/non-volatile solvent^{25, 43}. A long solvent evaporation step and a high volatile/non-volatile ratio give rise to a thicker top layer. Therefore, the large THF contents used to fabricate our membranes would in principle lead to thick top layers, but this effect is counterbalanced by the very short duration of the evaporation step.

Figure 4. SEM cross-section images of PS-*b*-P4VP membranes made of 18 wt% polymer solutions with different THF/NMP ratios. a) 0/100, b) 50/50, c) 60/40 and d) 70/30. Magnifications are 2000 $\times$ (a) and 1000 $\times$ (b-d). Insets show SEM images zoomed in on the polymer matrix (magnification 15,000 $\times$).

Besides the structure of the selective top layer, also the morphology of the support layer is examined, since the support layer should also be permeable and give the membrane mechanical strength. In Figure 4, the SEM cross-section images for the four different membranes are shown. The insets show the polymer matrix at a higher magnification. The images show that the THF/NMP ratio not only influences the structure of the top layer, but also influences the morphology of the support layer. Using only NMP as solvent (0/100), a symmetric homogeneous membrane is obtained with an interconnected network of small pores. This morphology looks similar to the structure of the surface (Figure 1a). This is not surprising, since with the use of only non-volatile NMP no significant solvent evaporation takes place that is required to create an asymmetric layer. The membranes that are fabricated using a mixture of THF and NMP as solvent (Figure 4b-d) all show a polymer matrix of highly interconnected pores, formed by short worm-like cylinders that are randomly linked with each other. The diameters of these cylinders and the cylinders that form the structures of the top layer seem similar, which suggests that these cylinders are also formed by micelles. Apparently, the BCPs throughout the whole film have the possibility to self-assemble in cylindrical micelles prior to phase inversion. However, the films also have larger voids in the polymer matrix. For the case of the 50/50 membrane, random large and small voids can be seen, as well as cracks that start at these voids. The 60/40 and 70/30

membranes have finger-like pores directly underneath the top layer, which become larger deeper inside the film. These so-called macrovoids are typically seen in ultrafiltration membranes made by phase inversion. They are often found when the solvent and nonsolvent have a high affinity and show instantaneous demixing²³. Surprisingly, in our cases macrovoids start to appear only when high amounts of THF are used, while THF and water are known for delayed demixing²³.

Figure 5 shows the effect of the polymer concentration on the obtained surface structure of the membrane. The membranes are fabricated using a THF/NMP ratio of 60/40 and an evaporation step of 1 second. When a polymer concentration of 15 wt% is used, a porous structure with a cylindrical micellar structure is obtained (Figure 5a), but it is less ordered than the honeycomb-like structure obtained using the 18 wt% polymer solution (Figure 1c). Interestingly, the structure looks very similar as the structure of the membrane fabricated with a 18 wt% polymer solution and a THF/NMP ratio of 50/50 (Figure 1b). When the polymer concentration is increased to 21 wt% (Figure 5b) the structure becomes even more ordered than the structure obtained using 18 wt% polymer. Thus, changing the polymer concentration can enhance the ordering of pores. The structure has pores of 35 ± 6 nm and a porosity of 31%. These values are lower than the ordered structure of the 18 wt% 70/30 membrane (Figure 1d). This can be explained by the higher polymer concentration used to make the structure in Figure 5b, which normally leads to a more denser morphology in phase inversion²³.

The formation of the structure of the top layer using dry-wet phase inversion is a combination of thermodynamics and kinetics. An interesting theoretical approach has been published that explains the formation of different structures⁴⁴. During the solvent evaporation step, the composition of the BCP, THF and NMP mixture changes continuously. When the film is immersed in the coagulation bath, the solvent concentration decreases because of solvent-nonsolvent exchange, until an unstable composition is reached

Figure 5. SEM surface images (magnification 100,000 $\times$) of PS-*b*-P4VP membranes made of a) 15 wt% polymer solution and b) 21 wt% polymer solution. Both solutions were made using a THF/NMP ratio of 60/40.

where the BCP solidifies. The BCP micelles do not freeze instantaneously after immersion of the swollen film in the coagulation bath, but still have seconds to rearrange to form the final structure⁴⁵. The formed structure depends on this final composition and the path towards it. In this liquid induced phase inversion, the initial composition of the solution is determined by the evaporation step and has a major influence on the path towards solidification. Because two different solvents are used together, the different solvent/nonsolvent pairs should also be considered. The mutual affinity and miscibility of THF and water is lower than that of NMP and water. As a result delayed demixing occurs when THF and water are exchanged, while NMP and water exchange instantly²³. THF will be more present in PS, since THF does not dissolve P4VP well⁴⁶. Also because water has a more favorable interaction with P4VP than with PS, NMP and water exchange is likely to start in the swollen P4VP domains. In summary, many parameters determine the final structure of the membrane. Unfortunately, a perfect combination of BCP type, suitable solvents, solution composition and duration of solvent evaporation has to be found empirically⁴⁴.

