

# Phase Inversion Membranes with an Organized Surface Structure from Mixtures of Polysulfone and Polysulfone–Poly(ethylene oxide) Block Copolymers

LAWRENCE F. HANCOCK

Circe Biomedical, Inc., One Ledgemont Center, 128 Spring Street, Lexington, Massachusetts 02173

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**ABSTRACT:** Phase inversion precipitation of a polysulfone and polysulfone–poly(ethylene oxide) block copolymer solution yields a membrane with an organized surface structure. The poly(ethylene oxide) block of the polysulfone–poly(ethylene oxide) block copolymer segregates to the surface of the membrane. Measurement of the  $^1\text{H}$   $T_{1\rho}$  of the component materials, X-ray photoelectron spectroscopy, and differential scanning calorimetry reveal the organized surface structure of the membrane. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1353–1358, 1997

**Key words:** membrane; poly(ethylene oxide)-*block*-polysulfone; hydrophilic

## INTRODUCTION

The surface composition of phase inversion membranes is critical to their performance and utility.<sup>1</sup> It affects performance through its contribution to the characteristic retention and solution flux of a membrane. It affects utility through its influence on the amount and nature of solute species, which adsorb to the membrane in process applications and compromise its performance.

In order to alter the surface composition of a membrane, one may choose a new material. This, however, is often problematic as it is necessary to compromise between competing material attributes. For instance, the hydrophilicity of poly(ethylene oxide) (PEO) and its ability to inhibit protein adsorption are certainly qualities of interest for typical membrane applications. However, PEO's limited mechanical strength, low melting point, and water solubility make it a poor candidate for membrane fabrication.

Alternatively, one may modify the surface composition of membrane through post treatment. Post treatments that have been used include coat-

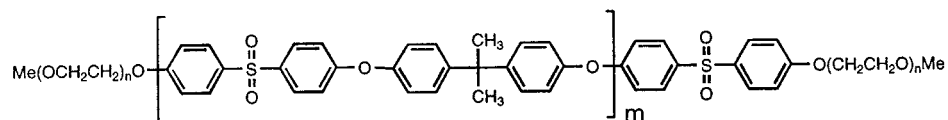
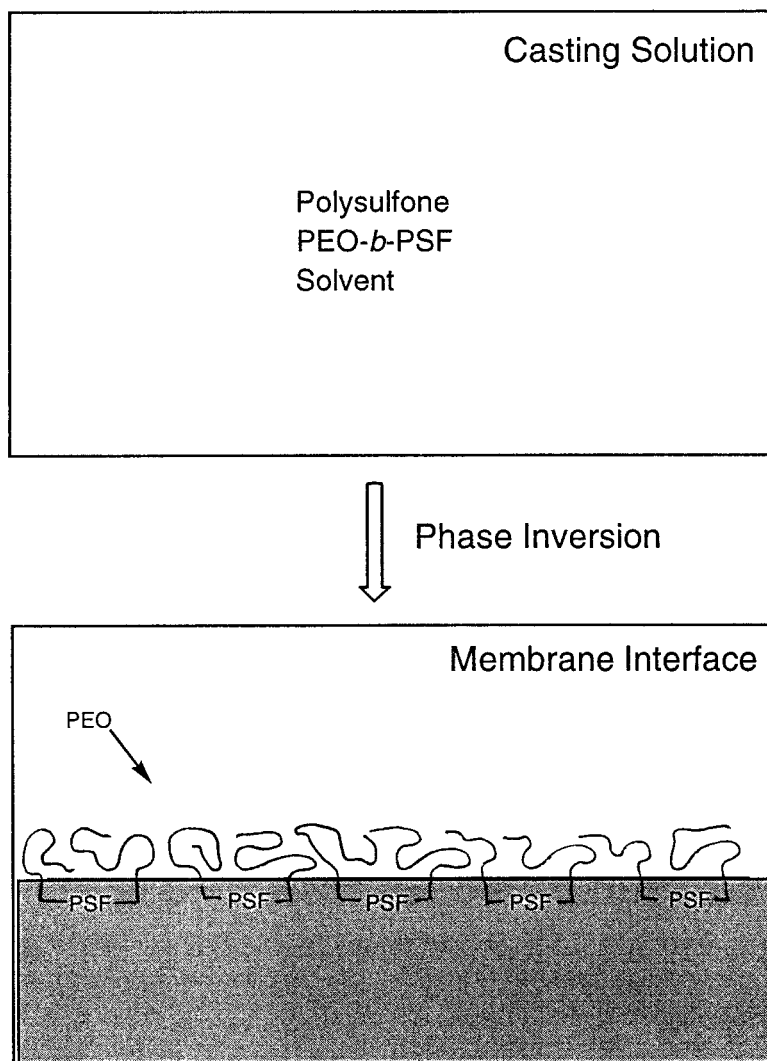
ings<sup>2–5</sup> and surfactant adsorption,<sup>6–8</sup> as well as reactive processing such as plasma oxidation,<sup>9</sup> plasma polymerization,<sup>9</sup> photo reactive grafting,<sup>10–11</sup> or radiation-induced grafting.<sup>9,12–14</sup> For coatings and surfactant adsorption, the question always exists as to the stability of the adsorbed layer once it is challenged by various solutes and solvents. Reactive post treatments leave open questions regarding uniformity of the surface modification at both the external membrane surface and the internal pore surface.

