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Synthesis of Ultrafine Poly(styrene-maleic anydride) and Polystyrene Fibers by Electrospinning

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ABSTRACT: Fiber formation from atactic polystyrene (*a*PS) and alternating poly(styrene-maleic anhydride) (PSMA) synthesized by free radical polymerization (AIBN, 90°C, 4 h) were investigated by electrospinning from various solutions. *a*PS was soluble in dimethylformamide (DMF), tetrahydrofuran (THF), toluene, styrene, and benzene, whereas PSMA was soluble in acetone, DMF, THF, dimethylsulfoxide (DMSO), ethyl acetate, and methanol. *a*PS fibers could be electrospun from 15 to 20% DMF and 20% THF solutions, but not from styrene nor toluene. PSMA, on the other hand, could be efficiently electrospun into fibers from DMF and DMSO at 20 and 25%, respectively. Few PSMA fibers were, however, produced from acetone, THF, or ethyl acetate solutions. Results showed that solvent properties and polymer–solvent miscibility strongly influenced the fiber formation from electrospinning. The addition of solvents, such as THF, generally improved the fiber uniformity and reduced fiber sizes for both polymers. The nonsolvents, however, had opposing effects on the two polymers, i.e., significantly reducing PSMA fiber diameters to 200 to 300 nm, creating larger and irregularly shaped *a*PS fibers. The ability to incorporate the styrene monomer and divinylbenzene crosslinker in *a*PS fibers as well as to hydrolyze PSMA fibers with diluted NaOH solutions demonstrated potential for post-electrospinning reactions and modification of these ultrafine fibers for reactive support materials. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2709–2718, 2009

Key words: poly(styrene-maleic anhydride); polystyrene; solvent effects; electrospinning; monomer and crosslinker additives

INTRODUCTION

Electrospinning of polymer solutions or melts with a wide range of chemical structures has been extensively reported to create fibers with diameters one to two orders of magnitudes smaller than those of natural and conventionally spun fibers.[1,2] Polystyrene (PS), one of the first polymers to be electrospun,[3,4] is a chemically and structurally versatile polymer because of its easy synthesis by several polymerization mechanisms to a variety of tacticities and chain lengths[5] and its high reactivity to generate chemically diverse materials including the Merrifield resins for the preparation of solid-support catalysts and ligands.[6]

Few have reported on electrospinning of PS copolymers[7–9] and their mixtures.[10] Electrospinning of PS block copolymers has produced microphase-separated features in fibers, including PS spherical domains on polydimethylsiloxane-*b*-polystyrene (PDMS-*b*-PS)[7] and styrene-butadiene-styrene (SBS) fiber surfaces[8] and PS inner core in the sheath-core structure of poly-styrene-*b*-polyisoprene (PS-*b*-PI) fibers.[9] Electrospinning of the mixtures of polyacrylonitrile-*co*-polystyrene (PAN-*co*-PS) and PAN led to fibers with PAN-*co*-PS sheaths that could carry drugs and surface-active agents.[10]

Polystyrene maleic anhydride (PSMA) is a copolymer that is even more chemically versatile than PS because of the highly charged maleic anhydride (MA) moiety. MA, although does not homopolymerize under normal conditions, can copolymerize with styrene to an alternated styrene-MA copolymer.[11] PSMA has been tuned to achieve specific hydrophile-lipophile balance (HLB) and to be used as dispersant for stability and suspension of organic pigments after neutralization with alkali.[12] The styrene moiety can be readily modified by electrophilic aromatic substitution to contain functional groups. In our laboratory, polystyrene-dithiocarbamates have been synthesized to chelate with divalent metal ions of Hg(II), Pb(II), and Cd(II).[13] We have also generated hydrophilic PSMA by hydrolyzing the MA moiety to dicarboxylic acid and functionalizing the styrene phenyl with dihydroxyphosphino to chelate with Pb(+2) Cu(+2), Cr(+3), and Ni(+2).[14] Others have incorporated an anionic surfactant-stabilized enzyme, α-chymotrypsin (CT), with 3 : 1 PS : PSMA mixture in toluene to show 65% biocatalytic activity

of the free enzyme.[10] Although PSMA has found a wide range of applications, they are notably used as dispersants in soluble forms while more limited as blends and composites in solid forms. If PSMA can be made into solids, in particular as high-specific surface fibers, its chemical versatility makes it a significant asset as reactive solid support.

The goal of this work was to investigate the effects of solvents on the electrospinnability of aPS and PSMA solutions and the morphology of fibers formed. First, PSMA was synthesized to a molecular weight high enough for fiber spinning. The solvent additives on PSMA fiber formation via electrospinning and the resulted fibers structures were compared with those of aPS. The presence of monomer and crosslinker on aPS fiber formation as well as aqueous hydrolysis of PSMA fibers in 0.005N NaOH were also examined to test the potential for postfiber chemical modification.