Micelle formation is a crucial first step that leads to ordered membrane structures. The state of these micelles, i.e., which blocks form the shell and core, is important since the polymer that forms the shell will determine the surface properties of the membrane. For PS-*b*-P4VP, the state of micellization in a mixed-solvent system has been a point of discussion⁴⁷. It is claimed that P4VP forms the shell of the micelles in a DMF/THF solvent solution when THF starts to evaporate, since the evaporation of THF leads to a higher concentration of DMF, which is more favorable to P4VP²¹⁻²². However, it was found that thread-like micelles having PS as the shell side are formed in DMF, even though DMF is favorable to P4VP. The incompatibility of the two polymer blocks drives the formation of micelles, having the minority P4VP blocks as micelle core⁴⁷. It is likely that PS also forms the shell side of the micelles in our case. The used BCP also has a majority PS block, and the used polymer solutions contain a high concentration of THF, which is PS favorable.

To conclude this paragraph, PS-*b*-P4VP membranes are fabricated using different THF/NMP ratios as solvent. A very short solvent evaporation step prior to precipitation coagulation is required to fabricate an asymmetric membrane with a thin top layer. The THF/NMP ratio and polymer concentration dramatically change the structure of both the top layer and the support layer. In the next paragraphs, the effect of the formed structure on the permeability and actual filtration properties will be examined.

Membrane performance

In all experiments, the freestanding membranes were placed on top of a non-woven that acted as an additional mechanical support. Because of the relatively large voids of the non-woven and its high permeability ($\sim 750,000 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, as determined experimentally) it is assumed that the non-woven has no influence on the results of both the permeability and filtration experiments.

Figure 6. Permeabilities (pure water) of membranes made with solutions with different THF/NMP weight ratios.

Figure 6 shows the pure water permeability of membranes made with 18 wt% polymer solutions with different THF/NMP ratios. A permeability of $270 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ is obtained when pure NMP (0/100) is used. The permeability dramatically increases to $\sim 1320 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ when the THF/NMP ratio is increased to 50/50. When the THF content is further increased to 60/40 and 70/30, the permeability decreases again to 344 and $349 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, respectively. Although these permeabilities differ a lot, they all are in the range of permeabilities of other freestanding BCP membranes made by phase inversion ($40 - 3000 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)^{17-18, 38, 48}. The thicknesses δ of all fabricated membranes are in the same order of magnitude ($\delta \approx 87 \mu\text{m}$, $77 \mu\text{m}$, $75 \mu\text{m}$ and $66 \mu\text{m}$ for THF/NMP = 0/100, 50/50, 60/40 and 70/30, respectively), which indicates that the large differences in permeabilities are mainly the result of differences in the membrane structure. Since the hydraulic resistance of the membranes will be mainly caused by the support layer¹⁸, it is best to explain the permeabilities with the SEM cross-section images in Figure 4. The structure of the 0/100 membrane is denser and has smaller voids than the membranes that were fabricated with THF in the polymer solution. This explains the lowest obtained permeability for this type of membrane. When THF is added to the polymer solution, the polymer matrix shows an interconnected network of pores formed by worm-like tubes. A THF/NMP ratio of 50/50 also shows large voids and cracks in the polymer matrix that can act as a highway for water. This is most probably the reason for the very high permeability of $1320 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. It should nevertheless be noted that this membrane (50/50) was very fragile and therefore difficult to work with. When higher THF contents (60/40 and 70/30) are used, structures with fingerlike macrovoids are formed. Such structures are often seen in other membranes made by phase inversion. These structures normally also have denser regions that decrease the permeability. As these membranes do not show any cracks within the polymer matrix, the permeability is lower than that of the 50/50 membrane.

As shown in this paragraph, the different morphologies of the polymer matrices result in different permeabilities. However, since all morphologies consist of interconnected pores, the permeabilities of all membranes are high. Since the permeability is also determined by the thickness of the membrane, higher permeabilities would be possible by fabricating

Figure 7. Rejection of 30 and 10 nm silver nanoparticles and BSA using membranes fabricated with polymer solutions with THF/NMP ratios of 0/100, 50/50, 60/40 and 70/30. Filtrations were performed in a dead-end setup at 1.0 bar.

thinner membranes on top of other support materials. This, however, is beyond the scope of this work.

Figure 7 shows the rejection of 30 and 10 nm silver nanoparticles and BSA for the membranes fabricated with different THF/NMP solvent ratios. Because the filtrations were performed in a dead-end setup, it is expected that accumulation of rejected solutes in the cell module influences the performance of the membrane in time in terms of permeability and rejection. Therefore, only the first 10-20 ml of permeate (of which the first 5 ml was not taken into account) were used for analysis.

