Membranes with Oriented Polyelectrolyte Nanodomains

Hong Chen, Giuseppe R. Palmese, and Yossef A. Elabd*

Department of Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania 19104

Received June 19, 2006. Revised Manuscript Received July 28, 2006

Polymer−polymer nanocomposite membranes with polyelectrolyte nanodomains oriented normal to the plane of the membrane were prepared using track-etched membranes as a host matrix. The oriented nanodomains of polyelectrolyte were synthesized in tubular and fibril forms by a plasma-induced surface graft polymerization, where nanodomains with aspect ratios as high as 240 were obtained. The morphology of nanodomains was confirmed by scanning electron microscopy, attenuated total reflection Fourier transform infrared spectroscopy, and energy dispersive spectroscopy. The specific conductivity of the polyelectrolyte nanodomains increased with decreasing domain size with the highest value 6 times higher than that of the isotropic bulk polyelectrolyte gel membrane. Mechanical strength of the nanocomposite was similar to the matrix in both the dry and the hydrated state, unlike the bulk polyelectrolyte gel membrane. The membranes synthesized in this study with oriented polyelectrolyte nanodomains demonstrate the ability to enhance transport in the desired direction for applications such as fuel cells.

Introduction

The transport and selectivity of polyelectrolyte membranes are critical for the efficacy of a variety of processes, including fuel cells,[1] batteries,[2] actuators and sensors,[3] water purification,[4,5] pervaporation,[6] selective barriers, and stimuli-responsive materials.[7,8] Recently, enhanced transport properties have been observed in polyelectrolyte membranes with organized and oriented nanodomains. Ding et al.[9] observed increased proton conductivity when comparing a graft copolymer (polystyrene grafted with polystyrene sulfonic acid side chains) to a random copolymer (polystyrene copolymerized with polystyrene sulfonic acid), which was attributed to a more organized ionic nanostructure observed by transmission electron microscopy. Cable et al.[10] stretched Nafion to induce orientation of the ionic nanostructure and observed a 40% increase in proton conductivity when comparing measurements in and normal to the plane of the membrane (anisotropic conductivity). Maki-Ontto et al.[11] also reported anisotropic conductivity (an order of magnitude difference) in proton conductive block copolymers that were sheared to induce an oriented lamellar nanostructure. Anisotropic conductivity was also observed in proton conducting triblock copolymers of sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) by Elabd and co-workers.[12,13] A lamellar morphology with a preferred orientation in the plane of the membrane was confirmed by small-angle X-ray scattering, and the proton conductivity measured in plane was over an order of magnitude higher than when measured normal to the plane.

However, the orientation of ionic domains, which usually occurs in the plane of the membrane, is not desired for many applications. Several investigators[14−16] have successfully oriented cylindrical nanodomains in diblock copolymers normal to the plane of the film with the use of mechanical sheer, electric field, magnetic field, and other surface treatments. The diameter of these domains is ∼10 nm, but the orientation or length of the nanodomains thus far has been limited to ∼10 nm (i.e., small aspect ratios). To induce orientation of nanodomains normal to the plane of the membrane over a larger length scale (∼1 μm) is difficult.

Track-etched polymer membranes, which have straight cylindrical pores that are oriented normal to the plane of the membrane, provide a promising platform to design membranes with nanodomains with high aspect ratios oriented in the desired direction. Presently, track-etched membranes are commercially available in polyester and polycarbonate with various thicknesses (6 μm or above), pore sizes (10 nm to micrometers), and porosities (∼0.05% to ∼20%). Filling the pores of a track-etched membrane with a polyelectrolyte results in a new class of polymer composite membrane,

---

* To whom correspondence should be addressed. Phone: 215-895-0986. Fax: 215-895-5837. E-mail: elabd@drexel.edu.

(1) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.
(2) Kerr, J. B. *Lithium Batteries* **2004**, 574.
(3) Kim, K. J.; Shahinpoor, M. *Handb. Polyelectrolytes Their Appl.* **2002**, *3*, 1.
(4) Smith, B. F.; Robison, T. W.; Sauer, N. N. *Environ. Separat. Heavy Met.* **2002**, 141.
(5) Bolto, B. A.; Dixon, D. R.; Gray, S. R. *Environ. Sci. Res.* **1996**, *51*, 99.
(6) Tieke, B. *Handb. Polyelectrolytes Their Appl.* **2002**, *3*, 115.
(7) Hoffman, A. S. *Adv. Drug Delivery Rev.* **2002**, *54*, 3.
(8) Galaev, I. Y.; Mattiasson, B. *Trends Biotechnol.* **1999**, *17*, 335.
(9) Ding, J. F.; Chuy, C.; Holdcroft, S. *Macromolecules* **2002**, *35*, 1348.
(10) Cable, K. M.; Mauritz, K. A.; Moore, R. B. *Chem. Mater.* **1995**, *7*, 1601.
(11) Mäki-Ontto, R.; de Moel, K.; Polushkin, E.; van Ekenstein, G. A.; ten Brinke, G.; Ikkala, O. *Adv. Mater.* **2002**, *14*, 357.
(12) Elabd, Y. A.; Napadensky, E.; Walker, C. W.; Winey, K. I. *Macromolecules* **2006**, *39*, 399.
(13) Elabd, Y. A.; Beyer, F. L.; Walker, C.W. *J. Membr. Sci.* **2004**, *231*, 181.
(14) Zhu, Z. Q.; Kim, D. H.; Wu, X. D.; Boosahda, L.; Stone, D.; LaRose, L.; Russell, T. P. *Adv. Mater.* **2002**, *14*, 1373.
(15) Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M.T.; Russell, T. P. *Science* **2000**, *290*, 2126.
(16) Xu, C.; Fu, X. F.; Fryd, M.; Xu, S.; Wayland, B. B.; Winey, K. I.; Composto, R. J. *Nano Lett.* **2006**, *6*, 282.