EXPERIMENTAL

Materials

Styrene monomer (Aldrich, St. Louis, MO) was freed from the 4-tert-butylcatechol inhibitor using an inhibitor removal column (Aldrich), then kept in the fridge before utilization. Divinylbenzene (DVB), constantly kept in the fridge, was used as received. MA (Aldrich) was recrystallized from chloroform and dried under vacuum. The initiator 2,2′-azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from ethanol, dried under vacuum, and kept constantly in the fridge. Toluene, acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), all obtained from Aldrich, were used without further purification. Sodium hydroxide (NaOH) and hydrogen chloride (HCl), obtained from Fisher Scientific, were used without further purification. Atactic polystyrene (aPS), with an average molecular weight M_v of 260 kDa, was obtained from Aldrich.

Synthesis of polystyrene maleic anhydride

PSMA was synthesized by free radical polymerization of styrene and MA initiated by AIBN at a fixed monomer, styrene [S]/initiator AIBN [I] ratio of 2000. Styrene (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. The polymerization was initiated by the addition of AIBN and was kept at 90°C for 4 h under reflux and nitrogen atmosphere, following a procedure previously used in our laboratory.[14] The viscosity molecular weight (M_v) was derived from the intrinsic viscosity [η] measurement of serial dilutions of PSMA in THF with a Cannon-

Fenske viscometer according to Mark-Houwink-Sakurada equation[15]:

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

Electrospinning

Homogeneous solutions were prepared by dissolving PS and PSMA at concentrations varying from 5 to 30%, respectively, in each solvent under constant stirring at room temperature. A broader assortment of fibers was formulated by using mixtures of solvent–solvent or solvent–nonsolvent. Electrospinning was performed using a previously reported setup.[15] About 5 mL of solution was placed in a glass tube, which was titled downward. A stainless electrode was immersed in the solution and connected to a power supply (Gamma High Voltage Supply, ES 30-0.1P). For PS, a grounded counter electrode was connected to collectors that included aluminum foil, copper plate, and mesh, as well as water. PSMA fibers were collected on aluminum foil. The electrospinning voltages varied from 5 to 15 kV and the distance of the capillary tip to the grounded collector varied from 12 to 25 cm. The collected electrospun membranes were dried under vacuum at room temperature for 10 h.

Hydrolysis of PSMA fibers

Hydrolysis of the electrospun PSMA membrane was also conducted for 15 min in aqueous 0.005N NaOH solution. The membrane was then rinsed with 0.005N HCl and water, and then dried at 25°C under vacuum.

Characterization

The viscosities of PSMA and PS solutions were measured according to ASTM D 445 using a Cannon-Fenske viscometer (Cannon Instrument Company, USA). The fiber and membrane morphology was observed with a scanning electron microscope (SEM; XL30-SFEG, FEI/Philips) at 5 kV accelerating voltage with gold coating. The average fiber diameters were analyzed by 20 measurements from SEM images using analysis® prosoftware from Soft Imaging System GmbH. Differential scanning calorimetry (DSC) analyses were conducted (DSC-60 Shimadzu, Japan) using $\sim$5 mg samples at a 10°C/min heating rate in dry N_2. Thermal stability studies of the fibers were also measured using a thermogravimetric analyzer (TGA; TGA-50 Shimadzu, Japan) from room temperature to 500°C at 10°C/min heating rate in dry N_2.

Maximum liquid retention capacity (C_m) was determined by immersion uptake of hexadecane, a

TABLE I
Physical Properties[17] of Solvents and Nonsolvents for PSMA (700 kDa)
and PS (280 kDa) at 25°C

Solvents	T_b (°C)	η (cp)	γ (dynes/cm)	δ (cal/cm³)$^{1/2}$	ε_R	ρ (g/cm³)
Acetone[a]	57	0.31	23.7	9.7	21	0.79
Cyclohexane[b]	81	1.06	25.0	18.8	2.4	0.78
Toluene[b]	111	0.59	27.0	18.2	2.4	0.87
Styrene[b]	145	1.10	32.0	–	2.4–2.7	0.91
THF[a,b]	64	0.55	28.0	18.6	7.5	0.89
Ethyl acetate[a,b]	77	0.43	23.4	18.1	6.0	0.9
DMF[a,b]	153	0.79	35.0	12.1	38	0.94
DMSO[a,b]	189	1.99	42.9	12.0	47	1.10
Water[c]	100	1.00	72.8	–	80	1.00

[a] Solvent for PSMA.
[b] Solvent for PS.
[c] At 20°C.