The 0/100 membrane completely rejects both 30 and 10 nm silver nanoparticles and has a BSA rejection of 0.65. The membranes made with THF/NMP mixtures never show complete rejection of the nanoparticles, but always have a rejection between 0.90 and 0.98. However, the BSA rejection is much lower compared to the 0/100 membrane, with BSA rejections of 0.13 for the 50/50 membrane, and even lower values of 0.06 and 0.02 when the THF/NMP ratio is increased to 60/40 and 70/30, respectively. The differences in rejections for the different membranes are the result of the different structures of the top layer of the membrane. Although the structure of the 0/100 membrane is less ordered compared to the membranes made with a THF/NMP mixture, the pores are much smaller. Therefore, the 0/100 membrane rejects smaller particles, including BSA that has a diameter of ~ 7 nm³⁷. For the membranes made with THF/NMP mixtures, one would expect a sharper size cut-off for the membrane with a more ordered pore structure. Indeed, the 70/30 membrane shows a higher difference between the rejections of the 10 nm nanoparticle and BSA than the 50/50 and 60/40 membranes, which means that the pore size distribution is smaller when the pore structure is more ordered. This again demonstrates the key advantages of the BCP membranes, i.e. the ordered pores proved to have a high selectivity and a high porosity.

Figure 8. Left) Flux of a PS-*b*-P4VP membranes made of 18 wt% polymer and a THF/NMP ratio of 60/40 at different pH values. Right) HR-SEM surface (magnification 100,000 $\times$) image of the membrane after immersion in aqueous HCl solution (pH 1.5).

Figure 8 (left) shows the flux response of the BCP membranes at different pH values. When the pH is lowered from 6 to 4, the flux remains similar, but decreases dramatically when the pH is further decreased to 3, 2 and 1. The original flux is restored when the pH is increased back to 6. This phenomenon is analogous to other membranes prepared with PS-*b*-P4VP^{21-22, 27, 48-49}.

P4VP responds to changes in pH via protonation and deprotonation of the pyridyl group⁵⁰. In the protonated state (below the pK_a of 5.2), the polymer chains are in an extended conformation because of electrostatic repulsion of the charged pyridyl groups, while the chains are coiled in the deprotonated state⁵¹⁻⁵². These conformations respond to a swollen state and a collapsed state of the polymer chains⁵³. As a result, the diameter of the pores decreases at low pH and consequently leads to a lower permeability of the membrane. It should be noted that protonation of P4VP also leads to a water-soluble hydrophilic state⁵³⁻⁵⁴, however, the decreasing effective pore diameter is the main phenomenon that contributes to the change in permeability.

Figure 8 (right) shows an HR-SEM image of the surface of the membrane after immersion in the aqueous HCl solution at a pH of 1.5. Although some of the initial honeycomb-like pores still exist, a significant amount of pores seems to have collapsed. This means that these membranes are pH-responsive in terms of permeability, but are also irreversibly damaged once they operate at low pH values. The reason of the pore collapse lies probably in the micellar state of PS-*b*-P4VP. As mentioned before, it is most likely that (for our membranes) P4VP forms the core of the cylindrical threads. Once this core swells, a collapse of the interconnected network of these cylindrical threads seems inevitable.

5.4 Conclusions

Different membranes made of self-assembling PS-*b*-P4VP can be fabricated using a combination of solvent evaporation followed by phase inversion. Using a solvent mixture of volatile THF and non-volatile NMP, an asymmetric membrane having a very thin top layer

and a highly porous and permeable support layer can be fabricated by using only 1 second of solvent evaporation, which is a big benefit from a processing point of view.

Changing the ratio of THF/NMP leads to membranes with different structures, hence, different performances. When only NMP is used as solvent, a symmetric porous membrane is fabricated. No selective layer is formed because no solvent evaporation takes place, as NMP is a non-volatile solvent. When a THF/NMP mixture is used as solvent, PS-*b*-P4VP starts to form cylindrical micelles that end up as a network of interconnected cylinders, thereby creating a highly permeable structure of interconnected pores. The short solvent (THF) evaporation step prior to phase inversion is enough to create a very thin selective layer of honeycomb-like ordered pores. The ordering of pores can be optimized by varying parameters such as polymer concentration and THF/NMP ratio. The best structures were obtained using a 18 wt% polymer solution with a THF/NMP ratio of 70/30 and a 21 wt% polymer solution with a THF/NMP ratio of 60/40, though it is likely that more combinations exist that lead to these structures.

The THF/NMP ratio also influences the morphology of the support layer, and determines the permeability of the membrane. Large voids and cracks underneath the defect-free top layer give rise to a high permeability ($1320 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for a 50/50 THF/NMP ratio), but make the membrane less mechanically strong. The membrane having the honeycomb-like top layer (70/30) shows a morphology with finger-like macrovoids underneath the top layer, which results in a permeability of $349 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$.