10.1021/cm061422w CCC: $33.50 © 2006 American Chemical Society
Published on Web 08/29/2006

where the filler can enhance or regulate transport in the desired direction and the track-etched membrane can provide mechanical stability and durability. Compared to dense membranes, these composite membranes can be tailored by the type of filler, pore size, and porosity of the membrane to provide tunable transport properties.

Several investigators have examined transport properties of track-etched membranes filled with polyelectrolytes. Fang and Leddy[17] examined the flux of cations in track-etched polycarbonate filled with Nafion using steady-state rotation disk voltammetry. In their study, as the diameter of the nanopores decreased, cation flux increased, as much as 20-fold over the flux through solution-cast Nafion films. Recently, Vorrey and Teeters[18] studied the effects of track-etched polycarbonate filled with poly(ethylene oxide) (PEO) on electrical conductivity. Conductivity increased by 2 orders of magnitude from 400 to 30 nm pore size, where transport in the 400 nm pore size composite was similar to that of pure PEO. Enhanced transport was attributed to the increased interfacial zone between the filler and track-etched pore[17] and the orientation of polyelectrolyte chains confined in the track-etched pore.[18] Results from these two studies[17,18] are intriguing and prompt further investigation into polyelectrolytes confined within nanopores.

In both works,[17,18] the polyelectrolytes were physically sorbed within the membrane and no visiual or chemical evidence of pore filling was provided. The work in this study differs from previous work in that the polyelectrolyte is chemically grafted (covalently bound) within the track-etched membrane and both visual and chemical confirmation is provided. In this work, membranes with oriented (normal to the plane) domains (10−2000 nm) of polyelectrolyte, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), were prepared. Commercial polycarbonate track-etched (PCTE) membranes were used as the host matrix and PAMPS was filled into the pores via plasma-induced surface graft polymerization. The graft bonds provide robust linkages between the polyelectrolyte domains and polycarbonate matrix, increasing the durability of the composite and eliminating potential leaching of the polyelectrolyte under hydrated conditions. Tubular and fibril PAMPS domains were synthesized by controlling the reaction conditions and were confirmed by electron microscopy, energy dispersive spectroscopy (EDS), and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The proton conductivity of the composite membranes was investigated at various nanodomain sizes and morphologies. The impact of the PAMPS content and hydration on mechanical stability was also examined.

Experimental Section

Materials. PCTE membranes were purchased from GE-Osmonics and were used without further treatment. Track-etched membranes are prepared by bombarding a polymer membrane with heavy energetic ions followed by chemically etching tracks into pores.[19] Several properties of the membranes used in this study are listed in Table 1, where porosity is defined as the void volume fraction. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS; 99%; Aldrich) and *N*,*N*′-methylenebisacrylamide (BisA; ≥98%; Aldrich) were used as received. Ultrapure deionized, reverse osmosis water (resistivity ∼ 16 MΩ cm) was used.

Table 1. Properties of PCTE Membranes

sample	thickness (μm)	pore size (nm)	porosity (%)
PCTE10	6	10	0.05
PCTE50	6	50	1.18
PCTE100	6	100	3.14
PCTE400	10	400	12.56
PCTE800	9	800	15.07
PCTE2000	10	2000	6.28

Plasma Treatment. The PCTE membranes were irradiated in a dielectric barrier discharge plasma configuration, consisting of two electrodes (19 × 19 cm^2) separated by 0.4 cm, at ambient conditions. Details of this plasma apparatus are described elsewhere.[20,21] The membranes were placed on the grounded lower electrode. Oxygen was introduced into the chamber at a flow rate of 1 L/min for 10 min. The samples were then exposed to plasma for 120 s at 1 W/cm^2. After the plasma treatment, the chamber was purged with oxygen for 2 min. The membranes were then removed for the graft reaction.

Graft Polymerization. The graft polymerization of AMPS onto plasma-treated track-etched membranes was performed in a round-bottom flask under a nitrogen atmosphere. Care was taken to keep the transfer time of the treated membranes from the plasma chamber to the grafting reaction flask less than 5 min. A calculated amount of AMPS was dissolved in deionized water in the flask to make 20 wt % monomer solution at a total weight of 20 g. The monomer solution was bubbled with nitrogen for 20 min before the addition of the PCTE membranes. Graft polymerization was initiated by elevating the temperature of the reaction mixture to 50 °C. After 4 h, PCTE membranes were removed from the reaction system and then thoroughly washed with deionized water. Graft polymerization with 2 wt % (of monomer) BisA cross-linker was conducted using the same procedure. The membranes were immersed in deionized water for 2 days after the reaction, and the excess gel surrounding the membranes was gently removed with tweezers.