low viscosity, and surface tension, and thus completely wetting liquid as follows:

$$C_m = (W_m - W_d)/W_d.$$

Water contact angle (θ) was determined by a surface tensiometer (Kruss, K14) according to a previously reported method of measuring the simultaneous wetting and wicking of a liquid in a vertical sample trip with its lower edge forced into contact with a liquid.[16] The water-wetting contact angle (θ) was determined by 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 water-surface tension, respectively. The vertical liquid-retention capacities C_v are derived from vertically held specimens that contact the liquid only at the lower edges and reflect the liquid transported by capillary wicking only. The C_v value of the sample is the vertical uptake of a total wetting liquid, such as hexadecane, in the sample before (W_d) and after (W_v):

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

RESULTS AND DISCUSSION

Solubility of PSMA and *a*PS

The AIBN-initiated free radical copolymerization of styrene and MA was highly efficient, reaching a yield greater than 94%. Synthesis at a 2000 [S]/[AIBN] molar ratio produced an alternating copolymer of PSMA with M_v of 700 kDa. This molecular weight is more than twice of the homopolymer PS used.

PSMA was soluble in acetone, DMF, THF, DMSO, ethyl acetate, and methanol, whereas *a*PS was soluble in DMF, THF, toluene, styrene, and benzene

(Table I). The distinctly different solubility between *a*PS and PSMA is consistent with their molecular structures. The nonpolar *a*PS easily dissolves in nonpolar aromatic solvents, whereas the more polar MA moiety of PSMA enables its dissolution in more polar solvents. PS was most soluble in DMF at 60%, followed by 55% in THF, 50% in toluene, and 40% in styrene. The solubility of PSMA was highest in acetone and DMF, both at 50%, followed by 40% solubility in THF and DMSO and 30% in ethyl acetate.

Among the solvents for PS and PSMA, DMF and THF are the only two in which both polymers share. This exception in solubility behavior of these polymers is probably due to the fact that both solvents are aprotic and lack of any acidic hydrogen. *a*PS has higher solubility in both solvents than PSMA, i.e., 60% in DMF and 55% in THF, when compared with the 50% and 40% of PSMA in the respective solvents. This is consistent with the fact that PSMA is more polar than *a*PS, and thus is less soluble than *a*PS in these less polar solvents. Nevertheless, the solubility of both polymers in either solvent is substantial.

*a*PS fiber formation

Single solvents

Electrospinning of *a*PS was investigated in four solvents in which PS was most soluble, i.e., DMF (60%), THF (55%), toluene (50%), and styrene (40%), at various concentrations up to 20%. The viscosities of *a*PS solutions increased with the concentrations, and the concentration dependence of solution viscosity were similar between the solutions of styrene and DMF, both higher than the 15 and 20% toluene solutions (Fig. 1). The higher viscosity dependence of the styrene and DMF solutions on PS concentrations indicated greater polymer–polymer interactions in these solvents. Although the viscosities of these two solutions were similarly concentration-
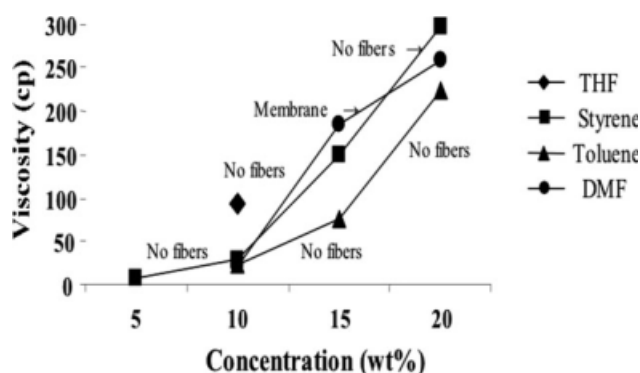
Figure 1 Relative viscosity of PS in THF, styrene, toluene, and DMF at 25°C.

dependent, only the DMF solutions with *a*PS concentrations between 15 and 20% could be electrospun into fibers. Fibers were also observed from electrospinning of the 20% THF solution but not from the toluene solutions (Table II). Some beaded structures were observed on the fibers electrospun from THF but fewer beads were noted with DMF. It is expected that fiber formation from these solvents or electrospinnability of these solutions is associated not only with solution viscosity or chain entanglement alone but also with other solvent properties.