Filtration experiments with 30 and 10 nm silver nanoparticles and BSA show that a sharper size cut-off is obtained when the pores are more ordered. This indicates that the ordered honeycomb-like pores indeed have a lower pore size distribution and result in better filtration performance.

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6

General discussion and outlook

Three approaches have been followed in order to fabricate UF membranes with ordered, isoporous pores. In this chapter, the results and conclusions of each individual approach are briefly revisited, and future research and challenges are discussed. Special attention is given to the limits and limitations of the methods and challenges for upscaling the fabrication process.

Downscaling of microsieves by solvent-shrinkage

Polymeric microsieves can be fabricated via phase separation micromolding and can subsequently be downscaled in size by solvent shrinkage¹. However, the smallest dimensions of a microsieve that can be obtained are limited due to several factors. First, the initial pore sizes of the fabricated microsieve are limited to the micrometer scale, due to limitations of the dimensions of the mold. Obviously, if molds can be produced with smaller pillars, it would lead to microsieves with smaller pores. This, however, was not the scope of this thesis. The need for smaller pores was the incentive for the investigation of downscaling microsieves via solvent shrinkage. An important feature that came with solvent shrinkage was that the pore sizes of the microsieves can be tuned by varying the duration of the solvent shrinkage. Microsieves with different performances can therefore be fabricated using just one type of mold. The pore size could be decreased to the point that the pores collapsed and disappeared. However, from a practical point of view, the solvent shrinkage method has two limits: A limit in smallest isoporous pores and a limit in isotropic shrinkage. At higher shrinkage values, the pores start to shrink with different rates and start to deform. Hereby the pores lose their uniformity and consequently the microsieve is not isoporous anymore. The maximum obtained isotropic shrinkage is limited to the porosity of the polymer matrix, as shrinkage of the microsieve occurs due to densification of the polymer matrix. Allowing for greater isotropic shrinkage is possible, but only by increasing the intrinsic porosity of the initial microsieve. In this work the deviation from isotropic shrinkage already started before the maximum isotropic shrinkage was reached¹. This deviation occurs because the perforated pores shrink with a higher rate than the periodicity, thereby decreasing the surface porosity of the microsieve. The obtained results suggest that the ratio of the two shrinkage rates (perforated pores/periodicity) could be tuned by varying the ratio pore size/periodicity and the morphology of the polymer matrix. In theory, the periodicity could shrink with a higher rate than the perforated pores. In that case, deviation of isotropic shrinkage would be beneficial, as the surface porosity would increase. However, more knowledge about the effects of the geometry of the microsieve and the polymer matrix morphology on the shrinking behavior is required.

This work focused mainly on the downscaling of polymeric microsieves, but there are other aspects about polymeric microsieves that still need to be investigated. One of the key questions is if the performance of microsieves, in terms of selectivity and permeability, is better than that of commercial membranes. Although some preliminary experiments on this topic have been performed², this question remains mostly unanswered. Another issue is

upscaling of the fabrication process. Until now, expensive, fragile and small inorganic molds have been used, which limits the sizes of the obtained microsieves. If these inorganic molds could be replaced by more robust and flexible polymer molds, it would become possible to upscale the fabrication process to a continuous process. This continuous process could also include a shrinkage step, to further control the pore size. Although it seems not possible to fabricate hollow-fiber microsieves, a continuous process for producing flat-sheet microsieves will make it possible to fabricate large areas of microsieves. Future research about microsieves should therefore first focus on the performance of microsieves and possibilities to upscale the fabrication process. This could also lead to renewed interest in microsieves, as polymeric microsieves were only studied in a small amount of publications in recent years. And even though it is questionable whether or not PSuM can eventually be used for fabricating membranes in the UF range, polymeric microsieves are still a highly promising type of membrane for applications such as disinfection, microfiltration and fractionation.

Composite membranes with nanoporous BCP top layer

A combination of self-assembling diblock copolymers and homopolymers can be used to fabricate a thin nanoporous layer³. This thin nanoporous block copolymer BCP layer can be used as the selective top layer of a composite membrane. By varying the homopolymer content, the pore size can be tuned and consequently membranes with different performances can be fabricated⁴. While the composite BCP membrane is a promising method, both the block copolymer/homopolymer system and the fabrication of composite BCP membranes have their limits and limitations. The block copolymer/homopolymer system has a limit in the maximum size of isoporous pores, a limitation in available structures and a limitation in available BCP/HP/solvent combinations. The composite BCP membrane has a limitation in its fabrication method⁴.

