

Organic and Aqueous Compatible Polystyrene–Maleic Anhydride Copolymer Ultra-Fine Fibrous Membranes

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ABSTRACT: Polystyrene–maleic anhydride copolymer (PSMA, $M_v = 700$ kDa) was synthesized and efficiently processed into 400 to 600 nm diameter fibers via electrospinning from either 20 wt % dimethylformamide or 25 wt % dimethylsulfoxide solution. Crosslinking of PSMA was effective by adding glycerol and poly(vinyl alcohol) (PVA) ($M_w = 31$ – 50 kDa) in the dimethylformamide and dimethylsulfoxide solutions, respectively. The PSMA fibers containing glycerol at 29.4 mol% were auto-crosslinked whereas those with 12.9 mol% (2 wt %) glycerol and 15.4 mol% (0.75 wt %) PVA required heating to induce intermolecular esterification. Heat-induced crosslinking with glycerol was more effective in rendering the PSMA fibrous membranes insoluble in all solvents whereas that with PVA remained soluble in most solvents except for acetone and tetrahydrofuran. The crosslinked fibrous membranes

had improved thermally stability and retained physical integrity upon exposure (2 hr at 40°C) to carbon disulfide, the solvent for Friedel–Craft reactions of the styrene moiety. Hydrolysis (0.01N NaOH) of the auto-crosslinked fibrous membrane significantly improved its hydrophilicity by reducing the water contact angles from 90.6° to 62.5° in a matter of seconds. These ultra-high specific surface PSMA fibrous membranes have shown superior organic and aqueous solvent compatibility to be used as highly reactive and easily retrievable supports for solid-phase synthesis. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 784–793, 2009

Key words: poly(styrene-*co*-maleic anhydride); ultra-fine fiber; electrospinning; crosslinked; membrane; solvent compatibility; glycerol; poly(vinyl alcohol)

INTRODUCTION

Merrifield resins,¹ in the form of micrometer size beads of divinylbenzene-crosslinked copolymers of styrene and chloromethylstyrene, have been widely used as solid supports for organic synthesis. For these solid supports to work, efficient swelling of the resin beads by appropriate reagents must take place to facilitate the loading and diffusion of the reactants, the mixing of reagents as well as the separation of products. In the case of Merrifield resins, their use is limited by their incompatibility with some organic solvents and nonwetting or swelling in aqueous solutions. The loose-beaded forms also require additional centrifugation, filtration, collection, and handling.

It is therefore desirable to design new resins that are both organic and aqueous compatible and in continuous forms that do not require extra separation processes. Fibrous membranes produced by electrospinning consist of ultra-fine fibers with typically sub-micrometer diameters² and offer many advantages including one to two order higher specific surfaces than beaded resins, simple separation,

and easy handling. The main challenge of this approach to reactive resins is to create intermolecular crosslinking within and among the fibers to be compatible with, yet to retain their physical integrity in, common organic solvents. Furthermore, the fibrous membranes can be made aqueous compatible if hydrophilic functional groups are introduced.

We have coupled electrospinning of binary water-soluble polymer systems with post-fiber formation crosslinking to generate ultra-fine fibers with 3D polymer network and stimuli-responsive swelling behaviors.^{3,4} In addition to the expandable polymer networks within the fibers, the fibrous membranes were intrinsically porous with fiber diameters and interfiber pore dimensions from less than 100 nm to several hundred nanometers. The ultra-high specific surfaces of these ultra-fine fibrous membranes enabled them to exhibit instantaneous size and shape change behaviors at the onset of external signals, such as temperature and pH,³ while swell in both organic and aqueous media.⁴

Maleic anhydride (MA) is highly reactive and can be copolymerized with styrene to form polystyrene maleic anhydride (PSMA). PSMA is chemically more versatile than polystyrene because of the dual reactivity of both styrene and MA. The chemical reactivity of the MA moiety has made PSMA polymers common additives in blends or composites to

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achieve desirable interfacial effects and as dispersants in the soluble forms in its most notable application.⁵ The PSMA polymers in these cases tend to be low molecular weights. On polystyrenes of higher molecular weights, MA has been incorporated via acylation⁶ and grafting⁷ reactions. We have also synthesized divinylbenzene-crosslinked PSMA and introduced dicarboxylic acid and dihydroxyphosphino functionalities to allow complexation with divalent metal ions, i.e., Pb(+2), Cu(+2), Cr(+3), and Ni(+2).⁸ To synthesize long-chain PSMA and to process the copolymer into solids, in particular, ultra-fine fibers would take advantage of its chemical versatility and excellent physical attributes of continuous, flexible, and ultra-fine specific surfaces for reactive solid supports.

More recently, we have synthesized PSMA and electrospun the copolymer into millimeter-thick membranes of sub-micrometer to micrometer size fibers.⁹ By using mixed solvents or adding nonsolvents, the fiber diameters could be further reduced, and in the case of toluene or cyclohexane, to 200–300 nm. However, these PSMA fibrous membranes remain soluble in solvents. While adding styrene or divinylbenzene crosslinker in the electrospinning solution allowed electrospinning, the fibers generated could not be rendered insoluble in common solvents for PSMA.

The objective of this work was to create cross-linked PSMA fibrous membranes by ways of electrospinning of binary polymer systems. The first criterion is to find common solvents that dissolve both polymer components and, at the same time, are amenable to electrospinning. To render PSMA insoluble in its solvents, the second component must be capable of forming multiple covalent bonds with PSMA.

