

Hydrophilic Polystyrene/Maleic Anhydride Ultrafine Fibrous Membranes

Corine Cécile, You-Lo Hsieh

Fiber and Polymer Science, University of California, Davis, California 95616

Received 9 April 2009; accepted 14 June 2009

DOI 10.1002/app.31003

Published online 10 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polystyrene/maleic anhydride (PSMA) was synthesized to reach a viscosity-average molecular weight of 700 kDa and fabricated into ultrafine fibrous membranes consisting of fibers with an average diameter of 300 nm. These ultrafine PSMA fibers were rendered insoluble in organic solvents by reactions with hydrazine and ethylenediamine (ED). The highly efficient incorporation of diamines into the fibrous membranes was easily achieved by brief immersions in either dilute (0.5 wt %) hydrazine for 1 min or ED ether solution for 2 min. Heating at 150°C for 5 min produced crosslinked PSMA with very little or no solubility in acetone with the retention of

the fibrous membrane structure. The ED-crosslinked membranes were particularly stable to both bases and acids as well as hydrophilic solvents, had a 46° water contact angle, and absorbed 22 times the amount of water as the as-spun fibrous membrane. This post-fiber-formation crosslinking approach was robust, highly efficient, and fast and required very little crosslinking reagent. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 723–730, 2010

Key words: crosslinking; fibers; functionalization of polymers; polystyrene

INTRODUCTION

Crosslinked polystyrene (PS) and copolymers of styrene (S) have expanded from the homopolymer's vast industrial and consumer products to more notable and chemically versatile solid support and functional resin applications. For instance, the well-known Merrifield resins¹ are divinylbenzene-crosslinked copolymers of S and chloromethylstyrene for organic synthesis. Copolymerizing S with the highly reactive maleic anhydride (MA) produces alternating polystyrene/maleic anhydride (PSMA) copolymers that are commonly used as additives in blends or composites to achieve desirable interfacial effects and as dispersants in the soluble form.² The PSMA copolymers for these applications tend to be low in molecular weight. As part of higher molecular weight PS, MA has been incorporated as side chains via acylation³ and grafting reactions.⁴ In our laboratory, divinylbenzene-crosslinked PSMA was synthesized with dicarboxylic acid and dihydroxyphosphino functionalities to allow complexation with divalent metal ions, such as, Pb^{2+} , Cu^{2+} , Cr^{3+} , and Ni^{2+} .⁵ More recently, we synthesized PSMA with a sufficient chain length [viscosity-average molecular weight (M_v) = 700 kDa] to be electrospun into fi-

brous membranes with fibers 200–800 nm in diameter, micrometer size pores, and super flexibility.⁶ The electrospinning of binary mixtures of PSMA with polyols, that is, either 31–50 kDa poly(vinyl alcohol) (PVA) or a small glycerol triol, followed by heat-induced esterification yielded crosslinked ultrafine fibrous membranes that were insoluble in solvents for PS and PSMA and carbon disulfide, a solvent for Friedel–Craft reactions.⁷ These highly porous and ultrahigh specific surface PSMA fibrous membranes could be hydrolyzed to be hydrophilic and also to swell instantaneously at the onset of organic solvent exposure, which facilitated the diffusion of reactants and products alike. Therefore, these ultrafine fibrous PSMA membranes not only overcome many limitations of the Merrifield resins, such as incompatibility with some organic solvents and nonwetting or nonswelling in aqueous solutions, but they also offer an easily handled continuous form without the need for the additional separation of centrifugation, filtration, and collection for their recovery, as needed with the beaded Merrifield resins.

Another way to crosslink PSMA fibrous membranes is by post-fiber-formation reactions. Post-fiber-formation crosslinking is desirable, as it prevents any additive effects on the binary solution properties and, thus, electrospinning and fibrous structures. To enable crosslinking with the anhydride functionality in PSMA fibrous solids, the more reactive amines may be necessary. PSMA has been reacted with primary (1-octylamine), secondary (1-

Correspondence to: Y.-L. Hsieh (ylhsieh@ucdavis.edu).

methyl hexylamine, 1,1-dimethyl propylamine, and dibutylamine),⁸ and tertiary amines.⁹ The reaction with 1,8-naphthalimide created a pendant luminescent moiety in PSMA.¹⁰ Furthermore, the opening of the MA ring of PSMA has been shown to impart biocompatibility and biological activity.^{11,12} In this study, the crosslinking of ultrafine fibrous PSMA membranes was investigated by reactions with diamines, that is, hydrazine and ethylenediamine (ED). The high electron deficiency of MA should facilitate charge-transfer interactions and promoted intermolecular crosslinking via amidation between the diamines and anhydride moieties. In fact, the reaction of hydrazine with PSMA in the powder form has been previously reported.¹³ ED was also included. If proven to work, it would be far more desirable because of its availability and demonstrated biocompatibility.

EXPERIMENTAL

Materials

All chemicals used were from Aldrich Chemical Co. We freed S (99%) of the inhibitor by passing it through an inhibitor-removal column (Aldrich, St. Louis, MO). MA (99%) was recrystallized from chloroform and dried *in vacuo*. The 2-2' azobisisobutyronitrile (AIBN; 98%) initiator, was recrystallized from ethanol and dried *in vacuo*. Acetone, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and cyclohexane were all 99.8% pure and were used without further purification. The crosslinkers, hydrazine (98% purity) and ED (99% purity), were used as received.