A limit in the maximum size of isoporous pores exists because pores start to lose their uniformity when a higher content of homopolymer is used. Using higher homopolymer contents, the homopolymer chains start to distribute more randomly over the block copolymer domains (microphase separation) and eventually start to form their own separated domains (macrophase separation). This leads to a very substantial increase in pore size distribution. When larger block copolymers are used, the transition from microphase to macrophase separation already occurs using lower homopolymer contents. However, larger block copolymers produce larger pores at fixed homopolymer contents since their nanodomains are larger. Thus, the largest isoporous pores that can be obtained are a compromise between large BCPs combined with low homopolymer content and small BCPs combined with a high homopolymer content. Still, for small pores, very uniform top layers can be created.

Another limitation is the amount of block copolymer/homopolymer/solvent combinations that can be used. A requirement for the block copolymer/homopolymer/solvent combinations is that both the block copolymer and the homopolymer should be soluble in the chosen solvent. Since the homopolymer is chemically very different than the majority block of the block copolymer, solvents that are selective towards one of the polymer types can often not be used. This can be seen as a disadvantage of this method since selective solvents could enhance the ordering of BCP nanodomains⁵.

But probably the biggest current limit is the obtained structure of the BCP film. An important property of a membrane is a high permeability, which can only be achieved if the membrane is very porous and has interconnected pores. The cylindrical nanostructure of the BCPs, however, theoretically already has as drawback that it would make the porous channels of a composite membrane less interconnected. Furthermore, in the *ideal* case of BCP self-assembly, the cylinders of the BCP nanodomains are oriented perpendicular to the surface while spanning the entire thickness of the BCP layer. This would lead to straight-through pores when the cylindrical blocks are removed. But in this case, many pores would be dead-end pores as the support layer has a limited surface porosity, leading to a low effective porosity. It would be interesting to create a composite membrane with a nanoporous BCP layer with a *gyroid* morphology⁶, and compare the performance of this new membrane with the membranes made in this work. Though having a higher tortuosity than packed cylinders, the gyroid morphology would lead to a network with interconnected pores.

The orientation of the BCP cylinders, however, changes deeper inside the film. If this orientation changes from perpendicular to parallel to the surface, even more pores will be blocked⁵. Results in this work show that the orientation of the cylinders indeed changes deeper inside the film, but the pores still seemed to be interconnected⁴. The composite membranes, however, did not have a high permeability. The highest obtained permeability is $19.4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. This is low compared to commercial UF membranes⁷, which are in the range of $100\text{--}1000 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. Apparently, the effective porosity is still low and can only be increased if more pores of the BCP layer are connected to pores of the support membrane.

The fabrication of a composite membrane by coating a thin layer on top of a support membrane also has its limitations. To obtain a high effective porosity, the surface of the support membrane should be very porous. A high permeability would also be obtained if the pores are large. However, a highly porous support membrane with large pores would require a thicker coating (top layer) for complete coating and mechanical stability of the layer. Unfortunately, for nanoporous BCP layers, the permeability decreases dramatically because of changes in BCP nanodomain orientation, as discussed before. The ideal composite membrane is thus a compromise between the porosity and pore size of the support membrane and the thickness of the BCP top layer.

Another phenomenon that could decrease the permeability of the composite membrane is the intrusion of the cast polymer solution into the pores of the support membrane. Only a short duration between casting the polymer solution and solidification of the polymer could already make it possible for the polymer solution to enter the pores of the support. This would create a dense intermediate layer with a high resistance. Prefilling the pores of the support membrane, preferably with a liquid immiscible with the used solvent, could prevent intrusion. Preliminary experiments were performed in this work but were not successful since evaporation of the filling liquid caused defects in the BCP top layer. Therefore, the filling liquid should be non-volatile as well.

Freestanding BCP membranes via dry-wet phase separation

Freestanding, asymmetric BCP membranes, having an isoporous top layer, were fabricated via dry-wet phase separation. Dry-wet phase separation involves a solvent evaporation step followed by immersion precipitation in a coagulation bath. The evaporation step is necessary for the formation of asymmetric membranes with a selective, ordered, isoporous top layer.

Freestanding, asymmetric BCP membranes are relatively new⁸ and, therefore, knowledge on the fabrication method is still limited. Additives, for example, have been added in order to enhance the ordering of the pores⁹. Various other recipes for the polymer solution also lead to similarly ordered, isoporous structures¹⁰. Many parameters can be tuned for dry-wet phase separation, such as BCP type, solvents, composition of polymer solution, composition of coagulation bath, duration of the evaporation step and temperature. Therefore, it is important to increase the knowledge about BCP dry-wet phase separation by varying more of the mentioned parameters and explore more possibilities to fabricate asymmetric BCP membranes via dry-wet phase separation.