Toward these, two polyols, a low molecular weight poly(vinyl alcohol) (PVA) (31–50 kDa), and a short triol, glycerol, both capable of esterification with the MA of PSMA, were selected. PVA is a water-soluble and biocompatible polymer and, in high molecular weights, has been electrospun into nanofibers.¹⁰ Glycerol is also water soluble and

widely used in medical and pharmaceutical preparations.¹¹ To form homogeneous solutions with PSMA that are also conducive to electrospinning, dimethylsulfoxide (DMSO) and DMF were used as the solvents with PVA and glycerol, respectively. The polyol and solvent effects on the electrospinning process and the structure of the fibrous membranes were investigated. Esterification between PSMA and polyols was studied and the crosslinking efficiency was determined by the solubility in acetone, a solvent for PSMA. The stability of the crosslinked fibers in diverse solvent environments and, particularly in alkaline solution (hydrolysis), in carbon disulfide (Friedel-Craft) was also studied.

EXPERIMENTAL

Materials and reagents

Acetone, dimethylformamide (DMF), DMSO, glycerol, and tetrahydrofuran (THF), all from Aldrich, were used without further purification (Table I). PSMA copolymers were synthesized via free-radical polymerization in toluene for 4 hrs at 90°C, under reflux and nitrogen atmosphere following a procedure previously used in our laboratory.⁸ Because of the charge-transfer-forming ability of the MA, alternating MA copolymer with styrene¹² is formed. The [S]/[AIBN] molar ratio was of 2,000 to achieve an M_v of 700 kDa was determined with a Cannon-Fenske viscometer according to the Mark-Houwink-Sakurada equation. PVA was purchased from Aldrich with an M_v range of 31 to 50 kDa and was used without further purification.

Fiber formation of PSMA

PSMA was dissolved in either DMF or DMSO under constant stirring at ambient temperature. For electrospinning, each polymer solution was placed in a capillary with a stainless steel electrode immersed in the solution and connected to a power supply (Gamma High Voltage Supply, ES 30-0.1 P). Grounded counter electrode was connected to

TABLE I
Physical Properties (20°C and 25°C) of PSMA Solvents and Glycerol¹³

Solvent	Boiling Point (°C) T_b	Viscosity (cp) η (25°C)	Density (g/mL) ρ	Surface Tension (dyn/cm) γ (20°C)	Hildebrand Solubility Parameter (cal/cm ³) ^{1/2} δ	Dielectric Constant ϵ (20°C)
Acetone	57	0.31	0.79	23.7	9.76	20.7
DMF	153	0.79	0.94	35.0	12.1	36.7 (25°C)
DMSO	189	1.99	1.10	42.9	12.0	46.7
THF	64	0.55	0.89	28.0	18.6	7.6
Glycerol	182	934	1.26	64.0	16.5	56.0

TABLE II
Effects of Crosslinkers in 30 wt % PSMA Solution^a on Electrospinning

Crosslinkers	Concentration (wt % of PSMA)	Observation	Voltage (kV)	Continuous Electrospinning ^b Time (h)
Glycerol	None	Blocked jet	14	–
	1	Blocked jet	9	<0.5
	2	Fibers	5	~ 48
	4.5	Fibers	6	~ 24
PVA	None	None	5-15	–
	0.75	Fibers, beads	6	~ 48

^a Glycerol was added to the DMF solution and PVA was added to DMSO solution.

^b Collected at 7-inch distance for 5 mL solution.

aluminum foil collector. The electrospinning conditions of voltages between 6 and 11 kV and distances of 7 inches were used to deform the pendant drop at the tip of the capillary into a conical shape. At a critical voltage, electrostatic forces acting on the surface of the cone overcome the surface tension of the solution, and a jet is ejected and accelerated toward the grounded collector by the electrical field generated between the electrode and the counter electrode. The obtained PSMA membranes were detached from the collectors and dried under vacuum at room temperature for 10 hrs.

Preparation of crosslinked PSMA fibers

Glycerol at concentrations ranging from 1 to 4.5% (wt % of PSMA/DMF solution) was added dropwise to the 30% PSMA/DMF solution with fast stirring. PVA was added to the PSMA/DMSO solution at 0.75% (wt % of PSMA/DMSO solution). Fibers were formed through the electrospinning of the solutions and collected on Al foil. They were then dried in vacuum at ambient temperature for 12 hrs and detached from the aluminum foil. To induce esterification between the hydroxyls of either glycerol or PVA and the MAs of PSMA, the fibrous membranes were heated from 60 to 160°C for 2 min. The resulted membranes were immersed in acetone, THF, DMSO, and carbon disulfide for various lengths of time depending on the solvent. Once removed from the solvent and dried, their stability was observed and their appearance was compared with one of the original membranes.

Hydrolysis

Hydrolysis of selected fibrous membranes was carried out in aqueous 0.005N NaOH solution for 1 hr to hydrolyze the anhydride to sodium carboxylate. The membranes were then washed twice with 0.005N HCl followed by water to remove the traces of NaCl, and they were then dried under vacuum for 17 hrs at 60°C.

Characterization

The fiber and membrane morphology was observed with a scanning electron microscope (XL30-SFEG, FEI/Philips) at 5 kV accelerating voltage with gold coating. Differential scanning calorimetry (DSC) analyses were conducted (DSC-60 Shimadzu, Japan) using ~ 5 mg samples at a 10°C/min heating rate in dry N₂. Thermal stability studies of the fibers were also measured using a thermal gravimetric analyzer (TGA-50, Shimadzu, Japan) from room temperature to 500°C at 10°C/min heating rate in dry N₂. Water contact angle and liquid retention were determined by a surface tensiometer (KRÜSS, K14) according to our previous report.¹⁴ The method measures the simultaneous wetting and wicking of a liquid in a vertical sample strip with its lower edge forced into contact with a liquid.

The pore volumes of the PSMA fibrous membranes were determined by saturation in hexadecane, a completely wetting liquid. Saturation gives maximum liquid retention C_m that includes liquid retained in the interfiber pores as well as on the surface of the porous membrane. The maximum liquid-retention capacity (C_m) of the sample is the maximum uptake of a total wetting liquid, such as hexadecane, in the sample before (W_d) and after (W_v):

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

The water-wetting contact angle (θ) was determined by the wetting force in water (F_w) with p and γ , the sample-liquid interfacial perimeter and water-surface tension, respectively.