Synthesis of PSMA

PSMA was synthesized by the free-radical polymerization of S and MA initiated by AIBN at a fixed monomer/initiator ratio of 2000. S (7 mL, 61 mmol) and MA (5.98 g, 62 mmol) were dissolved in toluene (200 mL) in a three-necked, round-bottom flask with nitrogen bubbling. We initiated the polymerization by adding AIBN and kept the reaction at 90°C for 4 h under constant reflux and nitrogen, following a procedure previously used in our laboratory.⁵ The M_v value of PSMA was derived from the intrinsic viscosity ($[\eta]$) measurement of a 4-mg/mL THF solution with a Cannon–Fenske viscometer according to the Mark–Houwink–Sakurada equation¹⁴:

$$[\eta] = 0.7704 \times 10^{-4} (M_v)^{0.725}$$

PSMA fiber generation and reaction with diamines

PSMA fibers were generated by the electrospinning of 20 wt % PSMA in DMF at a 7 kV voltage with a

previously described apparatus.¹⁵ Briefly, about 5 mL of solution was placed in a glass tube connected to the stainless electrode of a power supply (Gamma High Voltage Supply, ES 30-0.1P, Ormond Beach, FL). Electrospinning was conducted at ambient temperature for about 8 h, during which a white fibrous membrane was collected on a ground aluminum target. The fibers were then dried *in vacuo* at ambient temperature for 24 h and detached from the aluminum collector. The PSMA fibrous membranes were reacted with the diamines by saturation in ether solutions of either 0.5 wt % ED or 0.5 wt % hydrazine for 5 min. The fibers were dried at ambient temperature for 24 h and heated at 150°C for 5 min. After 2 h, the fibers were immersed in acetone for 5 min, and their mass change was determined after the fibers were dried *in vacuo* at ambient temperature for 10 h.

Stability of the diamine-reacted PSMA fibers

The PSMA fibrous membranes were immersed in acetone for 5 min to remove the unreacted PSMA and then dried for 1 h. The weight change (%) of the fibers was calculated as follows:

$$\text{Change in weight} = (W_i - W_t)/W_i \times 100\%$$

where W_i and W_t are the masses of the dried fibers before and after immersion in acetone and drying, respectively.

The base and acid stabilities of the diamine-reacted PSMA fibers were evaluated by their appearance and mass change when they were immersed in aqueous alkaline and acidic solutions. The fibers were immersed in an aqueous 0.005N NaOH solution for 5 s, then washed several times with water, and dried *in vacuo* for 24 h. The fibers were immersed in 0.01N H₂SO₄ for 10 min, neutralized with 0.01N NaOH, rinsed with water, and dried *in vacuo* for 10 h.

Characterization

Differential scanning calorimetry (DSC) analyses were conducted (DSC-60 Shimadzu, Columbia, MD) with samples of about 5 mg at a 10°C/min heating rate in dry N₂. Thermal analyses of the fibers were also performed on a thermogravimetric analyzer (TGA-50, Shimadzu) at a 10°C/min heating rate in dry N₂. The IR absorption spectrum of was obtained by direct transmission of the entire fibrous membrane on a Fourier transform infrared (FTIR) spectrometer (Nicolet Magna IR 560, Ramsey, MN). The morphology of the fibrous membranes was observed with a scanning electron microscope (XL30-SFEG, FEI/Philips, Hillsboro, OR) at a 5-kV accelerating voltage after the membrane was

sputter-coated with gold. The water contact angle and liquid retention were determined by a surface tensiometer (KRÜSS, K14, Hamburg, Germany) according to our previous report.¹² The simultaneous wetting (F_w) and vertical liquid-retention capacity (C_v) of a liquid in a vertically hung sample strip with its lower edge forced into contact with a liquid were measured. The water-wetting contact angle (θ) was calculated from the wetting force in water (F_w):

$$\theta = \cos^{-1}(F_w/p\gamma)$$

where p and γ are the sample liquid interfacial perimeter and the water surface tension, respectively. C_v of the sample was determined by the vertical uptake of the total wetting liquid, that is, hexadecane, in the sample by the weights before (W_d) and after (W_v):

$$C_v = (W_v - W_d)/W_d$$

RESULTS AND DISCUSSION

PSMA fiber formation

The AIBN-initiated, free-radical copolymerization of S and MA was highly efficient, with a yield greater than 94%. Synthesis at a 2000 [S]/[AIBN] molar ratio produced a PSMA with a M_v of 700 kDa. PSMA was soluble in acetone, THF, ethyl acetate, DMF, methanol, and DMSO. The polar MA moiety in PSMA explained its solubility in polar solvents, such as acetone and methanol, and in the aprotic solvents DMF, DMSO, ethyl acetate, and THF. DMF was used because of its high dielectric constant ($\epsilon = 36.7$ at 25°C), low viscosity ($\eta = 0.79$ cP at 25°C), and low vapor pressure or high boiling temperature ($T_b = 153^\circ\text{C}$), all desirable characteristics for electrospinning. At 20 wt % in DMF, the PSMA solution had a viscosity of 570 cP and could be efficiently electrospun continuously at a 1-mL/h rate and a 14-kV voltage. A millimeter-thick fibrous membrane could be produced after 24 h. The fibers were smooth on their surfaces and relatively homogeneous in size with a 300-nm average fiber diameter (Fig. 2, shown later). Few beaded structures were observed among the fibers.

