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ABSTRACT

Block copolymers, having the ability to self-assemble into arrays of well-defined nanostructures, can be turned into thin films. Their application as membrane was so far strongly limited by the fact that these thin films have to be transferred manually onto a porous membrane support, or because of the very strict preparation conditions. A simple method is reported here to directly produce ordered nanoporous membranes on porous supports. Well-ordered membrane structures were prepared via a simple strategy exploiting blending of a block copolymer (PS-b-PEO) with a homopolymer (PAA), involving no thermal or solvent treatment. The membranes could be directly introduced on several types of porous membrane supports via straightforward spin or dip coating of very small amounts of polymer. Moreover, the permeability of the membranes could be readily tuned by removal of the PAA without changing membrane morphology. While already inherently stable in e. g. sodium hypochlorite solutions, the ch...

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Ordered nanoporous membranes based on diblock copolymers with high chemical stability and tunable separation properties†

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Block copolymers, having the ability to self-assemble into arrays of well-defined nanostructures, can be turned into thin films. Their application as membrane was so far strongly limited by the fact that these thin films have to be transferred manually onto a porous membrane support, or because of the very strict preparation conditions. A simple method is reported here to directly produce ordered nanoporous membranes on porous supports. Well-ordered membrane structures were prepared via a simple strategy exploiting blending of a block copolymer (PS-b-PEO) with a homopolymer (PAA), involving no thermal or solvent treatment. The membranes could be directly introduced on several types of porous membrane supports via straightforward spin or dip coating of very small amounts of polymer. Moreover, the permeability of the membranes could be readily tuned by removal of the PAA without changing membrane morphology. While already inherently stable in e.g. sodium hypochlorite solutions, the chemical stability of the membranes could be further enhanced via simple UV-radiation, clearly widening their potential application field.

Introduction

The field of nanostructured materials is progressing rapidly, and a number of novel possibilities arise from employing self-assembly processes. Block copolymers are particularly interesting building blocks in this context. Thanks to the incompatibility between the chemically distinct segments, block copolymers have the ability to self-assemble into arrays of various well-defined structures such as spheres, cylinders, lamellae, or more complex morphologies, and have already proven their great potential for diverse applications in solutions or in thin films for example.¹

Membrane technology is an emerging field with a clear impact on daily life through reverse osmosis or membrane bioreactors for water purification, artificial kidneys in medicine, gas separations in methane production and solvent recycling.²–⁵ Nevertheless, the search for new membranes that combine good selectivity, permeability and stability is still a significant challenge. Being inversely proportional to thickness, high membrane fluxes inevitably require thin selective layers, while chemical stability directly determines the scope of applicability for a given membrane. For instance, chlorine resistance is of prime importance in water treatment where long-term stability of current commercial membranes remains problematic.⁶,⁷ Industrial membrane applications in ‘polymer-aggressive’ solvents like dimethylformamide (DMF) and tetrahydrofuran (THF) are currently still completely missing due to a lack of suitable resistant membranes.

Nanoscopically structured materials based on block copolymers have so far only scarcely been applied in membrane synthesis.⁸–¹¹ The reported approaches can be divided into two categories.

A first strategy is to self-assemble the block copolymer into a film where the cylinders that form the minor phase are oriented perpendicular to the film surface. The minor phase is then selectively removed to open up the pores.⁸ The film can be manually transferred from the solid substrate on which it was prepared onto a porous support to enable filtration experiments. Despite impressive ordered porous structures, often requiring a long thermal or solvent annealing step, the film transfer from a solid to a porous support severely excludes up-scaling and widespread application. Moreover, the pore size (typically not smaller than 10 nm) of these thin films cannot be substantially further reduced to allow for more critical separations. Other ordered structures based on ABC triblock copolymers were claimed to be applicable to membrane separations, and even though successful transfer to porous supports was shown, examples of real membrane separations remained absent.¹²

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The second strategy relies on the so-called ‘phase inversion’ process, where solidification of a cast polymer solution takes place during contact with a so-called non-solvent. Since both the selective layer and the support layer are made from the copolymer, this approach requires substantial amounts of often expensive copolymer. Most importantly, it can only be applied within a very narrow window of polymer types, concentrations, and solvent mixture compositions, since the controlled phase separation has to take place during the very fast, typically sub-second, membrane solidification. Also this new material was not yet tested in actual filtration experiments.\(^\text{11}\)

So, despite the established high potential of block copolymer based nanostructured materials for membrane separations, two critically important challenges still remain: direct introduction of ultrathin nanostructured block copolymer films onto porous supports to form a so-called thin-film composite membrane, and the proof that this type of membranes can actually achieve separation.