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

RESULTS AND DISCUSSION

Fiber formation with glycerol and PVA

PSMA was soluble in acetone, DMF, DMSO, and THF. The solubility was highest in DMF at 50 wt %, and

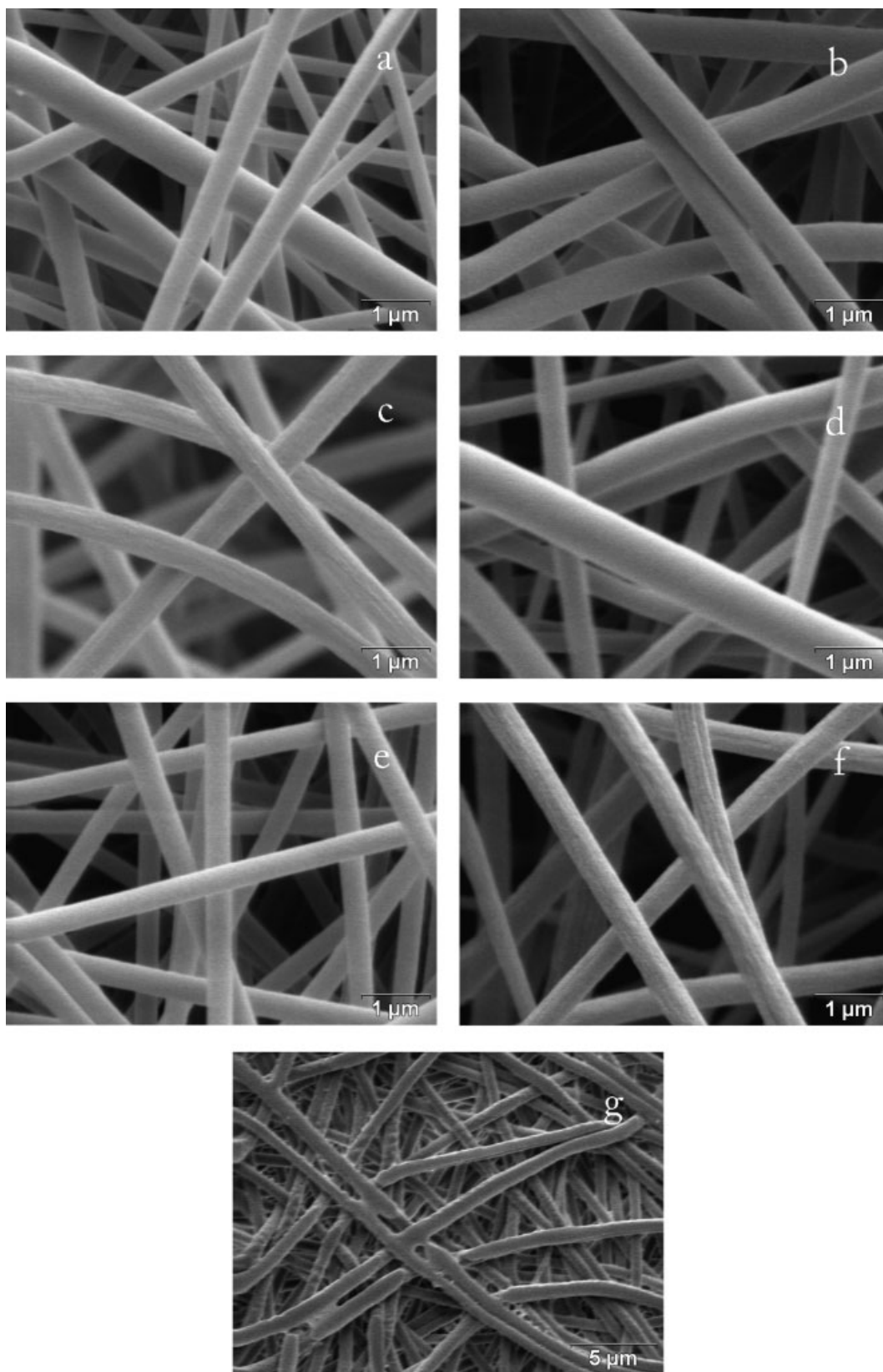


Figure 1 PSMA fibers electrospun from 30% DMF solutions with (a) 2% glycerol and (b) 4.5% glycerol; and from 30% DMSO solution with (c) 0.75% PVA; (d, e, f) a, b, c heated (160°C, 2 min); and (g) d immersed in acetone for 5 min.

followed by 40 wt % in DMSO. Fiber formation could be sustained by electrospinning of the PSMA solutions at 20 to 40 wt % in DMF or at 15 to 25 wt % in DMSO. Both DMF and DMSO have moderate surface tensions and relatively high dielectric constants, the characteristics highly desirable for electrospinning. The most efficient production of PSMA fibrous membranes was found with the 20 wt % DMF and the 25 wt % DMSO solutions.⁷

Heating the PSMA fibers electrospun from 20 wt % DMF solution at 160°C for up to 24 hrs did not alter their solubility in acetone. This observation conformed that the MA moiety in the structure was incapable of auto-crosslinking, pointing to the need for crosslinkers. The small triol glycerol and low molecular weight PVA polyol were thus added to the 30 wt % PSMA solutions.

Glycerol has three hydrophilic hydroxyl groups that are responsible for its hygroscopic nature and solubility in water. It is also soluble in most organic solvents and highly miscible with DMF. Therefore, DMF was the ideal solvent for the PSMA-glycerol mixtures. The maximum solubility of glycerol in the 30 wt % PSMA DMF solution was 5.9 wt % of the solution, or 38 mol% of PSMA (Table II). Glycerol was added at three levels of 1, 2, and 4.5 wt % of the PSMA solution or 6.5, 12.9, and 29.4 mol% of PSMA, respectively. Glycerol has higher surface tension and dielectric constant than DMF, thus should facilitate fiber generation. However, with 1 wt % glycerol, the PSMA concentration was still too high and solution too viscous to sustain continuous jet. Electrospinning efficiency was improved at higher glycerol contents of 2 and 4.5 wt %.