An attempt to crosslink the PSMA fibrous membranes by heating at 160°C for 24 h showed no effect on reducing the solubility in acetone. The fibrous membrane immediately became unobservable by the eyes when it was immersed in acetone; this indicated that the membranes either remained as completely soluble as the copolymer or partially soluble and disintegrated into fibers too small to be seen. In the former case, intermolecular crosslinking did not

occur. In the latter case, crosslinking might have occurred but either too little or intramolecularly. In any case, the use of crosslinkers was deemed necessary.

Preliminary reactions with the pure diamines and aqueous hydrazine

When the fibrous membranes were introduced to pure diamines, however, the PSMA fibers either dissolved, as in the case with hydrazine, or balled up into a gel, with ED. The reaction between either diamine with the MA of PSMA was fast, which caused the fibrous membranes to dissolve or deform. The reaction with the more reactive hydrazine was faster. These observations clearly showed that diluted diamines should be sufficient. Hydrazine is miscible with water and methyl, ethyl, propyl, and isobutyl alcohols, slightly miscible in hydrocarbons, and insoluble in chloroform and ethyl ether. The addition of 0.96 wt % hydrazine to DMSO, acetone, THF, and ethyl acetate resulted in solutions that stayed clear for at least 2 h, whereas the same concentration in DMF turned milky in 10 min. Because water is a nonsolvent for PSMA, aqueous media was thought to be suitable for the delivery of hydrazine to the fibers. However, the hydrophobic PSMA membranes stayed afloat on aqueous media. To wet the membrane and improve the liquid–fiber contact, 10% methanol, a solvent for PSMA, was added. The membranes saturated with 0.04 wt % hydrazine in either water or 9/1 water/methanol mixtures for 20 s kept their original membrane shapes but lost 10 and 26% masses, respectively, upon drying. Extending the exposure in these media to 20 min led to membranes that stayed moist even after extended drying. After drying *in vacuo* for 48 h, 24 and 17% weight gains were observed on membranes immersed for 20 min in the aqueous and 9/1 water/methanol solutions, respectively.

It was clear that reactions between PSMA and hydrazine occurred in all cases. Figure 1 shows the reaction with hydrazine. A six-member ring intermediate was likely when MA was condensed with a diamine-like hydrazine. The half-amide derivative should have easily formed because the facile ring closures in the maleic acid series could be stabilized by a resonance effect. However, the mass losses from the brief 20-s immersions indicated that some dissolution of PSMA also occurred; this was likely due to half amide formation. The higher mass loss observed for the sample immersed in the 9/1 water/methanol was consistent with partial dissolution. The increased moisture retention of those samples reacted for the longer 20 min indicated significantly improved hydrophilicity from the increased polar carboxylic and amine groups of the

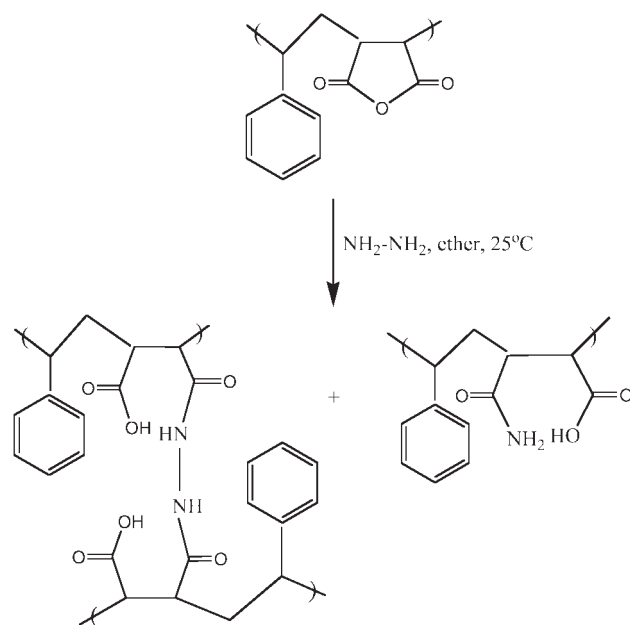


Figure 1 Crosslinking and grafting reactions between PSMA and hydrazine.

intermediates, a result of incomplete crosslinking. The reaction of PSMA fibrous membranes with diamines in solvents with high vapor pressures should have facilitated drying.

Crosslinking with the diamines in ether

Ether had a much lower surface tension (17.0 dyne/cm at 20°C) and wet the PSMA fibrous membranes far better than water. Exposure to ether also did not alter the PSMA fibrous structure; this made it a favorable media for reaction with hydrazine [Fig. 2(a,b)]. The fibers remained cylindrical with diameters mostly around 400 to 600 nm and a slight surface roughness [Fig. 2(a)].