This work reports on the surface modification of polysulfone membranes by the incorporation PEO-*b*-PSF in the membrane formulation. The block copolymer architecture of PEO-*b*-PSF makes it amphiphilic in character. On phase inversion precipitation, the PEO block of PEO-*b*-PSF segregates to the surface of the membrane, forming an organized surface structure. Scheme 1 depicts the chemical structure of PEO-*b*-PSF and the organized surface structure formed at the membrane interface.

## EXPERIMENTAL

### Membrane Fabrication

The preparation of PEO-*b*-PSF is described elsewhere.<sup>15</sup> Polysulfone (Amoco, Udel 3500) and *N*-

PEO-*b*-PSF

**Scheme 1** Chemical structure of PEO-*b*-PSF.

methyl pyrrolidinone (Spectrum, OmniSolv) were used as received.

Concentrated polymer casting solutions were prepared by weighing the appropriate constituents in a glass jar, sealing the jar, and then placing the jar on a roll mill or laboratory rocker until

a homogeneous solution was obtained. Membranes were prepared by pouring the casting solution onto a glass plate and then evenly coating the plate by drawing a retractable doctor blade across it (coating thickness was 0.008–0.015 in.). The plate was then immersed quickly and

smoothly into the coagulation bath. After a period of time in the primary coagulation bath, the membrane was removed and placed in a water bath for exhaustive extraction of water (6–24 h).

### $^{13}\text{C} \times ^1\text{H}$ -NMR

Solid-state NMR experiments were performed on a Chemagnetics 200 MHz spectrometer. A fixed spinning speed of 3600 Hz was used for all experiments. The rotating frame, spin-lattice relaxation time constant,  $T_{1\rho}$ , was measured by varying the proton–carbon cross polarization contact time from 0.8 to 20 ms and subsequent calculations.