This paper reports for the first time such simple synthesis method requiring only minimal amounts of copolymer. Membranes are obtained by directly depositing the ordered, block copolymer based, active layer on different porous supports of either ceramic or polymeric nature. The membranes have been tested in different filtration experiments, showing promising results and a wide application potential. Finally, an impressive chemical stability and easy tuning of the separation properties are demonstrated.

### Results and discussion

The general strategy reported here for the membrane preparation relies on the blending of a diblock copolymer with a homopolymer, as illustrated in Fig. 1. As starting materials, an asymmetric polystyrene-block-poly(ethylene oxide) (PS-\(b\)-PEO) diblock copolymer with a \(M_n\) of \(19k\) g mol\(^{-1}\) for the PS block and a \(M_n\) of \(6.4k\) g mol\(^{-1}\) for the PEO block, and a poly(acrylic acid) (PAA) homopolymer, both commercially available, were selected. Since PAA interacts specifically with the PEO block via hydrogen bonds and both polymers are fully miscible, the added PAA will be located in the PEO microdomains.

We first investigated the possibility to deposit the block copolymer based active layer directly on a porous support. Ceramic supports were first used due to their closer chemical similarity with the commonly used silicone wafers and the low surface roughness of the selected membrane, prepared from \(\alpha\)-Al\(_2\)O\(_3\) with a thin top-layer of \(\gamma\)-Al\(_2\)O\(_3\) having an average pore size of 3–5 nm. Solutions in THF of the PS-\(b\)-PEO with different amounts of PAA were spin-coated directly onto this porous support. Fig. 2 (top) shows Scanning Force Microscopy (SFM) images of films containing different amounts of PAA and with a thickness of only 200 nm, substantially less than the earlier reported transferrable membranes.\(^\text{8,12}\) An array of uniform cylinders perpendicular to the film surface is clearly observed when the weight fraction of PAA in the copolymer is less than 30%. The minor phase of combined PEO–PAA forms the cylindrical domains, and the major component PS constitutes the matrix. The average center-to-center distance between the cylindrical domains is about 25 nm. When the weight ratio of PAA exceeds 30%, lamellae perpendicular to the support are formed. The center-to-center distance is then 39 nm. The self-assembly in thin films of PS-\(b\)-PEO block copolymers is known to be very sensitive to the processing conditions (humidity, type of substrate, solvent used, film thickness,...).\(^\text{13,14}\) In the present case, adding even small amounts (5% w/w) of PAA to PS-\(b\)-PEO allows already to obtain perpendicular cylinders in a wide range of processing conditions, directly by spin-coating and without any further thermal or solvent treatment. This difference is probably linked to a strong increase in incompatibility between PS and PEO/PAA complex compared to PS and PEO. Such an increased incompatibility was shown recently for blends of PAA and Pluronics.\(^\text{15}\) Our system self-assembles thus upon mere solvent evaporation and even on a porous alumina support, turning it into a truly excellent candidate for further membrane exploration. Unlike earlier reports, the active layer can thus be applied straight onto a porous support to form a thin film composite membrane. Moreover, our approach requires only a small amount of a block copolymer, calculated to be less than 150 mg m\(^{-2}\) of membrane.