Although hydrazine is insoluble in ether, ED is slightly soluble in ether. We conducted the crosslinking reactions by immersing the membranes in 0.5 wt % dilute solutions of both diamines over various lengths of time and then drying and heating them at 150°C for 5 min. The mass of the hydrazine-crosslinked PSMA fibrous membranes increased very quickly with time, reaching 14% within 1 min (Fig. 3). The mass gain from the reaction with ED peaked at a higher level than hydrazine, at more than 20%, but also for a time that was twice as long. For the diamine exposure that lasted less than 1 min, the mass gain was less with ED than with hydrazine. As the reaction continued, the mass gain with ED exceeded that with hydrazine. The slower initial mass gain with ED was consistent the lower initial diffusion because of its larger molecular size. The eventual higher mass gain with ED was also consist-

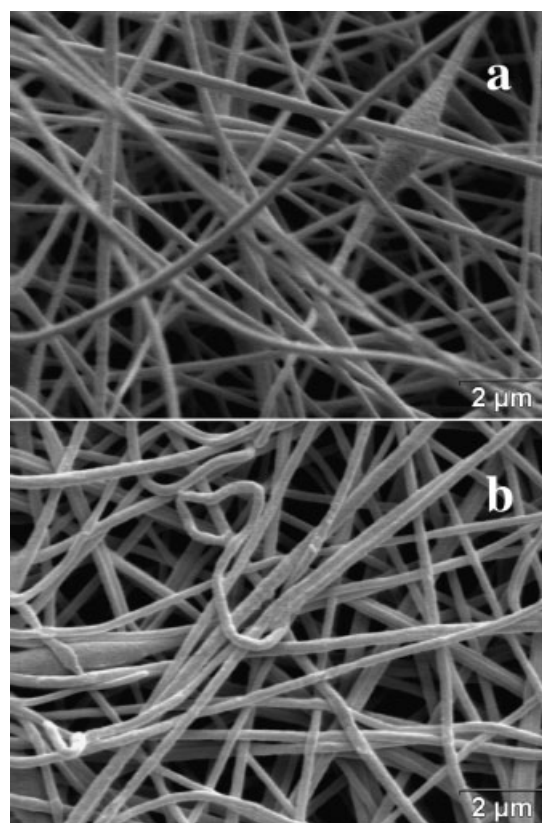


Figure 2 Morphology of the PSMA fibers (electrospun from 20 wt % PSMA in DMF): (a) before and (b) after 30 s of immersion in ether.

ent with its molecular mass and indicated similar molar inclusion in the two diamines.

The diamine-reacted membranes were immersed in acetone for 5 min to dissolve the uncrosslinked PSMA. Some mass loss was observed in most cases. Generally, the dissolution of PSMA was higher with shorter exposure times and showed improved crosslinking with longer immersion times. Crosslinking with hydrazine improved drastically between 30 s and 1 min, but persistent mass loss indicated incomplete crosslinking. The negligible mass loss of the

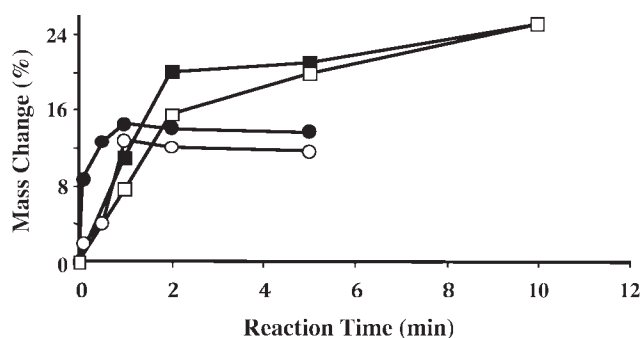


Figure 3 Mass change (%) of (●,○) hydrazine- and (■,□) ED-crosslinked (0.5 wt % in ether and heated at 150°C for 5 min) PSMA fibers (●,■) before and (○,□) after 5 min of immersion in acetone.

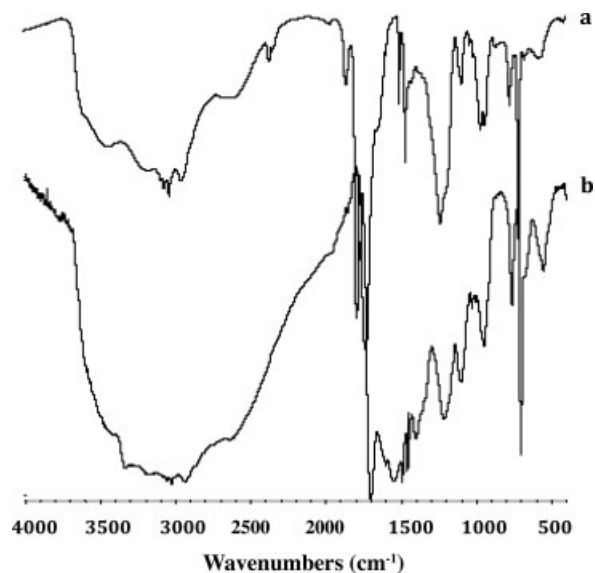


Figure 4 FTIR spectra of (a) the as-spun PSMA membrane and (b) the hydrazine-crosslinked (0.5 wt % in ether for 1 min) PSMA membrane.

fibers reacted with ED for 5 min or longer suggested not only better crosslinking with PSMA than with hydrazine but also possibly fully crosslinked fiber structures. On the basis of the mass loss from the acetone dissolution of PSMA, the optimal reaction times were 1 and 5 min for hydrazine and ED, respectively.

