



## Macromolecular Nanotechnology

# Composite membranes with hydrophilic nanopores derived from the self-assembly of block copolymer supramolecular complexes



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## ARTICLE INFO

## Article history:

Received 17 September 2014

Received in revised form 4 November 2014

Accepted 16 November 2014

Available online 22 November 2014

## Keywords:

Composite membranes  
Supramolecular complexes  
Nanopores  
Block copolymers  
Selectivity

## ABSTRACT

Selective composite membranes with high and controlled porosity have been fabricated using patterned silicon microsieves as support and nanoporous polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) membranes as selective layer. The desired morphology of the block copolymer layer is obtained by a supramolecular approach based on the hydrogen bonding of the PEO block with resorcinol. The formation of PS-*b*-PEO/resorcinol complexes allows to easily control the self-assembly of the block copolymer and to obtain normally oriented PEO/resorcinol nanocylinders by spin coating PS-*b*-PEO/resorcinol solutions. In a further step resorcinol works as a porogen and by its selective dissolution densely packed, normally oriented nanochannels coated by PEO chains have been obtained. These hydrophilic nanochannels have a diameter of approximately 20 nm and cross the membranes from top to bottom. The nanoporous polymer layer is crack-free and well adheres to the support microsieve. The composite membrane is permeable to methylene blue while blocks larger molecules, such as bovine serum albumin.

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## 1. Introduction

The capability of block copolymers to spontaneously arrange into well-defined ordered structures with nanoscopic size has proven to be particularly advantageous for templating nanoporous materials ranging from oxidic monoliths to inorganic and polymeric thin films [1–6]. Self-assembling of block copolymer templates has been also proposed as an alternative strategy to phase inversion [7,8], track-etched [9,10] and lithographic techniques [11] for the fabrication of nanoporous polymer membranes with high and controlled porosity.

The simplest strategy to obtain membranes from self-assembled block copolymers envisages the removal of the minority block (i.e. the lower molecular weight block of the block copolymer), while the majority one forms a continuous matrix. Block copolymer assemblies resulting in the cylindrical morphology and with cylinder orientation normal to the film surface are the most interesting ones as they allow the fabrication of membranes with highly ordered channels spanning the whole membrane thickness [12]. The main advantages of block copolymer-templated membranes over other types of polymer membranes are their narrow pore size distribution, high void fraction and smooth surfaces, resulting in superior selectivity, high fluxes and fouling resistance [13,14]. Pore size can be easily varied to optimize size selectivity, and

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additional separation mechanisms can be introduced by tuning the membrane surface properties through functionalization of the pore walls [15–17].

Most preparative protocols for nanoporous membranes derived from block copolymers consist in: (1) deposition of block copolymer solutions on proper supports, (2) annealing of the resulting thin films in order to optimize phase segregation and orientation of polymer domains, (3) pore generation. Through the deposition and annealing steps nanostructured thin films are obtained which consist of ordered nanosized domains (i.e. nanocylinders) embedded in a continuous matrix of the majority block [18]. In the third step block copolymer films are transformed in nanoporous membranes by elimination of a minor component through methods that do not compromise the integrity of the matrix material. This may be accomplished by selective degradation of the minority block or by selective dissolution of additional components, such as small organic molecules or homopolymers [19,6,20] confined within the minority block domains.

Recently block copolymer-derived membranes have been proposed as highly selective layers in composite membranes [21,22]. Highly selective separations and high flux have been obtained by membranes with an asymmetric film geometry consisting in a thin nanoporous layer, prepared from a block copolymer, and a support membrane. Both polymeric [23,24] and silicon macroporous supports [22] have been proposed for the fabrication of composite membranes.

In this contribution, we describe the fabrication procedure of nanoporous membranes with uniform pore size and high pore density obtained by spin-coating polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) solutions on commercial silicon microsieves. The desired morphology and orientation of the block copolymer domains is achieved by a supramolecular approach based on the complexation by hydrogen-bonding of the PEO block with hydroxyl groups of resorcinol (RES) molecules. The major advantage of the supramolecular approach is that the low molecular weight molecule (i.e. resorcinol) can be easily removed by solvent rinsing, leaving a nanoporous material with the same morphology as the parent material. In a previous paper we demonstrated that the changed interfacial interactions and the reduction in the crystalline PEO phase due to the presence of RES are able to force the complexed PS-*b*-PEO copolymers to self-segregate giving perpendicular oriented PEO/RES cylinders [25].