To broaden the possibilities, different porous polymer supports were screened as well, being the generally preferred support material for membrane preparation due to price and...
processability. Direct use of ultrafiltration membranes based on polyacrylonitrile (PAN) and diamine cross-linked polyimide (PI) failed, since the surface pores were too large. Indeed, the applied highly diluted coating solutions—required to obtain thin enough selective layers to increase fluxes—intruded the support pores, leading to defective selective layers. Pre-filling the support pores before spin coating was tried with an isopropanol/glycerol solution—a typical conditioner system for membranes, or with water. Dewetting however induced large pores (Fig. S1†). Fortunately, thanks to the high chemical stability of both selected supports, pore filling solvents possessing a higher compatibility with the coating solution could also be screened. THF was finally found to be the proper solvent to fill the pores. No intrusion was observed anymore and an unchanged morphology of the diblock polymer layer could be obtained (see Fig. S2†). To finally come to a really practical method, both at lab scale and in up-scaling, the thin copolymer layer was also successfully applied via dip-coating instead of spin-coating. Similar cylindrical and lamellar structures were obtained on all supports mentioned above, further proving the robustness and versatility of reported method.

Considering the dense nature of the copolymer layer, typical solvent fluxes in the nanofiltration (NF) range were anticipated. Permeances of 1.2–1.6 L m² h bar⁻¹ measured at 40 bars for pure methanol were indeed found, increasing slightly as a function of the PAA content (Fig. 3). The small changes with changing PAA content in domain sizes and in affinity of the PEO/PAA-domains for methanol possibly explain this effect on methanol transport. Molecular weight cut-off (MWCO) values, defined as the $M_w$ of a polyethylene glycol (PEG) solute that is retained for 90%, of

Fig. 2  Morphology of the thin film composite membranes with PS-$b$-PEO top layers containing different amounts of PAA on Al₂O₃ supports. (a–d) SFM of coatings containing 5%, 10%, 20% and 30% PAA respectively; (e and f) SEM pictures at 2 different magnifications of the cross-section of a composite membrane with a 220 nm thick PS-$b$-PEO top layer containing 20% PAA.
400–500 Da further confirmed the NF-nature of the prepared membranes.

Another interesting point of the reported approach is the possibility to remove the PAA homopolymer from the cylinders or lamellae of the selective layer to further tune the membrane properties. This can be easily done by soaking the films overnight in MilliQ water. The SFM pictures of the composite membranes after treating with water still show the highly ordered structures (see Fig. S3†), with the minor phase of PEO forming the cylindrical domains, and the major component PS constituting the matrix. The removal of the PAA was ascertained by Fourier Transform Infrared Spectroscopy (FTIR). Fig. 4 shows the FTIR spectra of a composite membrane with 20% PAA before and after the water treatment. The intensity of the carbonyl stretching band, characteristic of the PAA, obviously decreases drastically, confirming the successful removal of PAA from the thin films.

As shown in Fig. 3, this PAA-removal offers very interesting opportunities with respect to filtrations. With increasing content of PAA, and thus with increasing amount of material leached out from the original membrane, the methanol fluxes increase significantly, up to nearly three times for a membrane originally containing 30% PAA. Most interestingly, the retention power of the membranes hardly changes. This can be explained by the fact that: the inner morphology of the film and/or the actual barrier pore structure under operation conditions (in methanol) are presumably much different than what is expected. Moreover, the inner distribution of PAA in the cylinder will be another key

![Fig. 3](image1.png)

**Fig. 3** Separation properties of the self-assembled membranes before and after PAA removal. (a) Bar diagram of methanol fluxes, with the MWCO-values, obtained from the retention curves for polydisperse PEG-600 shown in (b), given on top of each bar.

![Fig. 4](image2.png)

**Fig. 4** FTIR spectra of a thin PS-\(\text{b}\)-PEO film containing 20% PAA before and after water treatment.

![Fig. 5](image3.png)

**Fig. 5** PALS results recorded on the alumina support and on a self-assembled membrane, prepared on the same alumina support, from a blend of PS-\(\text{b}\)-PEO with 20% PAA, before and after water treatment.
parameter that possibly determines the final retention of membranes. This method of PAA addition thus provides a simple way to make ordered nanoporous membranes with tuneable permeation properties, enabling an increase of the permeability while not affecting selectivity. Such effect is a rare, but highly desired combination in membrane technology. The strongly increased membrane fluxes after water treatment originate from the creation of extra free volume in the PEO phase due to the removal of the PAA, as evidenced by Positron Annihilation Lifetime Spectroscopy (PALS). The data of the $S$-parameter, vs. positron incident energy, are shown in Fig. 5a. 