The FTIR study of the hydrazine-reacted membranes (0.5% hydrazine in ether for 1 min) showed the appearance of the amide C=O at 1459 cm^{-1} and the disappearance of the 995-cm^{-1} C=O stretching vibration of MA (Fig. 4); this confirmed the reaction between the MA moieties of PSMA and hydrazine.

Thermal properties of the crosslinked PSMA

The DSC thermogram of the as-spun PSMA fibrous membranes exhibited two very small endotherms centered at 70 and 150°C and associated with dehydration and glass transition, respectively (Fig. 5). The mass loss associated with dehydration was about 7% and continued for another 9% up to 250°C before the onset of the major mass loss at 280°C . The decomposition of PSMA was observed as the major endotherm (348°C), followed by an exotherm at 409°C , which left only 2% ash. This was distinctively different than the onset of the unzipping of PS to S around 260°C , as indicated by a baseline shift without mass loss followed by the endothermic decomposition of S above 400°C accompanied by 100% mass loss.⁷ For PSMA, the mass loss and decomposition endotherm beginning at lower temperatures suggested different chemical changes and decomposition pathways than PS because of the MA moiety.

Upon reaction with hydrazine (0.5% in ether, 1 min), the endotherm at 348°C disappeared and was replaced with a broader exotherm that peaked near 409°C . Additional heating (150°C , 5 min) of the hydrazine-reacted PSMA fibers narrowed the exotherm considerably, but it still peaked at a similar temperature. Similar changes were also observed on the ED-reacted and heated membranes. The absence of the endotherm at 348°C in both the hydrazine- and ED-reacted PSMA fibrous membranes confirmed their association with MA and the conversion of the MA moiety from crosslinking.

Morphology of the crosslinked PSMA fibrous membranes

The crosslinking of the PSMA fibrous membranes with 0.5% diamine (1 min in hydrazine or 2 min in

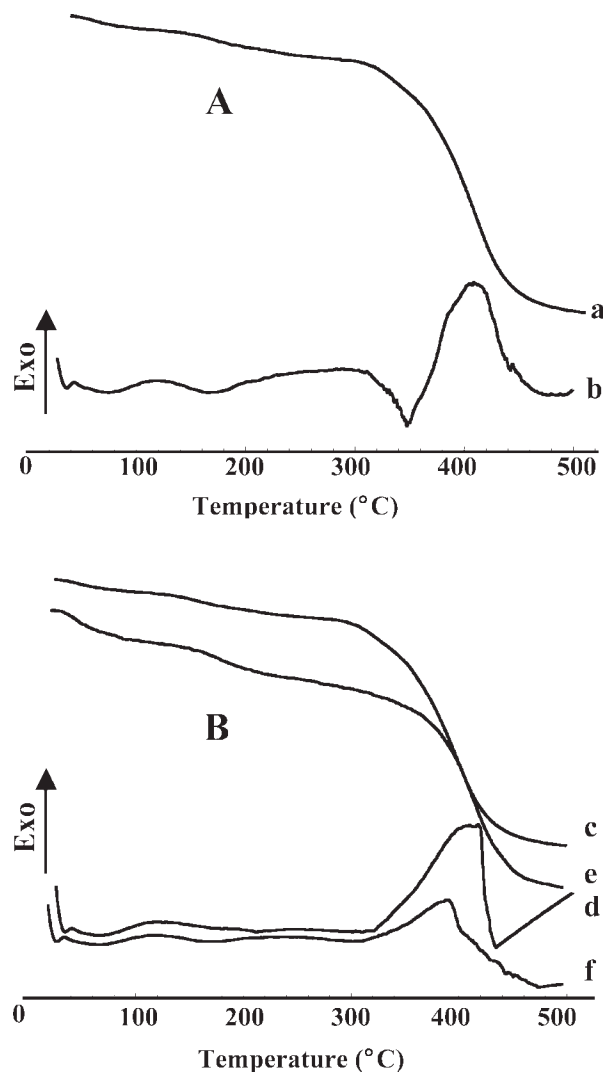


Figure 5 DSC of the PSMA fibers crosslinked with (A) 0.5% hydrazine for 1 min and (B) 0.5% ED for 2 min: (a) as-spun, (b) reacted, and (c) reacted and heated at 150°C for 5 min.