Characterization of Grafting. The grafting yield (G%; wt %) was calculated by $(W_g - W_o)/W_o \times 100$, where W_o and W_g are the dry weight of original and grafted membrane, respectively. For ATR-FTIR spectroscopy, the FTIR spectrometer (Nicolet 6700 Series) was equipped with a single-reflection diamond ATR attachment (Specac, Inc., MKII Golden Gate) and was used to characterize the surface grafting. The diamond ATR has a ∼0.5 mm^2 sampling area, where a consistent reproducible pressure is applied to every sample. Infrared spectra were collected at 4 cm^{-1} resolution and 32 scans. The morphology of the PCTE membranes, before and after grafting, was observed with scanning electron microscopy (SEM; model FEI/Phillips XL30) at 10 kV. The membranes were fractured in liquid nitrogen for cross-section images. All samples were sputter coated (Denton Desk II Sputtering System) with platinum at 40 mA for 30 s before observation. EDS and sulfur Kα maps were also collected on the cross-section of the grafted membranes using SEM coupled with an EDS microanalysis system. Membranes were uncoated in these experiments.

Proton Conductivity. Proton conductivity was measured using electrochemical impedance spectroscopy at frequencies between

---

(17) Fang, Y.; Leddy, J. *J. Phys. Chem.* **1995**, *99*, 6064.
(18) Vorrey, S.; Teeters, D. *Electrochim. Acta* **2003**, *48*, 2137.
(19) Fischer, B. E.; Spohr, R. *Rev. Mod. Phys.* **1983**, *55*, 907.
(20) Fridman, G.; Peddinghaus, M.; Ayan, H.; Fridman, A.; Balasubramanium, M.; Gutsol, A.; Brooks, A.; Friedman, G. *Plasma Chem. Plasma Process.* **2006**, submitted.
(21) Robinette, E. J.; Toughening Vinyl Ester Matrix Composites. Ph.D. Dissertation, Drexel University, Philadelphia, PA, 2005.

Table 2. Grafting Yields of Composite Membranes with Cylindrical PAMPS Nanodomains

	with tubular PAMPS domains			with fibril PAMPS domains[a]		
sample	G% (wt %)	wet thickness (μm)	thickness change (%)	G% (wt %)	wet thickness (μm)	thickness change (%)
PCTE10	2.5	6	0	2.1	19	217
PCTE50	3.5	7	16	11.8	27	350
PCTE100	10.2	11	83	18.5	30	400
PCTE400	15.4	18	80	22.5	46	360
PCTE800	4.9	13	45	30.1	44	389
PCTE2000	∼0	11	10	10.0	33	230

[a] Containing 2 wt % BisA cross-linker.

Table 3. Proton Conductivity of Composite Membranes with Cylindrical PAMPS Nanodomains

		with tubular PAMPS domains		with fibril PAMPS domains[a]	
sample	resistance (Ω)	effective conductivity (S/cm; $\times 10^{-3}$)	specific conductivity (S/cm; $\times 10^{-3}$)	effective conductivity (S/cm; $\times 10^{-3}$)	specific conductivity (S/cm; $\times 10^{-3}$)
PCTE10	234.8	0.09	127.9	0.04	22.4
PCTE50	40.1	0.85	50.4	2.12	43.5
PCTE100	7.2	1.68	29.1	1.64	29.8
PCTE400	14.0	5.08	15.1	8.21	13.3
PCTE800	116.5	1.89	5.5	3.47	3.7
PCTE2000	285.0	0.47	4.1	0.96	2.9

[a] Containing 2 wt % BisA cross-linker.

100 Hz and 1 MHz on a Solartron AC Impedance system (1260 impedance analyzer, 1287 electrochemical interface, Zplot software). Measurements were taken at room temperature (∼23 °C) and normal to the plane of the membrane with a two-electrode cell comprised of 1.22 cm^2 stainless steel blocking electrodes. All membranes were prehydrated in deionized water for at least 24 h and then quickly enclosed in a sealable cell to maintain hydration during impedance measurements. The real impedance was determined from the x intercept of the regression of the imaginary versus real impedance data over a high-frequency range (10 kHz to 1 MHz).[12,13]

Tensile Tests. Tensile tests of original PCTE and composite membranes were conducted on Instron 4200/4300/4400 at ambient conditions (∼23 °C and ∼50% relative humidity) with 2.54 mm/min crosshead speed. Samples were cut into 30 × 5 mm rectangular pieces, and a 10 mm gauge length was used. Tensile tests on hydrated (wet) samples were conducted by immersing the membrane strips in deionized water for 24 h and then removing and mounting quickly for tests. The sample transfer time was ∼1 min. Three to five pieces of each sample were tested, and the values reported are the average of those repeated experiments (Table 3).

Results and Discussion

Synthesis. Oxygen plasma treatment functionalizes the polymer surface with oxygen-containing groups, such as hydroxyl, carbonyl, and hydroperoxide groups.[22,23] The hydroperoxide groups are thermally labile in nature and upon heating initiate graft polymerization of AMPS, which introduces graft layers onto the surface (as shown in Figure 1). In addition, the oxygen-containing groups introduce hydrophilicity to the hydrophobic PCTE membrane. This facilitates the filling of pores with an aqueous reaction solution. It has been reported that the concentration of functional groups increases with exposure time to oxygen plasma.[24] However, over-exposure to plasma causes degradation to the polymer, demonstrated by reduced mass or dimension of the material. The grafting results and micrographs reveal that 120 s oxygen plasma exposure used in this work introduces a sufficient amount of functional groups for surface grafting, while having no obvious impact on the mass or dimension of the original track-etched membrane.