For the Al$_2$O$_3$ support, $S$ increases sharply near the membrane surface to a maximum that remains stable throughout the probing depth, representing the porosity of the support. The $S$ parameter of the composite membranes on the other hand reaches that same final level but shows a pronounced intermediate level, reflecting the porosity of the copolymer based top-layer. Upon PAA removal, the $S$ parameter of the polymer layer increases clearly, reflecting an increased free volume. The increased $\omega$-positronium lifetime of the composite membranes after water treatment further confirms the results (Fig. S4† and Table 1). The corresponding size of the free volume elements in the membrane grows from 0.97 nm to 1.02 nm. This analysis is further supported by the normalized porosity parameter ($R$) vs. the implantation energy plot (Fig. 5b). The thickness of the top-layer, which corresponds to an implantation energy of 2.7 keV in Fig. 5b, can be estimated to be around 200 nm, in good agreement with SEM results (Fig. 2). It is also interesting to note (Fig. 3) that the final performance of the membranes exceeds that of a commercial BPT/R6-E membrane (Bio Pure Technology, Rishon-Lezion, Israel).

The membranes prepared above can be used in a limited range of solvents only that do not dissolve the membrane polymer. However, the presence of isolated zones of two very different polymer systems opens unique and highly appealing possibilities for membrane development. Firstly, the strongly hydrophilic PEO regions create the potential to use this membrane in aqueous applications. For example, a PS-$b$-PEO membrane, prepared by extracting the PAA from a blend with 5% PAA, exhibited water fluxes of 6.4 L m$^{-2}$ h$^{-1}$ and retentions of Cl$^-$ ions of 80%. More importantly, the membranes showed a clear chlorine resistance with unaltered membrane morphology and performance (Fig. S5†) after soaking in 1000 ppm NaClO at pH $= 4$ for more than 20 hours. Secondly, the PS regions offer the possibility to further extend the chemical stability of the composite membranes in organic solvents. Simple cross-linking of the PS phase with a UV lamp left again the morphology of the membranes intact (Fig. 6 in ESI†), while introducing a chemical resistance toward all common organic solvents, including for instance acetone, DMF and dichloromethane (DCM) (Table 1). Moreover, the solvent resistant nanofiltration (SRNF) performance in these solvents was excellent, combining high fluxes with high selectivities (Fig. 6).

### Conclusions

A new class of nanostructured membranes was reported, exemplified here by using blends of a PS-$b$-PEO diblock copolymer and a PAA homopolymer as template. The membranes are

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<th>Toluene</th>
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*+: Resistant and --: not resistant (dissolved).
produced by a simple and versatile method by directly depositing the nanostructured thin active layer on several types of porous membrane supports of either inorganic or polymeric nature. This robust procedure is insensitive to the nature of the support and to the deposition conditions, keeping all options for further exploration and possible up-scaling intact. The membranes exhibit tuneable transport properties by changing the amount of PAA blended, but also by subsequent removal of this PAA from the top-layer. The intrinsically high chlorine stability of the membranes was extended to a general organic solvent stability via a simple UV irradiation, significantly broadening the impact of this new membrane type on the numerous fields exploiting membrane technology.

Reported membranes already show promising performances, especially in SRNF experiments. The simple procedure used to prepare the PS-b-PEO/PAA based membranes described here can in principle be generalized to other copolymer-homopolymer combinations, allowing for further tuning or developing new applications, and broadening thus further the application field.

**Experimental**

**Materials**

Porous Al₂O₃ supports, purchased from Pervatech, Netherlands, were composed of two layers: a porous α-Al₂O₃ coated with a γ-Al₂O₃. Before spin-coating the selective layer, the support was immersed in MilliQ water overnight and dried at 90 °C for 12 hours.

Cross-linked polyimide (PI) supports were prepared as reported previously.¹⁶ Polyacrylonitrile (PAN) supports were kindly provided by Sulzer Chemtech.