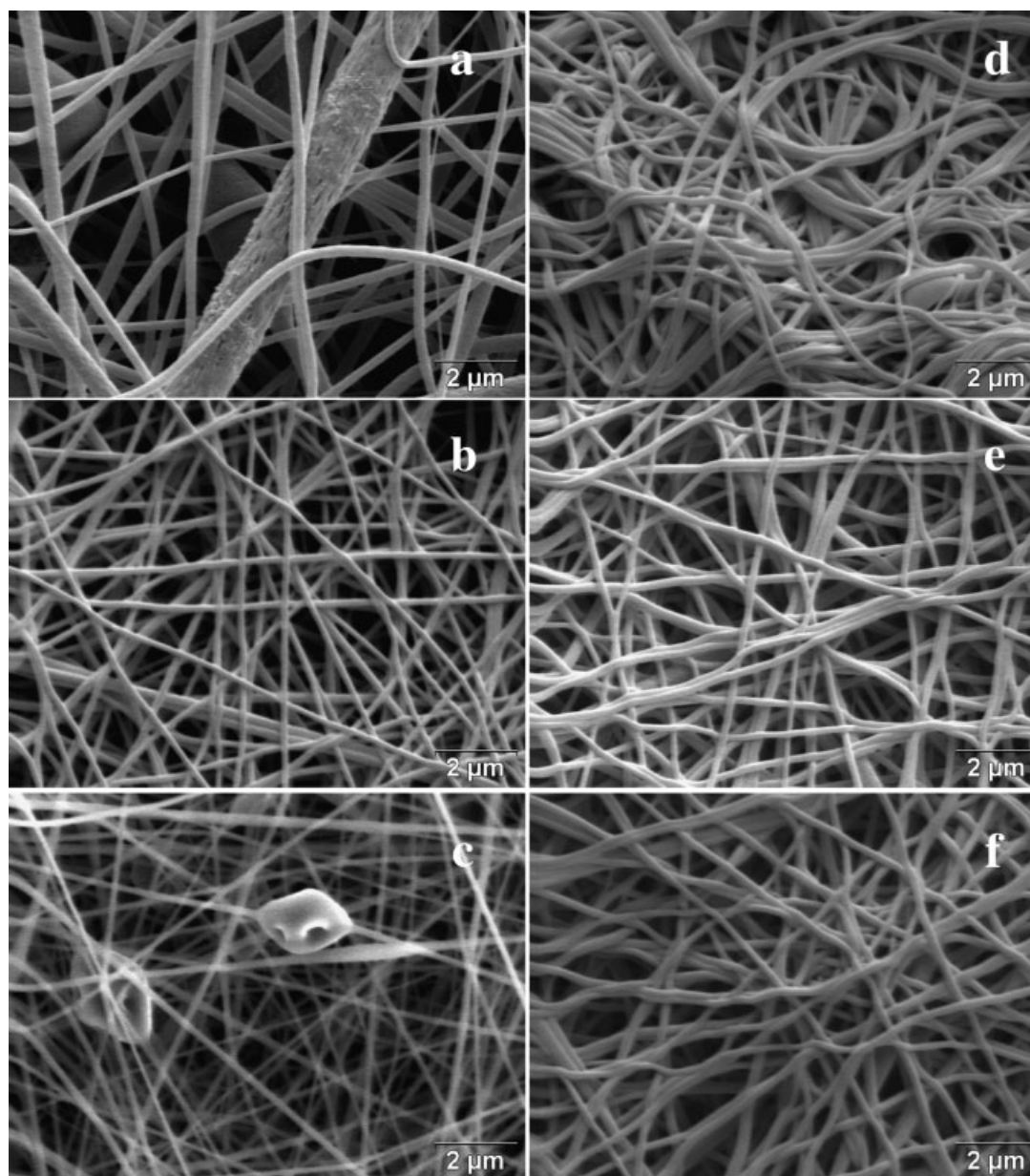


Figure 6 (a) 5-min immersion with 0.5 wt% hydrazine in ether, (b) sample a heated at 150°C for 5 min, (c) 5-min immersion with 0.5 wt% ED in ether, (d) sample c immersed in acetone for 5 sec, (e) sample c heated at 150°C for 5 min, and (f) sample e immersed in acetone for 5 sec.

ED, followed by heating at 150°C for 5 min) did not alter the fiber morphology significantly (Fig. 6). Some of the hydrazine-immersed fibers seemed to be enlarged slightly [Fig. 6(a)], but they appeared to be similar to the original as-spun fibers after the heat treatment [Fig. 6(b)]. The hydrazine-crosslinked fibers were insoluble in acetone for up to 24 h. The ED-immersed fibers showed even less change in appearance than those with hydrazine [Fig. 6(c)]. These fibers remained insoluble in acetone for 5 min but appeared relaxed, doubled in width, and merged with adjacent fibers [Fig. 6(d)]. Heating also

caused the fibers to appear similar to the as-spun fibers [Fig. 6(e)]. The fiber morphology did not appear to be altered by further exposure to acetone [Fig. 6(f)].

Hydrophilicity and porosity

The as-spun PSMA fibrous membrane had an average water contact angle of 77° and absorbed essentially no water (Table I). The very large standard deviation of the contact angle suggested a highly heterogeneous surface wettability. This water contact

TABLE I
Water Absorption, Pore Volume, and Water Contact Angle Values^a of the As-Spun and Hydrazine- and ED-Crosslinked (0.5 wt % in Ether for 2 min) PSMA Fibers

Crosslinker	Water absorption ($\mu\text{L}/\text{mg}$)	Pore volume ($\mu\text{L}/\text{mg}$)	Water contact angle ($^\circ$)
None	0.1 (0.1)	5.8 (1.5)	77.0 (31.3)
Hydrazine	6.6 (1.7)	7.5 (1.7)	69.0 (9.6)
ED	2.2 (0.1)	2.9 (0.6)	46.0 (5.5)

^a The values in parentheses are the standard deviations.