Our previous work[25] on surface grafting of polyester track-etched membranes shows that the grafting yield from oxygen−plasma initiation was tunable by the polymerization conditions. Higher grafting yields (up to 10 wt %) were obtained at higher AMPS concentrations (∼40 wt %) and longer polymerization times (∼4 h). Adding a small amount of bifunctional cross-linker (BisA, 2 wt % of monomer) enhanced the grafting yield significantly from below 10 wt % to above 20 wt %. The enhanced grafting by cross-linker could be explained by a proposed model for graft polymerization in the presence of both mono- (AMPS) and bifunctional (BisA) monomers (Figure 2). The pendent double bond of the cross-linker has three possibilities for reaction: (I) cross-linking with an adjacent growing grafted chain, forming loops on membrane surfaces, (II) cyclization, and (III) reaction with a macromolecular radical in the bulk. The grafting yield remains unchanged with routes I and II. Route III increases the amount of growing polymer chains connected to the matrix and consequently increases the grafting yield. A higher concentration of bifunctional cross-linker will, therefore, result in an increased amount of pendent double bonds available for initiation. The grafting yield will further increase if these double bonds react according to route III.

In this work, PCTE membranes with pore sizes ranging from 10 to 2000 nm and porosities between 0.05 and 15% were grafted with PAMPS or PAMPS gel (2 wt % cross-linker) at 20 wt % AMPS and 50 °C for 4 h (Table 2). In both reactions, the grafting yield was nearly proportional to the porosity of the PCTE membrane, peaking at 15 wt % with linear PAMPS and 30 wt % with PAMPS gel grafts.

---

[22] Denes, F. S.; Manolache, S. *Prog. Polym. Sci.* **2004**, *29*, 815.

[23] Robinette, E. J.; Palmese, G. R.; Kosik, W.; Hirvonen, J.; Demaree, D. E.; McKnight, S. H.; Fridman, G.; Gutsol, A.; Friedman, G.; Fridman, A. *J. Appl. Polym. Sci.* **2006**, submitted.

[24] Inagaki, N.; Narushim, K.; Tuchida, N.; Miyazaki, K. *J. Polym. Sci., Part B: Polym. Phys.*, **2004**, *42*, 3727.

[25] Chen, H.; Palmese, G. R.; Elabd, Y. A. *ACS Polym. Prepr.* **2005**, *46* (2), 1202.

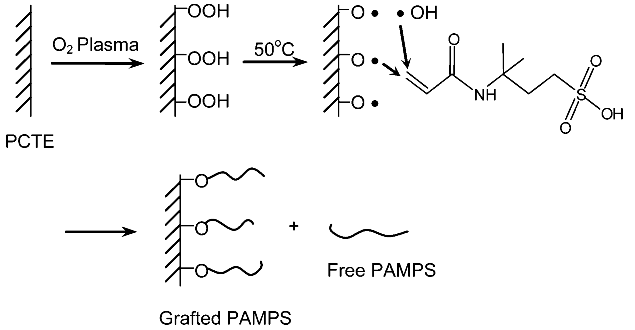

Figure 1. O_2−plasma initiated surface graft polymerization of the PCTE membrane with PAMPS.

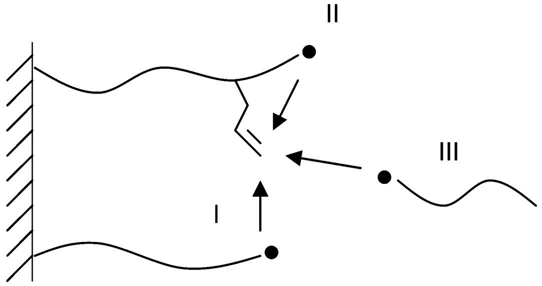

Figure 2. Schematic illustrating graft polymerization in the presence of divinyl cross-linker BisA.

Again, higher grafting yields were obtained with the presence of a cross-linker, where grafting increases in both the pore and the top/bottom surface of the membrane occur (evidenced by larger wet thicknesses in fibril compared to tubular PAMPS, shown in Table 2). It is interesting to note that the hydrated composite membrane thickness increases with increasing pore size and porosity (increasing grafting yield), while the planar area of the membrane remains constant. This suggests that the PAMPS in the pores contributes to the change in thickness when hydrated. Recently, Xu et al.[26] have demonstrated that hydrophilic cylindrical domains in the thin film (~30 nm) block copolymers expand like mushrooms covering the surface of the film when hydrated.

Morphology. Figure 3 shows micrographs of PCTE membranes (top (1) and cross-section (2) views) before (a) and after grafting with PAMPS (b) and PAMPS gel (c). The original membranes have a flat surface and uniform cylindrical pores randomly oriented normal to the plane of the membrane (Figure 3a). The pore walls of the original membrane appear rough, possibly as a result of the etching process.[19] After grafting, the pores on the top surface of the membrane were partially closed, while a smoother layer was observed on the pore walls (Figure 3b). This suggests grafting of PAMPS on the PCTE surface and pore walls (tubular PAMPS domains). Higher grafting yields obtained with the aid of BisA cross-linker resulted in the top surface completely covering the pores with a layer of PAMPS gel (Figure 3c1) and the pores fully filled with PAMPS rods or fibrils (Figure 3c2). Parts d2 and e2 of Figure 3 demonstrate that a broad range of domain sizes (50 and 2000 nm) can be filled by this grafting technique, where PAMPS nanodomains with aspect ratios as high as 240 were achieved in this work. The