Polystyrene-b-poly(ethylene oxide) (PS-b-PEO) with a molecular weight ($M_w$) of 25.4 kDa, a polydispersity of 1.06 and a PS fraction of 75 wt%, was purchased from Polymer Source, Dorval, Canada. Poly(acrylic acid) with a $M_w$ of 5 kDa and polydispersity of 1.2 was obtained by hydrolyzing poly(tert-butylacrylate), purchased from Polymer Source, by trifluoroacetic acid.

Preparation of composite membranes

A first set of composite membranes were prepared on the inorganic support by spin-coating THF solutions of PS-b-PEO blends with different amounts of PAA. The polymer concentration and the rotating speed during spin-coating were kept at 2% w/v and 1500 rpm, respectively, yielding films with a thickness of 200 nm as measured by AFM and SEM. A second set of composite membranes was prepared on polymeric supports by the so-called solvent casting method. The polymer supports were first taped onto a glass plate. The plate was placed on a platform tilted to form an angle of 60°. The polymer solution was deposited on the support by means of a Pasteur pipette. Before applying the polymer solution, the membrane support was filled with THF to prevent intrusion.

UV cross-linking was performed by irradiating the polymer films in air at a wavelength of 254 nm with a dose of 10 J cm⁻².

**Membrane filtration**

Filtrations were done in a stainless steel dead-end pressure cell with 15.2 cm² membrane area. Methanol was poured into the cell, and the cell was pressurized with nitrogen to 40 × 10⁵ Pa (40 bar). Permeate samples were collected in cooled flasks as a function of time, weighed and analyzed. The flux was calculated according to:

$$J = \frac{V}{AT}$$

where $J$ is flux (L m⁻² h⁻¹), $A$ is area and $T$ is time.

All measurements were based on at least three samples, and the average values were used. The average standard deviation on the measurements was about 5%.

**SFM and SEM measurement**

SEM (Philips XL FEG30) was carried out to study the cross-section of the membranes. The cross-section was obtained after breaking the membranes in liquid nitrogen. The SEM samples were first gold coated before use.

SFM experiments were performed by using a Multimode AFM with a Nanoscope IV controller (Veeco/Digital Instruments, Santa Barbara, USA). Samples were imaged in air in tapping mode with a drive frequency of 200–300 kHz. Silicon nitride oxide-sharpened tips (NCHR, Nanosensors, Germany) were used. AFM scratching to measure film thickness was done in contact mode. All measurements were based on at least three samples.

**Positron annihilation spectroscopy**

Variable low energy positron experiments were performed both at the Department of Subatomic and Radiation Physics of Ghent University, Belgium and at the new NEPOMUC facility of the FRMII research reactor in Garching, Germany, while the $R$ parameter and Doppler broadening experiments were performed at Ghent University. The positron lifetime measurements were performed at the FRMII research centre.

The positron beam at Ghent University is described elsewhere.²⁰ A magnetically guided continuous low energy positron beam from a moderated $^{22}$Na source can be accelerated and implanted into the samples with energies ranging from a few eV up to 30 keV corresponding to polymers with a maximum implantation depth of 10 micron. The annihilation radiation detected by a High purity Ge detector (resolution FWHM 1.2 keV at 511 keV) is parameterized into the $R$ and $S$ parameters.

The positron beam line used at the NEPOMUC²¹ slow positron facility at the FRMII is the pulsed low energy positron system (PLEPS). The continuous low energy positron beam from the neutron reactor, with an intensity of approximately 10⁹ low energy positrons per second, is modulated at 50 MHz into a pulse of approximately 250 ps. The lifetime spectra were decomposed using LT9 software.²² For each of the samples the evolution of the $R$ parameter profile measured at the Ghent University was used to determine the energy selection to perform the lifetime experiments at FRMII.

From the obtained $\alpha$-Ps lifetimes, the radius of the pores, which are considered to be free volume elements, can be
calculated using the Tau–Eldrup equation. The thickness of the membranes $d$ or the mean implantation depth $z$ of positrons can be related to the incident positron energy ($E$) according to the following equation:

$$z = \frac{C \times E^n}{\rho}$$

where $C$ and $n$ are constants and $\rho$ is the density of the polymer (in g cm$^{-3}$).

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References