A limit in dry-wet phase separation is the duration of the evaporation step. For each combination of parameters, a certain duration of the evaporation step exist that leads to the desired structure of ordered, isoporous pores. The evaporation step is preferably as short as possible from a processing point of view, but previous investigations required a drying step of at least 10 seconds. In this work this duration was shortened to only 1 second. It might be possible to use an even shorter evaporation step by varying other parameters, such as choice of solvents and composition of the polymer solution. Once again, our limit in knowledge requires more experiments. A shorter evaporation step would make it easier to upscale the fabrication process. Since the introduction of the first asymmetric BCP membrane made via dry-wet phase separation in 2007⁸ some attempts have been made to fabricate similar membranes via hollow-fiber spinning, but only with the selective layer at the outside of the fiber. The many parameters involved in hollow-fiber spinning make it very challenging to reproduce the structure that is obtained by the fabrication of lab-scale flat-sheet membranes. Upscaling the fabrication method described in this work¹⁰ thus seems

like the next step in the development of these asymmetric BCP membranes. The lowered limit in duration of the evaporation step will make it easier to upscale.

In this thesis, special attention was given to easy tuning of the pore sizes. Although tuning of pore sizes was demonstrated for the previous methods, during dry-wet phase separation with BCPs this is much harder. The ordered honeycomb-like structure could only be obtained when a specific combination of solution composition and other parameters was used, which means that tuning pore sizes by adjusting these parameters leads to the loss of the ordered structure. Probably the easiest way to “tune” the size of ordered pores is to vary the M_w of the BCP, although this means that for each type of membrane a different polymer has to be used.

A last critical remark regarding BCP based membranes in general is about the use of BCPs as material. The incentive for developing more efficient membranes is based on the reduction of costs. However, at this moment BCPs are expensive materials, which makes it very irrational to use BCPs for the development of more cost-saving membranes. BCPs are not produced in bulk quantities yet, which explains the high costs, and are not used on an industrial scale. If BCP membranes will eventually be produced on industrial scale, synthesis of BCPs should also be upscaled to a competitive process. For the fabrication of membranes via dry-wet phase separation, a composite membrane, having the asymmetric BCP layer as a thinner top layer, could be produced by e.g. using a triple spinneret¹¹, which would reduce the required amount of BCP.

Afterword

To finish this chapter, all three methods have their limits and limitations. For example, a limit that all methods currently have in common is upscaling. However, in this thesis, several limits and limitations have been changed and knowledge is obtained where to focus on in order to further change the limits and limitations. Although some limits and limitations will always be there, research, however, can change the limits and eventually allow the method to become competitive with state-of-the-art membranes.

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Summary

In this thesis, the focus is on three approaches that allow fabrication of films and membranes that contain ordered and uniform pores with pore sizes in the ultrafiltration range. Special attention is given to the tuning of pore sizes by varying simple parameters during the fabrication process.

For the first approach, solvent exposure is studied as a simple method to decrease the dimensions of polymeric microsieves (**Chapter 2**). Microsieves, having very uniform and straight-through pores, can be fabricated via phase separation micromolding (PSuM), which is a technique that combines the principle of polymer phase inversion to fabricate membranes with the use of microstructured molds to fabricate replicates. Pore sizes of microsieves are usually in the range of micrometers due to limitations in the size of the molds, but need to be reduced to below 1 μm to make the microsieve attractive for other aqueous filtration applications such as ultrafiltration (UF). Polyethersulfone (PES)/polyvinylpyrrolidone (PVP) microsieves were fabricated with (perforated) pores of 2–8 μm in diameter and a very open internal structure. The pore sizes of the microsieves were then further reduced by solvent-shrinkage, where the microsieves were immersed in mixtures of acetone and N-methylpyrrolidone (NMP). Microsieves shrink because of swelling and weakening of the polymers, and subsequent collapse of the open internal structure. Size reduction in terms of pore size and porosity of the perforated pores was monitored over time. The pore size of microsieves was reduced from an initial pore diameter of 2.6 μm to only 0.2 μm . A higher NMP concentration leads to a higher shrinking rate. Shrinking typically occurs in two stages: first, a stage where both the perforated pores and periodicity shrink, and second, a stage where the perforated pores continue to shrink while the periodicity remains constant. For the microsieve to retain a high porosity, it is desired that both the perforated pores and periodicity shrink at similar rates, a process called isotropic shrinkage. The shrinking rate of the periodicity depends on the geometry of the microsieve and the structure of the polymer matrix. The maximum obtained isotropic shrinkage is $\sim 35\%$, which is determined by the amount of voids in the polymer matrix.