In contrary to glycerol, DMSO was the only solvent among the PSMA solvents that easily dissolves PVA. DMSO was thus used to mix PVA with PSMA. Although electrospinning the 30 wt % PSMA solution did not produce fibers, adding 0.75 wt % PVA stabilized the jet and improved fiber formation. Relatively low voltages were necessary to generate thick fibrous membranes (Table II). The 0.75 wt % PVA, equivalent to 15.4 hydroxyl-to-maleic anhydride mol%, was the maximum concentration possible to keep the PSMA solution homogeneous.

The addition of glycerol at either 2 or 4.5 wt % to the 30 wt % PSMA solution in DMF did not seem to affect the fiber sizes or surface morphology [Fig. 1(a,b)]. The fibers were cylindrical and relatively uniform in diameters ranging from 400 to 600 nm, but showed slight surface roughness. Adding 0.75 wt % of PVA to the PSMA solution caused striated grooves on fibers [Fig. 1(c)] as well as few beaded structures. From the perspective of electrospinning, the difference between the two solvents, i.e., DMSO and DMF, is considered small. Although the higher viscosity and surface tension of DMSO would

TABLE III
Solubility of Glycerol- and PVA-Containing PSMA Fibers after 2 hrs Immersion

2 min-Heat Treatment	Solvent	2	Crosslinker (wt % PSMA)	
			Glycerol 4.5	PVA 0.75
None	Acetone	S	I	S
	THF	S	I	S
	DMSO	S	I	S
60°C	Acetone	S	I	I
	THF	NA	I	PS
	DMSO	NA	I	S
160°C	Acetone	I	I	I
	THF	I	I	I
	DMSO	I	I	S

S, soluble; I, insoluble; PS, partially soluble.

require higher driving force, its higher dielectric constant should have an opposite effect. The main difference between the two crosslinking systems may have to do with their solubility, i.e., PVA in DMSO and glycerol in DMF, their compatibility or miscibility with PSMA in the respective solvents and their molecular sizes. The observed surface striations on the fibers containing PVA suggest that PVA may be more phase-separated from PSMA and concentrates more on the fiber surfaces lowering the surface energy.

Heat-induced crosslinking

The as-spun PSMA fibers as well as those electrospun from solutions containing either 2 wt % glycerol or 0.75 wt % PVA were all soluble in acetone, THF, and DMSO as expected (Table III). The as spun PSMA fibers containing 4.5 wt % glycerol, on the other hand, became insoluble in these solvents, indicating auto-crosslinking at this higher glycerol content and ambient temperature. These observations showed that the electrospun PSMA fibers with lower quantities of either glycerol or PVA required further heating.

To induce esterification of PSMA fibers containing 2 wt % glycerol or 0.75 wt % PVA, the as spun fibrous membranes were heated for 2 min at either 60 or 160°C. The fibers that contained 2 wt % glycerol became insoluble in acetone, THF, and DMSO after being heated at 160°C, but not at 60°C. Heating at 60°C was sufficient to render the fibers containing 0.75 wt % PVA insoluble in acetone. However, heating at 160°C was necessary to render these fibers insoluble in THF, although the fibers remain soluble in DMSO (Table III). Under the conditions studied, heat-induced crosslinking with glycerol seemed to be more efficient than with PVA. Heating at 160°C for 2 min caused the fibers containing 2 wt % glycerol to become insoluble in all the three solvents

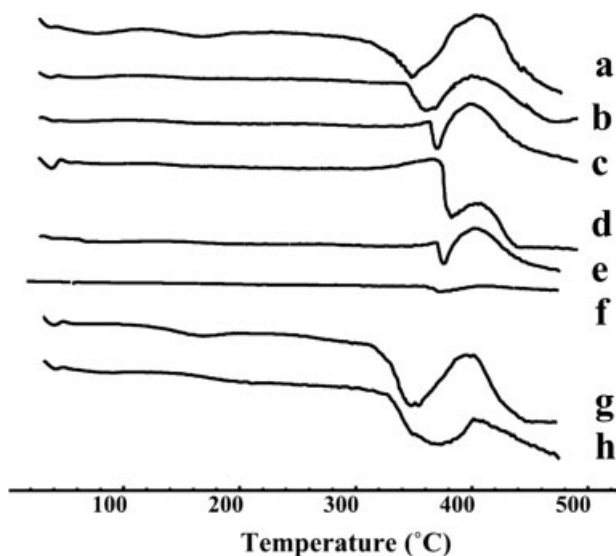


Figure 2 PSMA fibers electrospun from 30 wt % DMF solutions with (a) no glycerol, (b) 1% glycerol, (c) 2% glycerol, (d) 4.5 wt % glycerol (of PSMA) and heated (160°C, 2 min), (e) a, (f) d; and from 30 wt % DMSO solutions with (g) 0.75 wt % PVA (of PSMA), (h) g heated (60°C, 2 min).

whereas those with 0.75 wt % PVA were rendered insoluble only in acetone (60°C, 2 min) and THF (160°C, 2 min).