### X-ray Photoelectron Spectroscopy

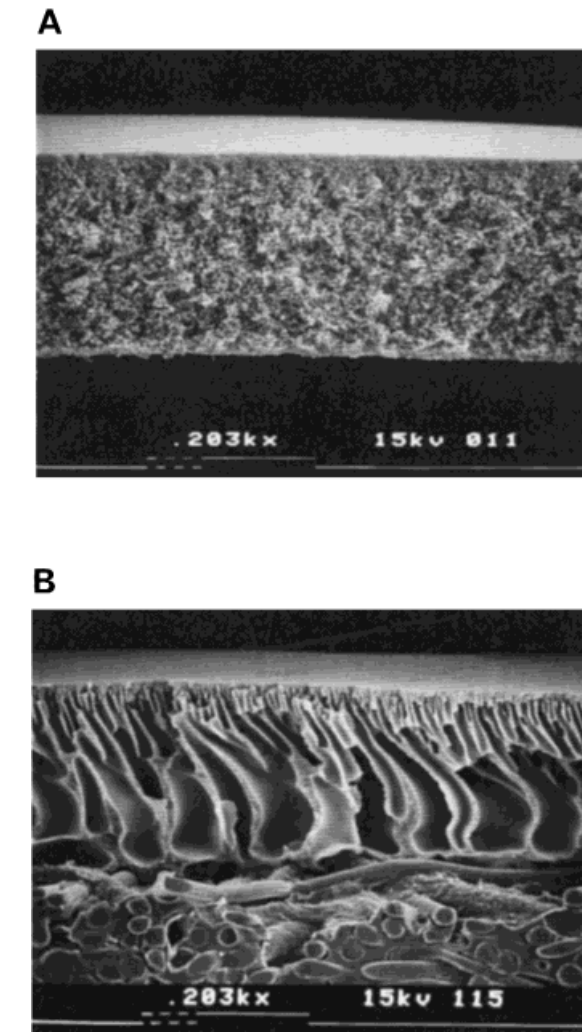
X-ray photoelectron spectra were obtained with a Physical Electronics Inc. PHI5600 spectrometer using a monochromated Al  $K\alpha$  (1486.6 eV) X-ray source (operated at 250 W) at a take-off angle of  $45^\circ$ . Membranes were covered with a metal mask to reduce charging during the analysis. Charge neutralization was achieved with an electron flood gun. The analysis area was  $800 \mu\text{m}$  in diameter. Quantitative analysis was performed by evaluating peak areas using atomic sensitivity factors provided by Physical Electronics Inc.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7. Thermograms were recorded at a heating rate of  $20^\circ\text{C}/\text{min}$ . Following an initial heating scan of each membrane, samples were cooled at a rate of  $10^\circ\text{C}/\text{min}$ , after which a second heating thermogram was recorded at a rate of  $20^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

Immersion of an *N*-methyl pyrrolidinone solution of polysulfone and PEO-*b*-PSF in water yields a porous membrane. Figure 1 displays representative electron micrographs of membranes 1 and 3. Table IA compiles the physical characterization of the materials used for membrane fabrication. Table IB summarizes the composition of the casting solutions used in this study. As is commonly observed in phase inversion membrane formation, it is possible to form membranes with specific macrostructures and porosities by controlling the precipitation process. The composition of the casting solution and the coagulant are often used to



**Figure 1** Electron micrographs representative of membranes 1 and 3. (A) shows a cross section of Membrane 1. Membrane 1 is  $175 \mu\text{m}$  thick and has a spongy homogeneous structure characteristic of microporous membranes. (B) shows a cross section of membrane 3. Membrane 3 is  $175 \mu\text{m}$  thick and has an anisotropic structure characteristic of ultrafiltration membranes.

control the precipitation process. Membrane 1 employs a water/solvent mixture in the coagulating bath; water is the coagulant and its dilution with solvent serves to slow the phase inversion kinetics. Membrane 1 is microporous membrane with surface pores ranging from  $0.1\text{--}0.5 \mu\text{m}$  (not shown) and a spongy homogeneous cross section. When water alone is used as the coagulant (membrane 3), phase inversion is rapid producing a relatively dense surface skin. The skin forms quickly and limits the transport of coagulant to the underlying casting solution. Consequently, the underlying casting solution precipitates more slowly, producing a porous support structure with

**Table IA Material Characteristics of Casting Solution Constituents**

Material Characterization	Wt % PEO <sup>a</sup>	$M_n$ ( $\times 10^{-3}$ ) <sup>b</sup>	$M_w$ ( $\times 10^{-3}$ )	$M_w/M_n$
Polysulfone (Udel 3500)	0	40.3	67.4	1.7
PEO- <i>b</i> -PSF-A	29	18.9	47.5	2.5
PEO- <i>b</i> -PSF-B	26.9	34.6	47.4	1.4
PEO- <i>b</i> -PSF-C	27.7	—	—	—

<sup>a</sup> % PEO determined from <sup>1</sup>H-NMR (Bruker 300 MHz).