The second approach focuses on the fabrication of composite membranes with a thin top layer based on self-assembling diblock copolymers (dBCPs) and homopolymers (**Chapter 3 and 4**). The block copolymers self-assemble into a morphology of hexagonally packed cylinders perpendicular to the surface, while the homopolymers reside in the core of the cylinders because of favorable interactions. Subsequent selective removal of the homopolymers leads to the formation of ordered, nanoporous layers. First, fundamentals of this approach are investigated, where layers are fabricated on model surfaces (**Chapter 3**). A system of polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) block copolymer, poly(4-vinyl pyridine) homopolymer and chloroform was used. The pore size and porosity can be tuned by varying the homopolymer content and molecular weight of the block copolymer. In this way, pore sizes were obtained between 10 and 50 nm. Uniformity of the pore size, however, is lost when the average pore size exceeded 30 nm because of macrophase

separation. In a continued investigation, composite ultrafiltration membranes were fabricated by coating a thin nanoporous BCP layer on top of a support membrane (**Chapter 4**). A system of polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) block copolymer, poly(acrylic acid) (PAA) homopolymer dissolved in tetrahydrofuran (THF) was used. The pore size and morphology of the polymer layer could be controlled by varying the content of homopolymers, as in agreement with results in Chapter 3. The polymer concentration of the coating solution influenced both the morphology and the thickness of the layer. The different pore sizes and morphologies lead to membranes with different molecular weight cut-offs (MWCO) and permeabilities. The work thus demonstrates clearly that membranes with different performances can be fabricated using just a single type of BCP by simply varying the homopolymer content.

In the third approach, freestanding, asymmetric BCP membranes having a selective top layer were fabricated via dry-wet phase separation (**Chapter 5**). A mixture of PS-*b*-P4VP, volatile THF and non-volatile NMP was used as polymer solution. After casting a film, THF was allowed to evaporate for a very short duration (1 second). The still liquid film was then immersed in a coagulation bath where the polymer solidifies. The evaporation step increases the polymer concentration locally at the top of the film, which results in a very thin top layer. It also gives the BCP time to form cylindrical micelles that can lead to an ordered honeycomb structure formed by threadlike cylinders. Changing the ratio of THF/NMP and polymer concentration leads to membranes with different structures, hence, different performances. The best ordered honeycomb structures were obtained using a 18 wt% polymer solution with a THF/NMP ratio of 70/30 and a 21 wt% polymer solution with a THF/NMP ratio of 60/40. The THF/NMP ratio also influences the morphology of the support layer, which determines the permeability of the membrane (349–1320 L·m⁻²·h⁻¹·bar⁻¹). Filtration experiments with 30 and 10 nm silver nanoparticles and BSA showed that a sharper size cutoff is obtained when the pores are more ordered. This indicates that the ordered honeycomb-like pores indeed have a more narrow pore size distribution that allows for more selective filtration.

In the general discussion, all three approaches were revisited, with a focus on the current limits and limitations of these techniques and with recommendations to address these.

Samenvatting

In dit proefschrift zijn drie methoden onderzocht voor het fabriceren van dunne polymeerlaagjes en membranen die poriën van dezelfde grootte bevatten in een regelmatige structuur. De grootte van deze poriën is geschikt voor ultrafiltratie. Extra aandacht is gegeven aan het controleren van de poriegrootte door eenvoudig parameters te variëren tijdens de fabricatie.

In de eerste methode is blootstelling aan oplosmiddelen onderzocht als techniek om de dimensies van polymeer microzeven (*microsieves*) te verkleinen (**Hoofdstuk 2**). Microzeven zijn geperforeerde membranen met poriën van dezelfde grootte en worden gefabriceerd door een techniek genaamd *Phase separation micromolding* (PS μ M). In PS μ M wordt fasescheiding van polymeeroplossingen, een techniek die vaak wordt gebruikt voor het maken van poreuze polymeer membranen, gecombineerd met replicatie van een microgestructureerde mal. De poriegrootte van microzeven zijn normaliter in de ordergrootte van micrometers door limitaties van de grootte van de structuren van de mal, maar dienen te worden gereduceerd tot $<1\text{ }\mu\text{m}$ om de microzeven aantrekkelijk te maken voor andere waterzuiveringstoepassingen zoals ultrafiltratie. Polyethersulfone (PES)/polyvinylpyrrolidone (PVP) microzeven waren gefabriceerd met (geperforeerde) poriën van $2\text{--}8\text{ }\mu\text{m}$ in diameter en een zeer open interne structuur. De poriegrootte van de microzeven werd daarna verder gereduceerd door krimp in een oplosmiddel, waarbij de microzeven werden ondergedompeld in een mengsel van aceton en N-methylpyrrolidone (NMP). Microzeven krompen door zwellen en zwakker worden van de polymeerketens, en vervolgens instorting van de open interne structuur. De poriegrootte van de geperforeerde poriën en de porositeit werden gevolgd als functie van de tijd. Poriën van microzeven werden verkleind van een initiële grootte van $2.6\text{ }\mu\text{m}$ tot een grootte van slechts $0.2\text{ }\mu\text{m}$. Een hogere NMP concentratie leidde tot een snellere krimp. Krimpen gebeurde in twee fases: eerst een fase waarin zowel de poriegrootte als de periodiciteit van de geperforeerde poriën krompen, en vervolgens een fase waarin de poriegrootte verder kromp maar de periodiciteit gelijk bleef. Om een hoge porositeit van de microzeef te behouden is het wenselijk dat de poriegrootte en de periodiciteit even snel krimpen, een proces dat *isotropisch* krimpen wordt genoemd. De krimpsnelheid van de periodiciteit hangt af van de geometrie van de microzeef en de structuur van de interne polymeermatrix. De maximaal haalbare isotropische krimp is $\sim 35\%$ en wordt bepaald door de hoeveelheid initiële lege ruimte in de polymeermatrix.

