Designing block copolymer architectures for targeted membrane performance

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Rachel Mika Dorin [a,1], William A. Phillip [b,1], Hiroaki Sai [a], Jörg Werner [c], Menachem Elimelech [d], Ulrich Wiesner [a,*]

[a] Department of Materials Science and Engineering, 214 Bard Hall, Cornell University, Ithaca, NY 14850-1501, United States
[b] Department of Chemical and Biomolecular Engineering, 182 Fitzpatrick Hall, University of Notre Dame, Notre Dame, IN 46556-5637, United States
[c] Department of Chemistry and Chemical Biology, Cornell University, 131 Baker Laboratory, Ithaca, NY 14850-1501, United States
[d] Department of Chemical and Environmental Engineering, Yale University, P.O. Box 208286, New Haven, CT 06520-8286, United States

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ABSTRACT

Using a combination of block copolymer self-assembly and non-solvent induced phase separation, isoporous ultrafiltration membranes were fabricated from four poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) triblock terpolymers with similar block volume fractions but varying in total molar mass from 43 kg/mol to 115 kg/mol to systematically study the effect of polymer size on membrane structure. Small-angle X-ray scattering was used to probe terpolymer solution structure in the dope. All four triblocks displayed solution scattering patterns consistent with a body-centered cubic morphology. After membrane formation, structures were characterized using a combination of scanning electron microscopy and filtration performance tests. Membrane pore densities that ranged from 4.53×10^{14} to 1.48×10^{15} pores/m^2 were observed, which are the highest pore densities yet reported for membranes using self-assembly and non-solvent induced phase separation. Hydraulic permeabilities ranging from 24 to 850 L m^{-2} h^{-1} bar^{-1} and pore diameters ranging from 7 to 36 nm were determined from permeation and rejection experiments. Both the hydraulic permeability and pore size increased with increasing molar mass of the parent terpolymer. The combination of polymer characterization and membrane transport tests described here demonstrates the ability to rationally design macromolecular structures to target specific performance characteristics in block copolymer derived ultrafiltration membranes.

1. Introduction

Porous polymeric membranes are typically produced using a phase separation technique. This technique involves preparing a casting dope by dissolving a polymer in a solvent, casting the dope into the desired form, allowing solvent to evaporate for a prescribed period of time, and finally precipitating the polymer. Rapid changes in the vapor composition or temperature of the atmosphere surrounding the cast film as well as non-solvent baths are commonly used to precipitate the polymer. Numerous efforts have been made toward the important goal of elucidating the interrelationships between the molecular architecture of the polymer, the membrane structure, and the ultimate performance of membranes obtained

from standard phase inversion methods. For example, the effects of adjusting the casting solution composition [1–3], incorporating additives into the dope [4] or phase inversion medium [5], and altering the casting procedure by changing the casting temperature, evaporation time, and film thickness [6,7], have been explored. The effects of polymer molar mass [8] and casting solution viscosity [9] on pore size and pore size distribution have also been studied.

Experimental evidence suggests that, due to this significant effort, the performance of ultrafiltration membranes produced using phase separation methods is reaching an upper limit. At this upper limit, a tradeoff between membrane selectivity and permeability exists [10]. A similar tradeoff is frequently discussed in the literature on gas phase membrane separations, which is summarized in the "Robeson Plot" [11], as well as reverse osmosis membranes [12]. For ultrafiltration, this performance limit is attributed to the distribution in pore sizes that results from the phase separation methods [12]. For state-of-the-art commercial membranes,

* Corresponding author. Tel.: +1 607 255 3487.
  E-mail address: ubw1@cornell.edu (U. Wiesner).
[1] These authors contributed equally to this work.

the upper bound suggests a normalized pore size deviation of ~20% [10]. Therefore, narrowing the pore size distribution of ultrafiltration membranes is one clear way to produce membranes whose performance could exceed the current performance ceiling. Given the significant efforts dedicated to standard phase inversion methods, accomplishing this goal requires developing new polymer chemistries and processing methodologies.

Significant improvements in the performance potential for ultrafiltration membranes have recently been described through the use of self-assembling block copolymers, which can be applied toward a variety of separation needs, including water purification [13], drug delivery [14], and virus filtration [15,16]. One particularly attractive method for producing membranes with uniform pores and high pore densities, which utilizes a combination of self-assembly and non-solvent induced phase separation (SNIPS) [17], is both scalable and offers impressive separation and permeability profiles. The SNIPS method has been demonstrated with both diblock copolymers [18–23] and triblock terpolymers [24,25]. Of fundamental importance for advancing SNIPS membranes is an understanding of the relationships between polymer molecular architecture, membrane formation, microstructure, and performance.

The highly controllable architectures of the block copolymers used in the emerging class of SNIPS membranes provide a unique capacity for designing molecules to achieve targeted membrane structures and performance. Studies correlating membrane structure with polymer molar mass have been initiated in diblock systems [26], but such relationships in triblock terpolymer systems have not previously been elucidated. Herein, we describe the fabrication of several triblock terpolymer SNIPS membranes and investigate the relationship between macromolecular architecture and membrane pore size, pore density, permeability, and solute rejection. We establish clear molecular structure–membrane characteristic correlations that open a path to the molecular design of ultrafiltration membranes.