The heating process caused the fibrous membranes to shrink to about one third of their original sizes and to become more rigid, but did not alter their white color. The fiber sizes were reduced slightly and became less uniform, but the fiber surfaces remained similar [Fig. 1(d–f)]. The fiber size reduction seemed to be greater with the fibers that contain higher amounts of glycerol [Fig. 1(d,e)] and with those containing PVA [Fig. 1(f)]. The fiber size reduction, which may have to do with dissolution of uncrosslinked PSMA and/or crosslinkers in the acetone wash, however, did not cause significant surface change. The PSMA fibers electrospun with 2 wt % glycerol and heated (160°C, 2 min) remained insoluble in acetone for 5 min, but swelled and enlarged to about 2 μm in diameters, and merged with adjacent fibers and at crossover points [Fig. 1(g)]. The PSMA fibers electrospun with PVA and heated (160°C, 2 min) were also insoluble.

The most likely crosslinking reaction is the formation of intermolecular ester bonds between the MA of the PSMA and the hydroxyls of either glycerol or PVA. The fibers containing 2 wt % glycerol became insoluble in all the three solvents whereas those with 0.75 wt % PVA remained soluble in DMSO indicated that esterification between the MA and the glycerol hydroxyl was higher than that in the PVA hydroxyl. The more effective crosslinking by glycerol, even at slightly lower molar content, may be attributed to better mixing and distribution of the

smaller glycerol among PSMA molecules than the much longer PVA. In addition to crosslinking, dehydration of the free carboxylic acids of PSMA could also occur on heating, creating additional intermolecular bonds. Furthermore, intramolecular ester bonds may also be formed, but would not contribute to the necessary intermolecular crosslinking to resist dissolution in solvents.

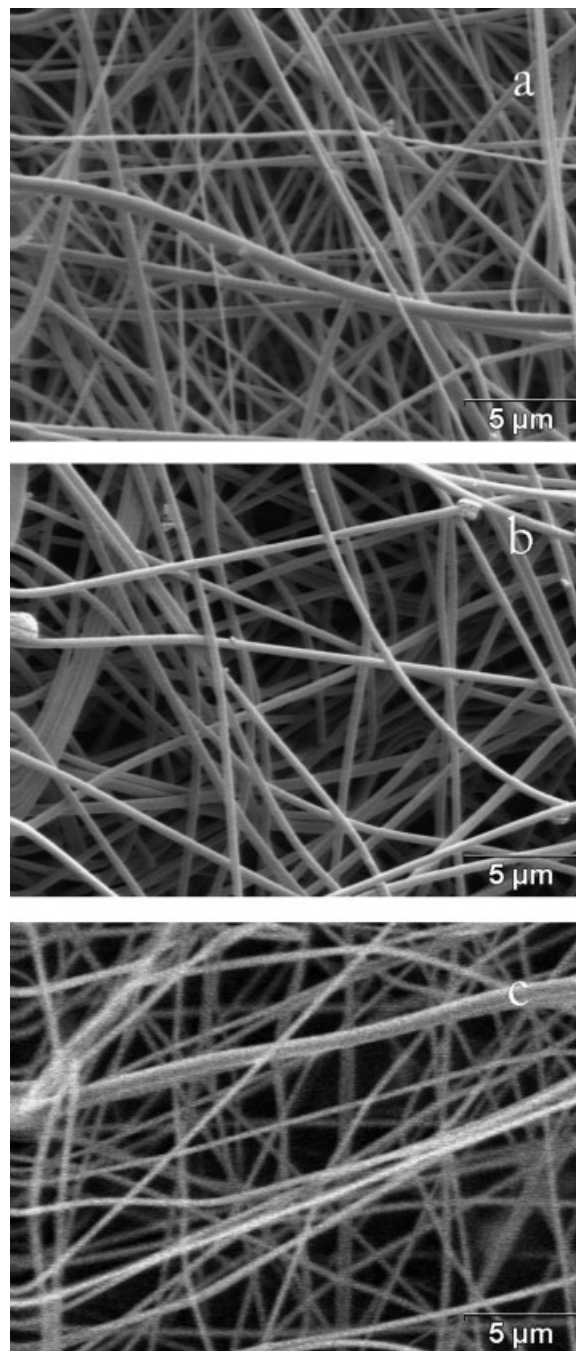


Figure 3 PSMA fibers electrospun from 30% DMF solutions with (a) 2 wt % glycerol (of PSMA), (b) 4.5 wt % glycerol (of PSMA) and heated at 160°C for 2 min and (c) 5 min.