De tweede methode focust op de fabricatie van composiet membranen met een dunne toplaag gebaseerd op zelf-ordenende blok copolymeren (*self-assembling block copolymers*) (BCP) en homopolymeren (**Hoofdstuk 3 en 4**). De blok copolymeren ordenen zich vanzelf in een structuur van hexagonaal gepakte cilinders die loodrecht op het oppervlak staan, terwijl de homopolymeren zich verdelen in het midden van de cilinders. Wanneer deze homopolymeren vervolgens weer worden verwijderd, wordt een nanoporeuze laag verkregen met geordende poriën. Eerst is fundamenteel onderzoek gedaan naar deze

methode, waarbij laagjes werden gemaakt op model-oppervlaktes (**Hoofdstuk 3**). Een systeem bestaande uit polystyreen-*blok*-poly(4-vinyl pyridine) (PS-*b*-P4VP) blok copolymeer, poly(4-vinyl pyridine) homopolymeer en chloroform was hiervoor gebruikt. De poriegrootte en de porositeit konden worden gecontroleerd door de hoeveelheid homopolymeer en de grootte van het blokpolymeer te variëren. Op deze manier werden poriegroottes verkregen tussen 10 en 50 nm. De uniformiteit van de poriegrootte ging echter verloren wanneer de gemiddelde poriegrootte boven de 30 nm kwam, door een proces genaamd *macrofase scheiding*. In het vervolgonderzoek werden composiet membranen gemaakt door een dunne BCP laag op een support membraan te coaten (**Hoofdstuk 4**). Een systeem bestaande uit polystyreen-*blok*-poly(ethyleen oxide) (PS-*b*-PEO) blok copolymeer, polyacrylzuur homopolymeer en tetrahydrofuran (THF) was hiervoor gebruikt. De poriegrootte en de structuur van de polymeerlaag konden worden gecontroleerd door de hoeveelheid homopolymeer aan te passen, overeenkomstig met de resultaten uit Hoofdstuk 3. De polymeerconcentratie van de coating oplossing had invloed op zowel de structuur als de dikte van de laag. De verschillende poriegroottes en structuren leidden tot membranen met verschillende scheidingseigenschappen en permeabiliteiten. Dit werk laat dus duidelijk zien dat membranen met verschillende eigenschappen kunnen worden gefabriceerd met slechts één type blok copolymeer door de hoeveelheid homopolymeer te variëren.

In de derde methode werden vrijstaande, asymmetrische BCP membranen met een selectieve toplaag gefabriceerd door middel van droog-nat fasescheiding (*dry-wet phase separation*) (**Hoofdstuk 5**). Een mengsel van PS-*b*-P4VP, vluchtig THF en (niet vluchtig) NMP was gebruikt als polymeeroplossing. Nadat een laag polymeeroplossing was gestreken, kon THF verdampen voor een korte periode (1 seconde). De nog steeds vloeibare laag werd dan ondergedompeld in een coagulatiebad waar het polymeer stold. De korte verdampingsperiode verhoogde lokaal de polymeerconcentratie in de top van de gestreken laag, en zorgde daardoor voor een hele dunne toplaag. Het zorgde er ook voor dat BCP micellen zich konden ordenen in een honinggraad structuur gevormd door kleine polymeerdraadjes. Door de verhouding THF/NMP en de polymeerconcentratie te variëren konden membranen met verschillende structuren, en daardoor verschillende eigenschappen, worden gemaakt. De beste geordende honinggraad structuren werden verkregen met een 18% (gewicht) polymeeroplossing met een THF/NMP verhouding van 70/30 en een 21% (gewicht) polymeeroplossing met een THF/NMP verhouding van 60/40. De THF/NMP verhouding beïnvloedde ook de structuur van de support laag en bepaalde de permeabiliteit van het membraan ($349\text{--}1320 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$). Filtratie proeven met 30 en 10 nm zilver nanodeeltjes en BSA toonden aan dat een selectievere scheiding plaats vindt wanneer de poriën meer geordend zijn. Dit duidt aan dat de poriën van de geordende honinggraad structuur inderdaad een kleinere poriegrootte verdeling hebben die zorgt voor een selectievere scheiding.

Tenslotte worden de drie methoden kort opnieuw besproken, met een focus op de limieten en limitaties van deze technieken en met aanbevelingen voor vervolgonderzoek.

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