angle showed PSMA to be not nearly as hydrophobic as PS, whose water contact angle was 90° , but slightly more hydrophobic than polyester.⁶ The overall pore volume of the membrane indicated by hexadecane retention was $5.8 \mu\text{L}/\text{mg}$. The hydrazine-crosslinked membranes wet similarly to the as-spun membranes, but the ED-crosslinked PSMA fibrous membranes became more hydrophilic, with a much reduced water contact angle of 46° . The more hydrophilic surfaces of the ED-reacted fibers may have indicated the presence of more amine groups on the fiber surfaces than the hydrazine-reacted fibers. Although hydrazine seemed to be more reactive

than ED, the presence of hydrocarbon chains in the molecules of ED may have improved the flexibility and accessibility on the fiber surfaces. Crosslinking with ED also nearly halved the pore volume of the membrane to $2.9 \mu\text{L}/\text{mg}$, as compared to the slightly enlarged or unaltered pore volume of the hydrazine-reacted membrane. This was consistent with the microscopy observation, where the ED-reacted fibers were more closely packed. The ED-reacted fibers were generally smaller, with an average diameter of 300 nm , compared to the wider range of fiber diameters ($0.2\text{--}2 \mu\text{m}$) for the hydrazine-reacted PSMA fibers. The water-absorbing capacities of the crosslinked membranes were 22 and 66 times that of the original as-spun PSMA fibrous membranes. Although the hydrophilicity and the water absorption of the two diamine reaction membranes differed, the proportion of absorbed water to the pore volume was slightly lower for the ED-reacted membrane (76%) than the hydrazine-reacted (89%) membrane. The lower ratio of the more hydrophilic membrane may have had to do with the pore sizes and size distribution, which controlled the wicking action.

The stability of crosslinked PSMA fibrous membranes The stability of the diamine-crosslinked PSMA fibrous membranes in acids and bases were

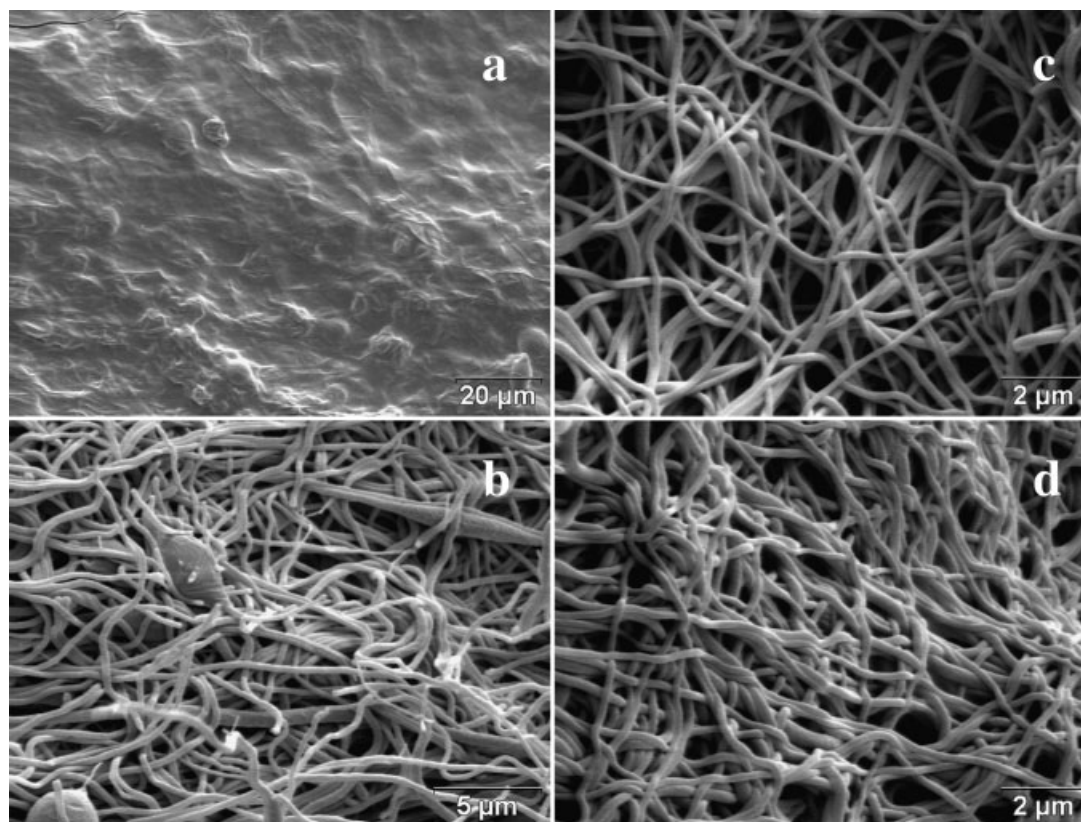


Figure 7 ED-crosslinked PSMA fibers (reacted in a 0.5 wt % solution for 2 min and heated at 150°C for 5 min) after exposure to NaOH: (a) surface of the membrane exposed to 0.01N NaOH, (b) internal fibers exposed to 0.01N NaOH, (c) fibers exposed to 0.005N NaOH for 5 min, and (d) fibers exposed to 0.005N NaOH for 5 min after acetone for 5 min.