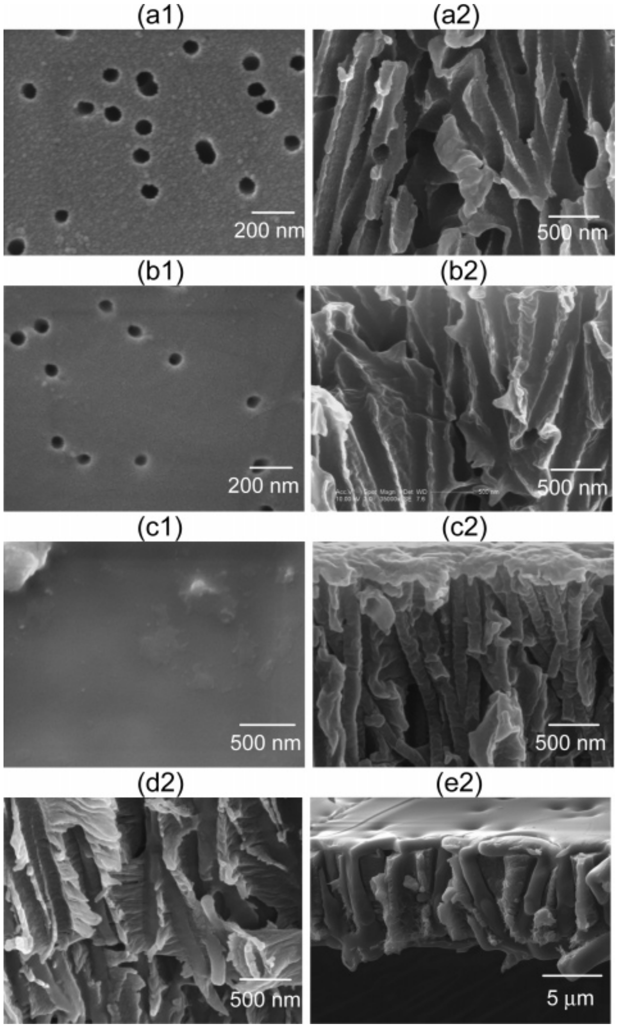

Figure 3. SEM images of (a) the original PCTE membrane (PCTE100, 100 nm pore size) and composite membranes with (b) 100 nm tubular PAMPS domains, (c) 100 nm fibril (cross-linked) PAMPS domains, (d) 50 nm fibril PAMPS domains, and (e) 2000 nm fibril PAMPS domains. 1, surface view; 2, cross-sectional view.

micrographs also reveal that, excluding the changes in surface morphologies, the bulk as well as the dimension of PCTE membranes is not altered by the grafting reaction, confirming that grafting is limited to the PCTE surface.

The surface grafting was further confirmed by ATR-FTIR with the appearance of new bands at 1055 cm^{-1} and 1658 cm^{-1} and a broad band between 3150−3650 cm^{-1} (Figure 4), which represent SO_3^-, C=O (Amide I), and N−H groups in PAMPS, respectively. Energy dispersive spectra (Figure 5) of the cross-section of a grafted pore in the membrane confirm PAMPS on the pore walls by showing the signals of the Kα shell of sulfur at 2.307 keV. To study the distribution of PAMPS on the pore walls, X-ray maps were collected on the cross-section of grafted membranes, where the yellow color represents the sulfur atoms in PAMPS (Figure 6). While no sulfur was observed in the original PCTE membrane, clear patterns of sulfur across the cross-section were obtained in the grafted membranes. These patterns suggest that PAMPS was uniformly grafted on the pore walls. In addition, prior to imaging, all composite membranes were thoroughly washed and stored in deionized water after polymerization. Because PAMPS is water soluble, this

---

[26] Xu, C.; Fu, X.; Fryd, M.; Xu, S.; Wayland, B. B.; Winey, K. I.; Composto, R. J. *Nano Lett.* **2006**, *6*, 282.

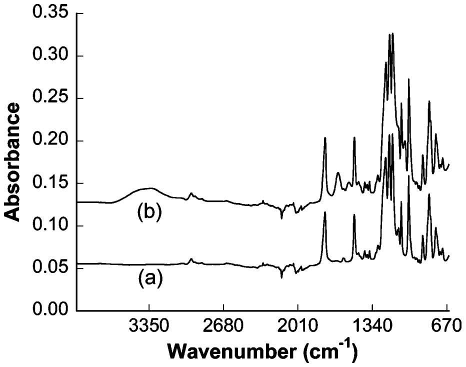

Figure 4. ATR-FTIR spectra of PCTE800 (800 nm pore size) before (a) and after (b) being grafted with PAMPS fibrils (cross-linked).

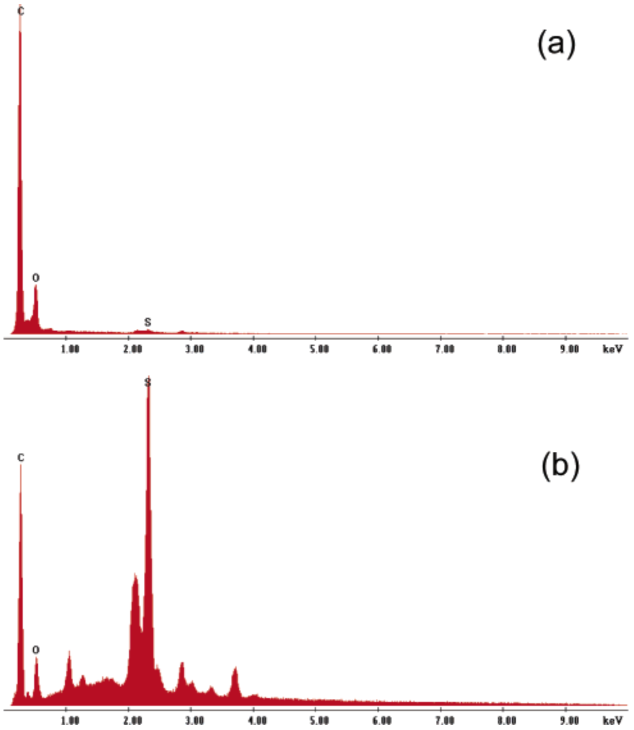

Figure 5. Energy dispersive spectra of the cross section of (a) PCTE2000 with tubular PAMPS domains and (b) PCTE2000 with fibril (cross-linked) PAMPS domains.

confirms covalent bonds between the track-etched membrane and polyelectrolyte.