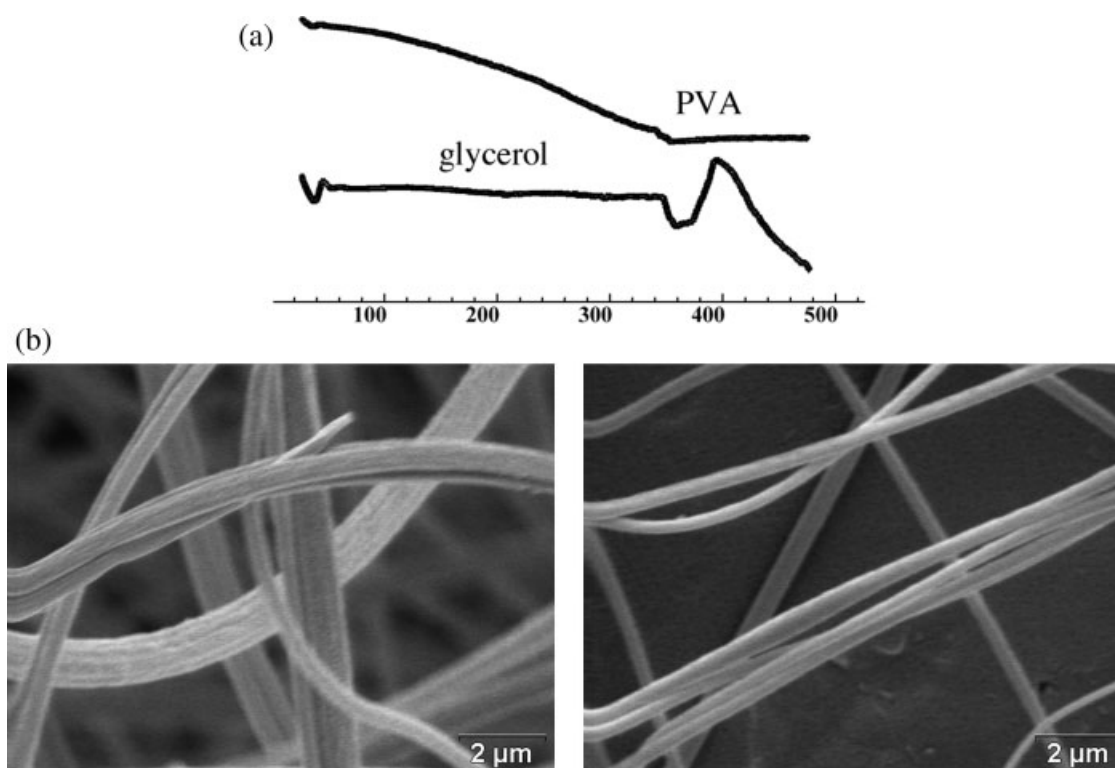


Figure 4 Carbon disulfide (48°C, 2 hrs) exposure on heated (160°C, 2 min) PSMA fibers. (a) DSC, (b) SEMs: left 0.75% PVA and right 2% glycerol.

Thermal properties

The DSC thermogram of PSMA showed two very weak endotherms at 70 and 150°C, attributing to the evaporation of adsorbed moisture and the glass transition, respectively [Fig. 2(a)]. The as-spun PSMA fibers also showed an endothermic peak at 348°C and an exothermic peak at 409°C, corresponding to the two stages of thermal degradation of the copolymer [Fig. 2(a)]. The decomposition at 348°C, higher than that of the homopolymer PS, is due to the presence of the MA moieties in the copolymer PSMA backbone. The exothermic decomposition at 409°C is believed to be caused by chain scission involving the styrene moiety, possibly by the unzipping mechanism.

The heated as-spun PSMA fibers showed significantly reduced peak sizes of both the endotherm and exotherm [Fig. 2(e)]. However, only the endothermic temperature was raised. This observation indicates that heating most likely induces chemical changes involving the MA moieties. The fact that these heated fibers remain soluble suggest that these changes and/or reactions are mainly intramolecular.

The addition of either glycerol [Fig. 2(b,c)] or PVA [Fig. 2(d)] caused the disappearance of the two endotherms at 70 and 150°C. The absence of the 70°C endotherm could possibly be due to hydrogen bonding between the free hydroxyls and carbonyls.

The disappearance of the glass transition at 150°C in the crosslinker-containing fibers could be due to the reduced segmental motions of the PSMA chains in the presence of the added crosslinkers. With added glycerol, the decomposition endotherm raised to above 360°C, while reduced in intensity [Fig. 2(b-d)]. These increases in endothermic temperatures seemed to be associated with increasing quantities of glycerol, suggesting higher extent of crosslinking. Similar thermograms of the heated PSMA [Fig. 2(e)] and the heated PSMA with 2 wt % glycerol [Fig. 2(c)] suggest that the crosslinking, although appearing to be intramolecular in the former and intermolecular in the latter, has similar effects on thermal decomposition of PSMA. The reduced decomposition peaks of heat-treated fibers, particularly those with 4.5% glycerol [Fig. 2(f)], might be caused by the increased crosslinking.

The PSMA fibers with PVA had similar decomposition transitions [Fig. 2(g)] as those without any crosslinker [Fig. 2(a)], but a slightly larger endotherm. Heating these fibers further broadened and raised the endotherm to a higher temperature [Fig. 2(h)]. The absence of the exotherm at 409°C may indicate ester interchange interfering with the chain scission.

Stability in carbon disulfide

For the crosslinked PSMA fibrous membranes to be effective resin supports, the stability was examined