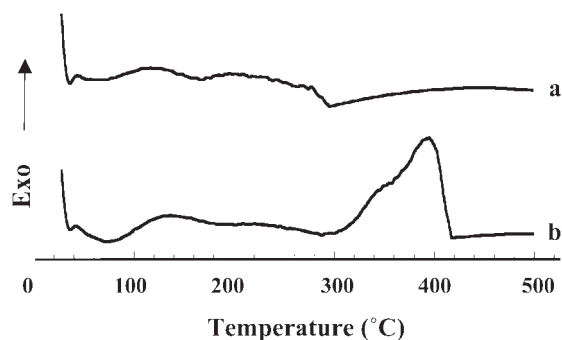


Figure 8 Thermal properties of PSMA fibers (20 wt % PSMA in DMF) after 10 min of immersion in aqueous 0.01N H_2SO_4 : (a) as-spun and (b) after the reaction with 0.5 wt % ED in ether for 2 min.

observed in H_2SO_4 and NaOH solutions at different concentrations and lengths of time. Exposure to 0.01N NaOH for 5 s at ambient temperature caused the hydrazine-crosslinked membrane to lose its fibrous structure immediately, and it balled into a gel-like material. Even at a reduced 0.005N NaOH concentration, the hydrazine-crosslinked membranes still became filmlike on the surface [Fig. 7(a)], whereas fibers located inside the membrane remained straight but slightly enlarged [Fig. 7(b)]. For the ED-crosslinked fibers, 5 s of exposure to 0.005N NaOH led the fibers to appear somewhat more relaxed and to merge at crossover points [Fig. 7(c)]. After further immersion in acetone for 5 min, the fibers became twisted and more closely packed but did not dissolve [Fig. 7(d)]. Therefore, the alkaline stability of the ED-crosslinked PSMA fibrous membranes was higher than that of their hydrazine counterparts, which again indicated superior chemical crosslinking in the PSMA fibrous membranes with ED versus hydrazine.

Acid hydrolysis of the ED-crosslinked PSMA fibrous membranes was also conducted by immersion in 0.01N H_2SO_4 for 10 min. The as-spun membranes stayed afloat on the surface of the solution, whereas the ED-crosslinked ones were completely immersed; this showed their higher hydrophilicity. DSC of the acid-hydrolyzed as-spun membrane showed that the membrane seemed to have lost both thermal transitions [Fig. 8(a)], whereas the ED-crosslinked fibers showed a broadened exotherm [Fig. 8(b)], even

wider than the ED-immersed fibers before heating [Fig. 5(b)]; this indicated that the ED-crosslinked fibrous membranes retained most of their structure.

CONCLUSIONS

Post-fiber-formation crosslinking of ultrafine fibrous membranes electrospun from PSMA was successfully demonstrated with two diamines. The immersion of the PSMA fibrous membranes in either hydrazine or ED at a 0.005% concentration followed by heating at 150°C for 5 min was shown to be highly efficient in rendering the fibrous membranes insoluble in acetone. Such crosslinking reactions with hydrazine and ED were quick and led to substantial mass gains of 14 and 20% in 1 and 2 min, respectively. Both amine-crosslinked PSMA fibrous membranes exhibited resistance to alkaline hydrolysis, with the ED-crosslinked membranes more superior and also resistant to acid (0.01N H_2SO_4). Furthermore, the ED-crosslinked PSMA fibrous membranes also became far more hydrophilic and absorbed 22 times more water than the as-spun membranes.

References

1. Belattar, N.; Mekhalif, T. *Mater Sci Eng C* 2004, 24, 507.
2. Zhou, Y.; Yu, D.; Xi, P.; Chen, S. L. *J Dispersion Sci Technol* 2003, 24, 731.
3. Wang, K.; Huang, W.; Xia, P.; Gao, C.; Yan, D. *React Funct Polym* 2002, 52, 143.
4. Li, H. M.; Chen, H. B.; Shen, Z.; Lin, S. *Polymer* 2002, 43, 5455.
5. McClain, A. R.; Hsieh, Y. L. *J Polym Sci Part A: Polym Chem* 2004, 42, 92.
6. Cécile, C.; Hsieh, Y. L. *J Appl Polym Sci* 2009, 113, 2709.
7. Cécile, C.; Hsieh, Y. L. *J Appl Polym Sci* 2009, 114, 784.
8. Hu, G. H.; Lindt, J. T. *Polym Bull* 1992, 29, 357.
9. McCormick, C. L.; Chang, Y. *Macromolecules* 1994, 27, 2151.
10. Li, C.; Pan, X.; Hua, C.; Su, J.; Tian, H. *Eur Polym J* 2003, 39, 1091.
11. Staudner, E.; Kyselá, G.; Kruppová, T.; Turayová, Z. *Eur Polym J* 1997, 33, 463.
12. Uglea, C. V.; Panaitescu, L.; Spiridon, D.; Ursu, D.; Popa, I.; Ottenbrite, R. M. *J Biomater Sci Polym Ed* 1996, 8, 269.
13. Chiang, W. W.; Ching-Liang, C. *Polymer* 1998, 39, 227.
14. Spridon, D.; Panaitescu, L.; Ursu, D.; Uglea, C. V. *Polym Int* 1997, 43, 175.
15. Liu, H. Q.; Hsieh, Y.-L. *J Polym Sci Part B: Polym Phys* 2002, 40, 2119.