Proton Conductivity. Proton conductivity of the composite membranes was measured normal to the plane of the membrane in a fully hydrated state (Table 3). Hydration increased the thickness of the composite membranes (see wet thicknesses in Table 2) due to swelling of PAMPS grafted on the top/bottom surface of PCTE membranes. But there was no change in the planar dimension of the hydrated composite membranes containing tubular PAMPS domains. The composite membranes with fibril PAMPS domains showed less than 10% expansion in the planar area after hydration. The robust PCTE matrix membrane provides dimensional stability for the polyelectrolyte. This may provide additional benefits to applications such as actuators and fuel cells.[27]

The resistance of the original PCTE membranes was on the order of 10−100 Ω. By incorporating tubular or fibril nanodomains of PAMPS, the resistance of composite membranes decreased significantly compared to the original PCTE membrane (Table 3). The highest conductivity obtained was ~0.01 S/cm in the composite membrane containing 400 nm fibril PAMPS domains. Overall, composite membranes with fibril PAMPS domains possess higher effective conductivities compared to the membranes with tubular PAMPS domains. The micrographs show that the composite membranes with fibril PAMPS domains also have a thick layer of PAMPS gel grafts on the top/bottom surface of the membrane (see Figure 3e2). This is further confirmed by the ~200−400% increase in thickness after hydration, while the composite membranes with tubular PAMPS only showed ~0−80% increase in thickness (Table 2). Apparently, in addition to the PAMPS nanodomains and the resistance of the matrix membrane, the layer of surface gel can also contribute to the overall or effective conductivity of the composite. To examine proton transport exclusively through the oriented PAMPS nanodomains (specific conductivity), the resistance of the matrix membrane and surface gel layer must be factored out.

Specific Conductivity. The specific conductivity was calculated using eq 5, taking the porosity and the thickness of the hydrated PAMPS layer on the top/bottom surface of the membrane into consideration.

$$R_t = R_1 + R_2 \tag{1}$$

$$R = \frac{L}{A\sigma} \tag{2}$$

$$\frac{L_t}{A_t\sigma_t} = \frac{L_1}{A_1\sigma_1} + \frac{L_2}{A_2\sigma_2} \tag{3}$$

$$A_t = A_1 = A_2$$

$$\sigma_1 = \frac{L_1}{\dfrac{L_t}{\sigma_t} - \dfrac{L_2}{\sigma_2}} \tag{4}$$

$$\sigma_p = \frac{\sigma_1}{\theta} \tag{5}$$

In the equations above, R is the resistance (Ω), σ is the conductivity (S/cm), L is the thickness of the membrane (cm), A is the area of the membrane (cm^2), and θ is the porosity (%) of the PCTE matrix membrane. Subscript 1 represents the PCTE matrix membrane, 2 represents the PAMPS layer on the composite surface, and t is the total composite membrane (with tubular or fibril PAMPS domains), while p represents the oriented PAMPS domains. In this study, an isotropic PAMPS bulk gel (not confined within a pore) membrane was synthesized by free-radical polymerization at 5 wt % (to monomer) BisA cross-linker. The conductivity of the bulk gel was measured as 0.02 S/cm and was used as σ_2 in the calculations. This value is similar to Nafion (0.02 S/cm; two-electrode method), the most frequently used polyelectrolyte membrane in fuel cells.[13,28,29]

---

(27) Yamaguchi, T.; Miyata, F.; Nakao, S. *Adv. Mater.* **2003**, *15*, 1198.

(28) Gardner, C. L.; Anantaraman, A. V. *J. Electroanal. Chem.* **1995**, *396*, 67.

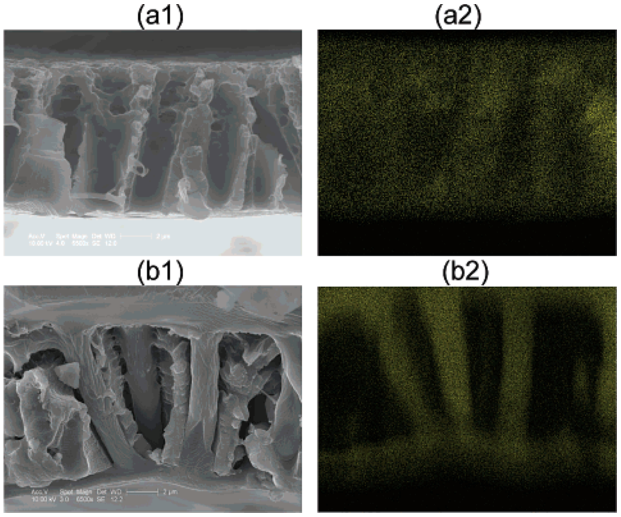

Figure 6. SEM micrographs (1) and X-ray maps (2) of the cross-section of (a) PCTE2000 with tubular PAMPS domains and (b) PCTE2000 with fibril (cross-linked) PAMPS domains. The yellow color in the X-ray maps represents sulfur Kα in PAMPS.