<sup>b</sup>  $M_n$  and  $M_w$  determined by gas permeation chromatography using a Hewlett Packard 1090 system equipped with 3 Phenomenex columns and eluted at 1.0 mL min with THF at 40°C.  $M_n$  and  $M_w$  are based on PMMA narrow molecular weight standards.

large finger-like macrovoids. Membrane 3 possesses the signature structure of an anisotropic membrane.

Nuclear magnetic resonance (NMR) characterization of the microporous sample, membrane 1, demonstrates that the PEO and PSF segregate into two distinct domains in the membrane and that the PEO domain is wholly accessible to a solution contacting the membrane. Table II presents the <sup>1</sup>H  $T_{1\rho}$ 's measured for samples of the respective homopolymers as well as membrane 1. Two conclusions are evident from the data. First, the polysulfone and the poly(ethylene oxide) of the membrane exist in two distinct domains. This is evident from the two unique  $T_{1\rho}$ 's obtained for each polymer constituent. Had the two segments coexisted as a single homogeneous mixture, a single  $T_{1\rho}$  would be observed due to rapid spin diffusion within the mixed phase. The second conclu-

sion arises from the decrease in  $T_{1\rho}$  observed for the PEO <sup>1</sup>H's when the membrane is exposed to a D<sub>2</sub>O solution of Cr(acac)<sub>3</sub>, a paramagnetic relaxation agent. This demonstrates that the PEO segments of the block copolymer are located at the active surface of the membrane; i.e., they are accessible to the D<sub>2</sub>O Cr(acac)<sub>3</sub> solution. Wetting the membrane with D<sub>2</sub>O alone demonstrates that changes in the relaxation time were the result of the paramagnetic agent and not simply to a restructuring of the membrane in response to exposure to D<sub>2</sub>O.

Results from X-ray photoelectron spectroscopic (XPS) analysis provide further evidence, indicating an organized surface structure with PEO segregated to the membrane surface. Table III presents results comparing membranes 2, 3, and 4. There are two sets of data for each example membrane. The first set reports results for the membranes dried to ambient conditions immediately following exhaustive extraction with water. The second set reports results for membranes that were heated in water at 120°C for 30 min in an autoclave and then dried to ambient conditions. The atomic ratio, O/S, provides a measure of the PEO-PSF surface composition. It is evident from both sets of data that as the proportion of PEO-*b*-PSF is increased in the formulation, the surface concentration of oxygen increases, and the con-

**Table IB Membrane Casting Solution Composition**

Membrane Formulations	Casting Solution	Coagulant
Membrane 1	5% Polysulfone 15% PEO- <i>b</i> -PSF-A 80% NMP	70% NMP 30% H <sub>2</sub> O
Membrane 2	5% Polysulfone 15% PEO- <i>b</i> -PSF-B 80% NMP	50°C H <sub>2</sub> O
Membrane 3	10% Polysulfone 10% PEO- <i>b</i> -PSF-B 80% NMP	50°C H <sub>2</sub> O
Membrane 4	20% Polysulfone	50°C H <sub>2</sub> O
Membrane 5	10% Polysulfone 10% PEO- <i>b</i> -PSF-C 80% NMP	25°C H <sub>2</sub> O
Membrane 6	5% Polysulfone 15% PEO- <i>b</i> -PSF-C 80% NMP	25°C H <sub>2</sub> O