2. Experimental

2.1. Polymer synthesis and characterization

Poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) (ISV) triblock terpolymers were synthesized *via* sequential anionic polymerization as previously reported [24]. The molar mass of three polymers, ISV43, ISV77, and ISV115, was determined using a combination of ^{1}H solution nuclear magnetic resonance (^{1}H NMR) and gel permeation chromatography (GPC) in tetrahydrofuran (THF) as a solvent on a Waters 510 GPC instrument equipped with a Waters 2410 differential refractive index detector. Volume fractions of each block were calculated using ^{1}H NMR spectra obtained on a Varian INOVA 400 MHz spectrometer using $CDCl_3$ ($\delta = 7.27$ ppm) signal as an internal standard. The ^{1}H NMR was also used to determine the molar mass and volume fractions of ISV91 using the signal for the *sec*-butyl lithium initiator as a reference. The ^{1}H NMR method of determining molar mass was found to be within 5% of GPC methods. Bulk films of ISV were prepared by dissolving the polymer in chloroform at <5 wt% and pouring the solution into a Teflon dish. The dish was covered with a glass dome to slow solvent evaporation, and the chloroform was evaporated overnight. Small-angle X-ray scattering (SAXS) on bulk samples was performed at the G1 station of the Cornell High Energy Synchrotron Source (CHESS) with a 250 cm flight path and an X-ray energy ranging from 8 to 10.6 keV. Two-dimensional patterns obtained on a phosphor-optical fiber coupled CCD were azimuthally integrated to generate the 1D SAXS patterns in the MATLAB software suite [27]. The scattering vector, q, is defined as $q = (4\pi sin\,\theta)/\lambda$, where θ is half of the total scattering angle. Bulk samples were sectioned at 50–70 nm using a Leica Ultracut UC7 cryo-ultramicrotome at −60 °C. Microtomed samples were selectively stained with either OsO_4 (g) for 30 min or with I_2 (g) for 2 h. Bright field transmission electron microscopy (BF-TEM) images were obtained using a FEI Tecnai F12 Spirit electron microscope equipped with a SIS Megaview III CCD camera, operated at an acceleration voltage of 120 kV.

2.2. Solution preparation and characterization

Solutions of ISV for SAXS and for membrane fabrication were prepared by first mixing 1,4-dioxane (DOX) and THF and subsequently dissolving the polymer in the solvent mixture overnight. Solutions for SAXS were centrifuged into 0.9–1.0 mm glass capillaries (Charles-Supper Co.) and flame sealed. SAXS data were taken at the CHESS beamline.

2.3. Membrane preparation and characterization

Membranes were hand-cast using a doctor blade (Testing Machines, Inc., K Control Coater) with a gate height of 200 μm, evaporated for a specified time (see Section 3.3), and plunged into deionized (DI) water. Membranes were dipped in ethanol, dried under ambient conditions, and coated with gold-palladium prior to SEM imaging, which was performed on either a Hitachi Ultra-High Resolution Analytical Field Emission Scanning Electron Microscope (FE-SEM) SU-70 or a Zeiss Leo 1550 FE-SEM. Membrane hydraulic permeability and solute rejection experiments were conducted in a stirred cell (Amicon 8010, Millipore Co.) pressurized with N_2 (g). Solute rejection tests were performed using single solute polyethylene oxide (PEO) solutions at a concentration of 1 g/L in DI water. PEO concentration in the feed and permeate were determined using a Shimadzu total organic carbon analyzer or a TA Instruments thermogravimetric analyzer Q500. Permeate water flux and PEO rejection measurements were run at applied pressure drops ranging from 20.7 to 137.9 kPa (3–20 psig) to maintain similar hydrodynamic conditions between samples. SEM micrographs were analyzed using ImageJ software to estimate the average pore diameter of membranes derived from each sample of ISV terpolymer [28].

3. Results and discussion

3.1. Triblock terpolymer characterization

Four ISV triblock terpolymers with total molar masses of 43, 77, 91, and 115 kg/mol, abbreviated as ISV43, ISV77, ISV91, and ISV115, respectively, were synthesized using sequential anionic polymerization. From results of earlier studies, volume fractions of 0.30, 0.55, and 0.15 were targeted for the polyisoprene (PI), polystyrene (PS), and poly-4-vinylpyridine (P4VP) blocks, respectively [24]. Experimentally determined volume fractions, f, molar masses, M_n, and dispersities (Đ) for each triblock terpolymer are summarized in Table 1, demonstrating that all four ISVs were similar in composition.

Table 1
Volume fractions (f), molar masses (M_n), and dispersities (Đ) of each block of the four ISV triblock terpolymers used in this study.

	f_{PI}	f_{PS}	f_{P4VP}	M_n (kg/mol)	
ISV43	0.27	0.55	0.18	43	1.02
ISV77	0.29	0.57	0.14	77	1.16
ISV91	0.32	0.55	0.13	91	1.20
ISV115	0.29	0.58	0.13	115	1.12