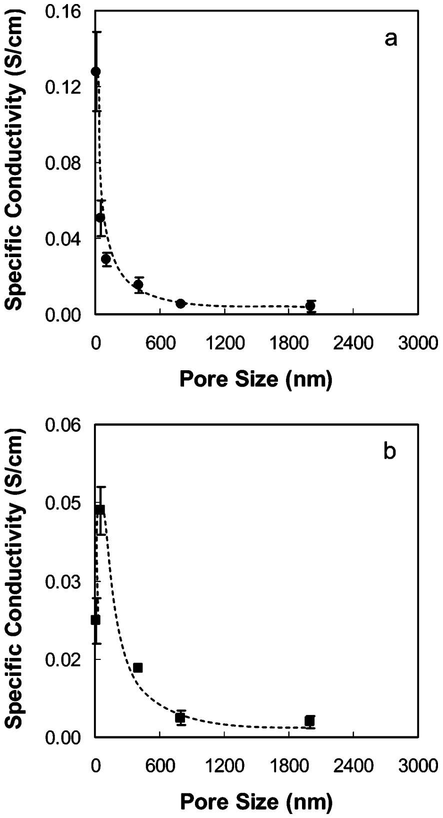

Figure 7. Specific proton conductivity versus pore/domain size of composite membranes with (a) tubular PAMPS domains and (b) fibril (cross-linked) PAMPS domains.

The specific conductivity of tubular PAMPS domains in the composites increased exponentially with decreasing domain size and exceeded the conductivity of isotropic PAMPS bulk gel at domain sizes less than 400 nm (Figure 7a; Table 3). The highest value at 10 nm tubular domains was 6 times higher than the isotropic PAMPS gel. A similar exponential increase was observed for the specific conductivity of the fibril PAMPS domains (50−2000 nm), where the maximum value (at 50 nm domain size) was ~2 times higher than the isotropic PAMPS gel (Figure 7b; Table 3). A decrease in specific conductivity was observed with 10 nm fibril PAMPS domains, which may suggest that the pores are not fully filled with PAMPS fibrils. Notice that the PCTE membranes at 10 nm pore size grafted with tubular and fibril PAMPS have similar grafting yields, yet the fibril PAMPS composite membrane has a higher hydrated thickness compared to the tubular form (6 vs 19 μm). This suggests that most of the fibril PAMPS is grafted to the top/bottom surface of the membrane and not in the pores.

Similar results (increasing transport with decreasing pore size) have been reported in literature with different explanations. Vorrey and Teeters[18] observed that PEO confined in track-etched pores below 400 nm was more conductive than a bulk PEO membrane. This observation was attributed to the orientation of the helices of the PEO polymer electrolyte chains, which allows interhelical electrical conduction. Fang and Leddy[17] studied the flux of cations through Nafion confined in track-etched nanopores. The flux increased with decreasing pore size and exceeded the value of the Nafion film at pore sizes below 300 nm. They ascribed this enhanced transport to the increased interfacial zone (surface area for transport) between Nafion domains and pore walls at small pore sizes. In both investigations,[17,18] the polyelectrolyte was physically sorbed within the track-etched pores, where in this study the polyelectrolyte is grafted (covalently bound) within the pores.

In addition to the explanation provided by Fang and Leddy,[17] it is well-known that Nafion phase separates in the solid state, where aggregates of ions form due to the electrostatic interactions between ion pairs, leading to the formation of two microphases: ion-rich (sulfonic acid-rich) and ion-poor domains. Upon hydration, the polymer transforms from an insulator to an ion conductor (percolation threshold), whereby isolated ionic domains become interconnected throughout the polymer. X-ray analysis on Nafion by Gierke et al.[31] suggests that ion-rich domains are approximately 5 nm in size and are interconnected by small narrow ionic channels on the order of 1 nm. Above this percolation threshold, protons transport through the polyelectrolyte via hydrolyzed acidic sites through this interconnected ionic network. A number of investigators[12,13,31−35] have demonstrated that transport properties in Nafion and other similar polyelectrolyte membranes are affected by the ionic nanostructure and follow a percolation model. In the work by Fang and Leddy[17] it is possible that when the pore size approaches a size scale similar to the interconnected ionic network, the ionic nanostructure becomes more oriented resulting in enhanced transport. Although there is limited information regarding the ionic nanostructure of PAMPS, the reduction in pore size

---

(29) Pourcelly, G.; Oikonomou, A.; Gavach, C.; Hurwitz, H. D. *J. Electroanal. Chem.* **1990**, *287*, 43.

(30) Siddhanta, S. K.; Gangopadhyay, R. *Polymer* **2005**, *46*, 2993.

(31) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci.: Polym. Phys.* **1981**, *19*, 1687.

(32) Hsu, W. Y.; Barkley, J. R.; Meakin, P. *Macromolecules* **1980**, *13*, 198.

(33) Gronowski, A. A.; Jiang, M.; Yeager, H. L.; Wu, G.; Eisenberg, A. *J. Membr. Sci.* **1993**, *82*, 83.

(34) Matsuyama, H.; Teramoto, M.; Tsuchiya, M. *J. Membr. Sci.* **1996**, *118*, 177.

(35) Xu, T. W.; Yang, W. H.; He, B. L. *Chem. Eng. Sci.* **2001**, *56*, 5343.