Starting from that finding ordered nanostructured films with normally oriented PEO/RES cylindrical domains were prepared. These films were subjected to a mild photo-degradation by UV treatment, both to improve their mechanical resistance by crosslinking the PS matrix, and to increase their hydrophilicity by introducing polar groups on the PEO chains. Pores were then generated by selective dissolution of RES embedded in the cylindrical PEO domains. PEO-coated nanochannels crossing the membrane thickness were thus obtained. Permeability and selectivity of the composite membrane were assessed by monitoring the diffusion of methylene blue ( $MW = 320 \text{ g mol}^{-1}$ ) and bovine serum albumin ( $MW = 66 \text{ kg mol}^{-1}$ ).

## 2. Experimental

### 2.1. Materials

PS<sub>308</sub>-*b*-PEO<sub>250</sub> ( $M_n = 32,000$ -*b*- $11,000$ ) was purchased from Polymer Source Inc. (Dorval, Canada) and used without further purification.

Resorcinol (RES  $\geq 99\%$ ) was obtained by Carlo Erba. Benzene, 2-propanol, diethyl ether, acetic acid (HAc), methylene blue (MB), bovine serum albumin (BSA), sodium dihydrogenphosphate and sodium hydroxide were purchased from Sigma Aldrich.

### 2.2. Preparation of nanoporous membranes

Copolymer benzene solutions (2 wt%) were stirred for half an hour to ensure complete dissolution of the copolymer. Then resorcinol was added in order to obtain mixtures with a molar ratio RES:EO of 1:2, 1:4 and 1:8. Prior to deposition solutions were filtered through 0.45  $\mu\text{m}$  PTFE membrane syringe filters. A few drops of each solution were spin coated onto proper supports at 1000 rpm for 20 s, using a 8" Desk-top Precision Spin Coating System, model P-6708D vs. 2.0. Films were dried in a hood at ambient temperature for at least 12 h and then were UV-irradiated for 8 h under a fluorescent lamp (Philips TUV T8) emitting UV-C rays at 15 W. Finally, nanopores were generated by immersing the films into solvents able to selectively dissolve RES. Following this procedure nanoporous polymer membranes were prepared on dense supports (mica, glass and silicon) and on commercial silicon microsieves by Aquamarijn Micro Filtration BV (Zutphen, Netherlands), having on top a Si<sub>3</sub>N<sub>4</sub> membrane with surface area of  $5 \times 5 \text{ mm}$ , thickness of 0.6 mm and pores of 5  $\mu\text{m}$  in diameter arranged in hexagonal setting.

### 2.3. Characterization

Surface morphology of both nanostructured PS-*b*-PEO/RES films and of nanoporous membranes obtained after resorcinol removal was studied by Atomic Force Microscopy operating in Non-Contact mode (AFM-NC). Analyses were performed in air at room temperature with a Park Systems Instrument, model XE-100. A silicon microcantilever with the reflective side coated with aluminum (force constant 20 N/m and resonance frequency of 265 kHz) and conical silicon tips (radius of curvature less than 10 nm, tip height 15–20  $\mu\text{m}$ , full tip cone angle less than 30°) were used. Scan rates were set between 0.5 and 1 Hz.

Field Emission Scanning Electron Microscopy (FESEM) images were obtained with a Zeiss Ultra Plus field emission SEM at 1.5–3.0 kV (range of acceleration voltage: 0.02–30 kW) equipped with an Inlens detector and a SE Everhart – Thornley Secondary Electron Detector. For FESEM analyses nanoporous membranes were prepared on silicon wafers. Areas close to fracture lines were observed in order to get information on the shape, size, distribution and alignment of the pores within the membrane thickness.

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