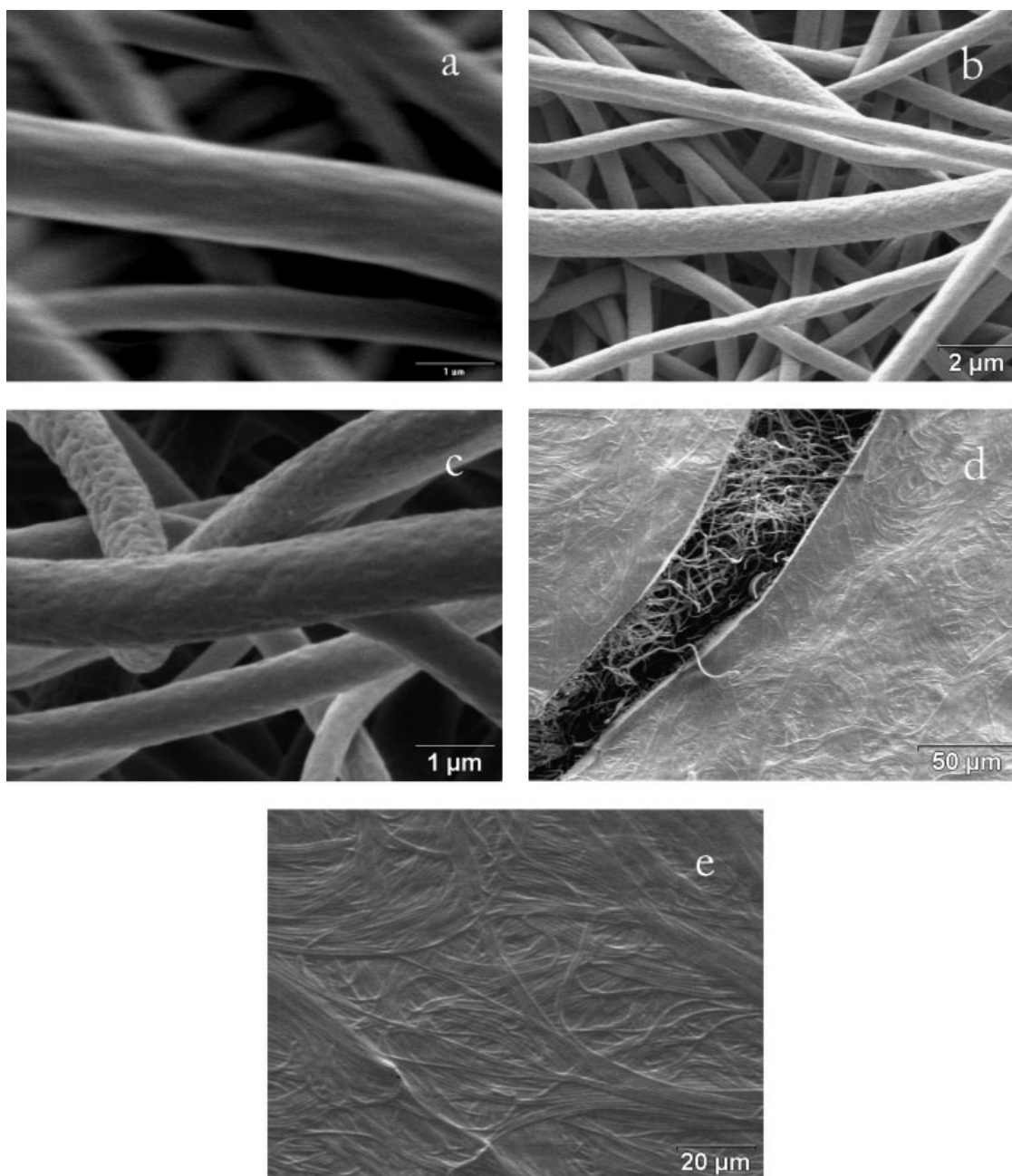


Figure 5 Aqueous hydrolysis (NaOH, 0.01N) of PSMA fibers electrospun with 4.5% glycerol and heated (160°C, 2 min) for: (a) 0.2, (b) 0.5, (c, d) 2, (e) 50 min.

in carbon disulfide, the solvent for Friedel-Craft reactions of the styrene moiety, at 48°C for 2 hrs (Fig. 3). Both the heated (160°C, 2 min) fibers with 0.75% PVA and 2% glycerol remained stable in carbon disulfide. For the membranes containing glycerol, no changes in their fibrous structures were observed after immersion for 2 hrs [Fig. 4(b)]. In addition to keeping their original stability, the thermal transitions of the fibers appeared at similar temperatures [Fig. 4(a)]. In comparison, the PVA-containing fibers lost their fibrous forms and turned into a gel-like structure instantly after immersion in

carbon disulfide (Table III). As a correlation between the DSC graphs and the scanning electron microscope images of the PSMA fibers crosslinked with glycerol or PVA, no thermal transition was observed likely due to chemical changes [Fig. 4(a)]. The better stability in CS₂ again confirmed the better cross-linked structure with glycerol.

Alkaline hydrolysis

Alkaline hydrolysis of the crosslinked PSMA membranes was intended to increase their surface

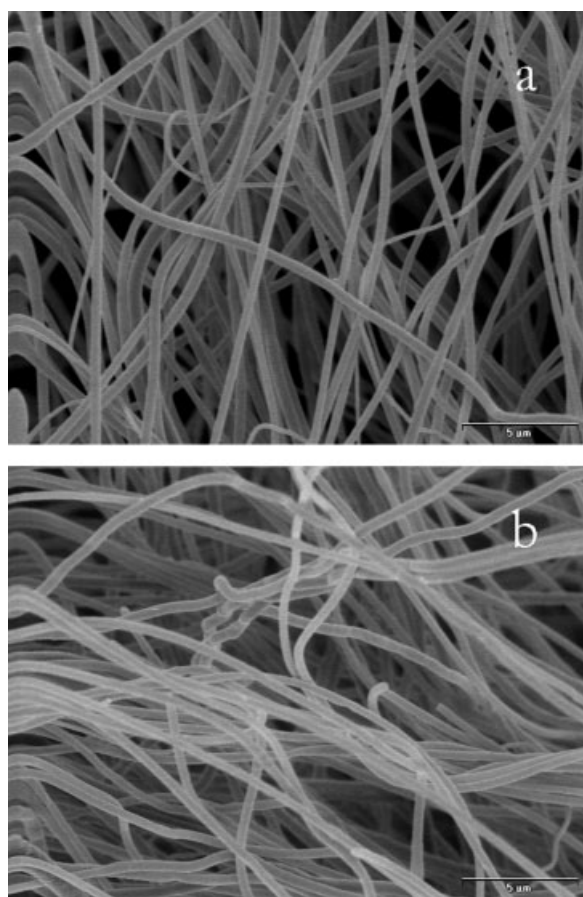


Figure 6 Effect of hydrolysis (NaOH, 0.005N, 1 hr) on PSMA fibers containing 2% glycerol (a) before and (b) after heating (160°C, 2 min).

hydrophilicity by transforming each of the free MA of PSMA into two carboxylic acid groups. This also allowed observation of the alkaline stability of the fibrous membranes and comparison with that in the organic media (carbon disulfide).

The auto-crosslinked glycerol (4.5 wt %) membranes were hydrolyzed in 0.01N NaOH at ambient temperature for varying lengths of time up to 50 min. After hydrolysis for 0.5 min [Fig. 5(a,b)], the fibers were retained in their fibrous forms [Fig. 5(a,b)]. The longer hydrolysis of 2 min caused the membrane surface to become a film-like material [Fig. 5(c)]. The fibers located inside the membrane retained their forms, but seemed slightly enlarged [Fig. 5(d)]. The morphological effects remained similar for hydrolysis that lasted 10 min. After the 50-min hydrolysis, the fibers were dissolved in acetone to sufficiently turn into a film-like material [Fig. 5(e)]. Instead of fibers, only a thin layer with homogeneous and smooth surface was observed.