Table 4. Mechanical Properties of PCTE and Composite Membranes with Cylindrical PAMPS Nanodomains

	breaking strength (MPa)		breaking elongation (%)		modulus (MPa)	
	dry	hydrated	dry	hydrated	dry	hydrated
PAMPS gel	72[a]	0.012[b]	3.2[a]	40[b]	3108[a]	0.03[b]
polycarbonate[c]	72		150		2480	
PCTE50	48 ± 4	86 ± 26	57 ± 5	22 ± 7	1228 ± 64	1304 ± 264
PCTE50 with tubular PAMPS	24 ± 13	19 ± 1	4 ± 1	5 ± 1	1087 ± 7	704 ± 417
PCTE50 with fibril PAMPS	30 ± 8	16 ± 3	4 ± 1	5 ± 1	1482 ± 265	503 ± 124
PCTE400	35 ± 5	33 ± 3	17 ± 7	23 ± 9	729 ± 124	653 ± 42
PCTE400 with tubular PAMPS	21 ± 3	21 ± 3	4 ± 1	6 ± 2	883 ± 229	568 ± 161
PCTE800	44 ± 6	40 ± 10	18 ± 13	8 ± 2	1000 ± 151	862 ± 145
PCTE800 with tubular PAMPS	23 ± 14	22 ± 5	5 ± 2	6 ± 1	775 ± 339	631 ± 81
PCTE800 with fibril PAMPS	53 ± 2	17 ± 5	11 ± 1	9 ± 2	1298 ± 166	304 ± 24

[a] Containing 5 wt % BisA cross-linker. [b] 98% swelling.[30] [c] General purpose grade.[36]

(<400 nm) may result in the orientation either of ionic networks or of polymer chains, resulting in the enhanced transport observed in Figure 7. A more in depth investigation on the PAMPS nanostructure confined within a nanopore is underway.

Another observation of interest was that although the effective proton conductivity of fibril PAMPS-containing composites was higher compared to those containing tubular PAMPS domains, the specific conductivity of fibril PAMPS domains was slightly lower than that of their tubular counterparts. This may be due to the existence of the cross-linker in fibril PAMPS, which reduces the mobility of polymer chains and hinders the transport of protons. The lower specific conductivity of fibril PAMPS domains also indicates that the thick PAMPS layer on the composite surface plays important role in the effective proton conduction of fibril PAMPS-containing composites.

It is interesting to note that the tubular PAMPS domains at 10 nm have a high specific proton conductivity of 0.13 S/cm. These data suggest that a composite membrane composed of PCTE membrane, with 10 nm pores and 16% porosity, filled with tubular PAMPS domains will have an effective conductivity similar to that of Nafion.

Mechanical Properties. The tensile properties of PCTE and composite membranes were investigated under both ambient and hydrated conditions. In spite of the porous structure, PCTE membranes possess mechanical properties comparable to the dense film (Table 4). No significant impact was observed for membranes at different pore sizes. The PAMPS gel synthesized at 5 wt % cross-linker was similar in strength but more brittle than the PCTE membranes in the dry state. As expected, the hydrophobic PCTE membranes showed no obvious changes in mechanical properties after being exposed to water. However, the PAMPS gel loses its strength by many orders of magnitude after hydration.

At all pore sizes, the breaking strength and elongation of PCTE membranes were reduced by ∼50% and ∼75%, respectively, after incorporating PAMPS tubules in the pores (Table 4). In comparison, the composite membranes containing fibril PAMPS domains show similar breaking strength and modulus compared to the PCTE matrix, while showing ∼50% decrease in breaking elongation.

Composite membranes containing tubular PAMPS domains retained the mechanical properties after hydration (Table 4), while the composite membrane containing 800 nm fibril PAMPS domains lost more than half its strength after hydration but was still on the same order of magnitude as PCTE membranes. This decrease in strength was less distinct at a smaller domain size. Overall, the mechanical data show that nanocomposites synthesized by surface grafting were able to retain the mechanical stability of the hydrophobic PCTE matrix even after hydration, unlike a bulk PAMPS gel membrane.

Conclusions

Track-etched membranes with cylindrical porous structure provide a promising matrix to prepare polymer membranes with oriented polyelectrolyte (PAMPS) nanodomains. The oriented PAMPS domains, with aspect ratios as high as 240, were synthesized in tubular and fibril (cross-linked) forms by plasma-induced surface graft polymerization. Oxygen plasma treatment of the polycarbonate track-etched host matrix improves pore filling of an aqueous reaction solution and ensures uniform grafting of PAMPS on the pore walls, which was confirmed by sulfur Kα maps. The specific conductivity of the tubular PAMPS domains increased with decreasing PAMPS domain size (2000−10 nm) with the highest value 6 times higher than the isotropic bulk PAMPS gel membrane. Mechanical properties of the nanocomposite were similar to those of the PCTE host matrix in both the dry and the hydrated state. Results from this study demonstrate that the polymer−polymer nanocomposites synthesized by pore-filling surface graft polymerization combine the mechanical stability of the hydrophobic matrix and the functionality of the polyelectrolyte domains, while enhancing transport in the desired direction for a variety of membrane processes. The development of track-etched membranes of various chemistries and porosities will provide a broader applicability of this work.

Acknowledgment. The authors acknowledge the financial support of the U.S. Army Research Office through Grant W911NF-05-1-0036. The authors are grateful to the Drexel Plasma Institute and the assistance of Alexandar Fridman, Alexander Gutsol, and Gregory Fridman.

CM061422W

---

(36) *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley: New York, 1999.