**Table II  $T_{1\rho}^H$  Relaxation Times Observed Via Solid-State <sup>13</sup>C  $\times$  <sup>1</sup>H-NMR**

Sample	$T_{1\rho}^H$ (PSF) (ms)	$T_{1\rho}^H$ (PEO) (ms)
PEO (5 kDa)	—	< 1
PSF	5.2	—
Membrane 1	5.5	7.9
post-D <sub>2</sub> O exposure	5.0	7.6
post-Cr(acac) <sub>3</sub>	5.1	4.9

**Table III XPS Analysis of PSF/PEO-*b*-PSF Membranes**

Sample	As Formed				Treated (H <sub>2</sub> O 120°C, 30 min)			
	%C	%O	%S	O/S	%C	%O	%S	O/S
Membrane 2 75% PEO- <i>b</i> -PSF-B 25% PSF	79.5	17.7	2.7	6.6	78.2	19.5	2.3	8.5
Membrane 3 50% PEO- <i>b</i> -PSF-B 50% PSF	81.5	15.6	2.9	5.4	78.7	18.8	2.5	7.5
Membrane 4 100% PSF	81.5	15.4	3.1	5.0	80.5	16.7	2.8	6.0

centration of sulfur decreases. Annealing the membrane in a hot water bath improves the PEO surface enrichment.

DSC provides further insight into the phase structure of PEO-*b*-PSF-PSF membranes. It is apparent that the aqueous annealing imposes a phase organization on the membrane with PEO forming an organized surface at the membrane interface. When prepared with a 5000 Da monomethyl poly(ethylene glycol), PEO-*b*-PSF is homogenous at compositions from 15 to 30%. This is based on the observation of a single, broad  $T_g$  intermediate of that observed for polysulfone.<sup>15</sup> Table IV summarizes the DSC results obtained for PSF, PEO-*b*-PSF-C, and membranes 5 and 6. It also compares the measured glass transitions with that which would be expected for a homogeneous PEO-PSF mixture. Polysulfone behaves as expected with a single glass transition observed at 187°C. A single, broad transition is observed for PEO-*b*-PSF-C at ~ 50°C. On the first DSC scan of membranes 5 or 6, a single glass transition is observed near that of polysulfone. On the second scan, again, a single glass transition is observed; however, it is shifted to a lower temperature, which corresponds to the predicted  $T_g$  for a

PEO-PSF mixture. The shift in the glass transition to a lower temperature results from the dissolution of the PEO component into the PSF to form a homogeneous mixture. The high  $T_g$  present in the initial scan of membrane indicates that a relatively pure PSF phase is present in the membrane samples.

## CONCLUSION

PEO-*b*-PSF organizes at the surface of phase inversion membranes when incorporated into conventional polysulfone membrane formulations. Solid-state NMR demonstrates that the PEO component forms a unique phase in the membrane which is accessible to an aqueous solution in contact with the membrane. XPS independently demonstrates an enrichment of PEO at the surface of the membrane. DSC provides evidence of a polysulfone phase in membranes which reverts to a homogeneous poly(ethylene oxide)-polysulfone mixture after it is melted. In total, the results demonstrate that it is possible to control the surface chemistry of microporous and ultrafiltration

**Table IV Summary of DSC Results Obtained for Membranes 5 and 6**

Sample	PEO <sup>a</sup> (wt %)	$T_g$ (Predicted) <sup>b</sup> (°C)	$T_g$ (Scan 1) (°C)	$T_g$ (Scan 2) (°C)
Polysulfone	0	185	187	—
PEO- <i>b</i> -PSF-C	27.7	70	~ 50	—
Membrane 5	7.7	146	186	142
Membrane 6	9.6	137	175	133

<sup>a</sup> Wt % PEO was determined by <sup>1</sup>H-NMR of a CDCl<sub>3</sub> membrane solution.

<sup>b</sup> Predicted  $T_g$ s were calculated from the Fox equation;  $T_g = 1/\sum w_i/T_{g_i}$  using 185°C for the  $T_g$  of PSF and -66°C for the  $T_g$  of PEO.

membranes through the incorporation of block copolymers directly in the membrane formulation.

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