For the fibers containing 2 wt % glycerol and heated (160°C for 2 min), hydrolysis was performed at a lower 0.005N NaOH concentration but for lon-

TABLE IV
Pore Volume (H , $\mu\text{L}/\text{mg}$) and Water Wettability (θ , $^\circ$) of PSMA Fibrous Membranes as Affected by Crosslinker (in wt % of PSMA), Heat Treatment and Aqueous Hydrolysis

	Pore Volume ($\mu\text{L}/\text{mg}$)	θ ($^\circ$)
As spun		
None	6.0 (1.5)	90.6 (22.9)
0.75% PVA	18.5 (6.3)	85.9 (0.0)
4.5% glycerol	17.7 (5.2)	78.8 (5.6)
Heated (160°C, 2 min)		
0.75% PVA	26.3 (8.1)	87.4 (0.9)
2% glycerol	8.7 (0.4)	90.8 (2.6)
4.5% glycerol	11.3 (9.6)	86.7 (1.5)
Hydrolysis (0.01N NaOH) of membranes with 4.5 wt % glycerol and heated (160°C, 2 min)		
5 sec	5.3 (5.5)	72.4 (11.6)
15 sec	3.3 (2.9)	64.9 (13.3)
30 sec	2.3 (1.1)	62.5 (9.8)

ger time (1 hr). No apparent alteration in neither fiber nor membrane morphology was observed (Fig. 6). However, alkaline hydrolysis caused the membranes to become very rigid and to lose weights, 6% mass loss for the PSMA and 4% for the glycerol-containing (2 wt %) fibers. These weight losses might be due to dissolution of the uncrosslinked fragments of PSMA and glycerol in the dilute alkaline solution.

Wetting and pore volume of fibrous membranes

The PSMA fibrous membranes were hydrophobic with a 90.6° water contact angle (Table IV). The fibrous membranes containing glycerol (4.5 wt %) and PVA became slightly more hydrophilic, with lowered water contact angles of 78.8° and 85.9°, respectively. The interfiber pore volumes of the fibrous membranes were significantly increased from 6.0

TABLE V
Mass Gain (in Fraction of Original) of PSMA Fibrous Membranes after 48 hrs of Imersion in Acetone, DMF or Water

	Heating	Acetone	DMF	Water
2% Glycerol	160°C, 2 min	2	1	2.3
4.5% Glycerol	None	1.4	0.9	1.2
0.75% PVA	60°C, 2 min	Soluble	Soluble	1.2

$\mu\text{L}/\text{mg}$ of the as-spun to 17.7 and 11.3 $\mu\text{L}/\text{mg}$ for those with glycerol and PVA, respectively.

Heat treatment (160°C for 2 min) seemed to affect the pore structure of the membranes more than the wetting behavior. The interfiber pore volume of the PVA-containing fibrous membranes was further increased, indicating even lower fiber packing, whereas the opposite was observed with those crosslinked with glycerol.

Hydrolysis (0.01N NaOH) of the PSMA fibers electrospun with 4.5 wt % glycerol was then conducted over a range of short reaction times. In a matter of seconds, hydrolysis significantly improved the membrane hydrophilicity. The water contact angles of the fibrous membranes were reduced to 72.4°, 64.9° and 62.5° after 5, 15, and 30 sec, respectively. The interfiber pore volumes also decreased to 5.3, 3.3, and 2.3 $\mu\text{L}/\text{mg}$, respectively.

Although addition of crosslinkers and heating affected the pore structure and slightly improved membrane hydrophilicity, hydrolysis significantly densified fiber packing as well as improved hydrophilicity of the crosslinked membranes.

CONCLUSION

PSMA ($M_v = 700$ kDa) synthesized by free-radical polymerization was soluble in acetone, DMF, DMSO, and THF, reaching highest solubility of 50 wt % in DMF and 40 wt % in DMSO. Electrospinning of PSMA solution, either 20 wt % in DMF or 25 wt % in DMSO, was highly efficient, generating uniform, cylindrical fibers with 400 to 600 nm diameters. The additions of glycerol and PVA polyols in these solutions did not alter electrospinning efficiency nor the fiber sizes, but increased interfiber pore volumes of the membranes by two- to three-fold, or reduced fiber packing significantly. The PSMA fibers with 29.4 mol% glycerol were auto-crosslinked whereas those with 12.9 mol% (2 wt %) glycerol and 15.4 mol% (0.75 wt %) PVA required heating to induce intermolecular esterification between MA and the hydroxyls of either glycerol or PVA. Heating caused the fibrous membranes to shrink in dimensions as well as become stiff, although the effects on fiber packing were opposite

between the two polyols. Hydrolysis (0.01N NaOH) of the auto-crosslinked fibers significantly improved the membrane hydrophilicity, by reducing the water contact angles from 90.6° to 62.5° in a matter of seconds while also densified fiber packing. Hydrolysis (0.005N NaOH, 1 hr) of the fibrous membranes crosslinked with glycerol (2%) did not affect fiber morphology, but caused the membranes to become more rigid. Crosslinking with glycerol was more effective in rendering the PSMA fibrous membranes insoluble in all solvents whereas that with PVA remained soluble in most solvents except for acetone and THF. The fibrous membranes crosslinked with glycerol also remained stable in carbon disulfide, the solvent for Friedel-Craft reactions of the styrene moiety. These findings showed that reactive PSMA could be efficiently synthesized and fabricated into ultra-high specific surface fibrous membranes that were stable in organic solvents and could be made hydrophilic by alkaline hydrolysis. These organic and aqueous compatible, yet resistant, reactive styrene-based membranes should find expanded and superior applications as highly reactive and easily retrievable supports for solid-phase synthesis.

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