Several physical properties of the solvents might affect the electrospinning of these *a*PS solutions (Table I). The conductivity of a solution determines how it is charged during electrospinning and ejected into jets toward the grounded target. The fact that neither styrene nor toluene solution led to any fiber is thought to be largely due to their extremely low dielectric constants (ε_R = 2.4 for toluene; ε_R = 2.4–2.7 for styrene). Styrene also has a relatively high viscosity. DMF, on the other hand, has a very high dielectric constant. In addition, the dipole moment of DMF (3.8 debye) is also high because of the presence of both carbonyl groups and the electronegative nitrogen. Polarization of a polymer solution is a function of the dipole moments of both the solute and the solvent molecules. Therefore, at any applied voltage, the solvent with a higher dipole moment is expected to generate a stronger electrical force, which induces an efficient forward driving force. Other solvents of a high dipole moment and conductivity, such as 1,2-dichloroethane, ethyl acetate, or methyl ethyl ketone (MEK), have also shown to facilitate electrospinning of PS.[7]

Effects of collecting targets

The effects of the targets to collect *a*PS fibers electrospun from 15% solutions in DMF were studied using Al foil, water, and copper mesh. The *a*PS fibers collected on Al foil were about 0.5 μm in diameter and

had striated fiber surfaces [Fig. 2(a)]. Increasing the *a*PS concentration from 15 to 20% doubled the fiber sizes and improved their surface smoothness [Fig. 2(b)]. Fibers collected on water and copper mesh were similarly packed as those collected on Al foil but also with smoother surfaces [Fig. 2(c,d)]. While all three collectors are conductive, Al foil is solid, copper mesh is porous, and water is diffusive to the mixable solvents. In electrospinning, the dissipation of residual charges in the jets affects how fibers repel each other, and thus their packing and arrangement in the membrane. Similar fiber packing among those collected on the three targets is consistent with their conductive nature. Similar fiber surface morphology between those collected on water and copper mesh suggests that although the mechanisms of solvent removal are different, i.e., diffusion into water versus evaporation into air, the rate may not be too dissimilar. These results showed that the solvents greatly affected the formation and morphology of fibers, whereas the targets, as long as conductive, had little influence. The effects of adding other solvents or nonsolvents were thus studied.

Mixed solvents

The effects of adding a nonsolvent (acetone or cyclohexane) or a solvent (THF or styrene) to the DMF solution of *a*PS on fiber morphology were examined. *a*PS fibers electrospun from DMF were relatively uniform in their diameters around 2 μm [Fig. 2(a)]. When mixed with 12 or 30% acetone, the fibers became slightly larger (∼ 3.0 μm) and more irregular in sizes and shapes; both increasing with acetone contents. This shape change is likely due to high volatility and faster evaporation of acetone, which is miscible with DMF but a nonsolvent for PS (Fig. 3). With 30% cyclohexane, the fiber diameters increased to about 4.5 μm, while their shapes remain

TABLE II
Additive Effects on Electrospinning of 20 wt % of PS from DMF (9–12 kV, Al Foil Collector)

Additive	Additive content, % of DMF	Fibers/fibrous membrane	Sizes (μm)
THF	12[b,c]	Membrane	∼1.5
	30[b,c]	Membrane	∼0.5
Cyclohexane	12–20[c]	Membrane	–
	30	Few	4.5
Styrene	24	Membrane	1.5
	24 + 5% DVB[a]	Membrane	0.5
	74	Membrane	1
Acetone	12[c]	Membrane	2
	30	Few	3

[a] DVB concentration in vol % of styrene.
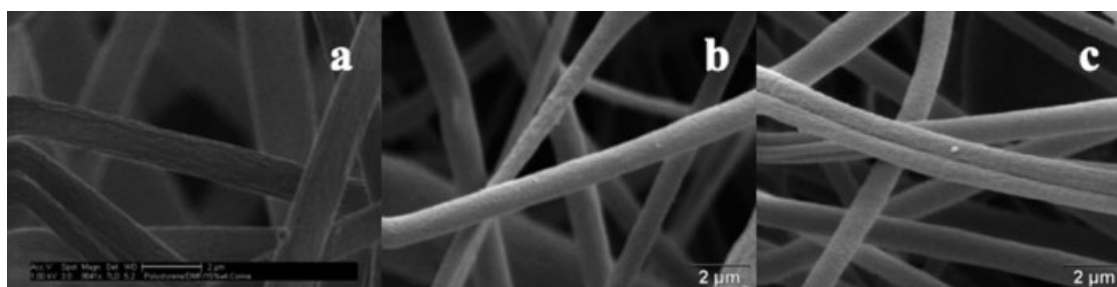[b] Collector copper mesh.
[c] 15 wt % PS concentration.

Figure 2 Collector effects on PS fibers electrospun from 15 wt % in DMF [except for (b) at 20 wt %]: (a) Al foil; (b) water; and (c) copper mesh.

unchanged (Table III). Both nonsolvents enlarged fiber sizes, but only acetone, with a much lower viscosity η but significantly higher dielectric constant ε_R than cyclohexane, led to a broad distribution of fiber diameters.

With the addition of another solvent, such as THF, some smaller fibers with diameters ranging from 0.5 to 1 μm appeared among the 2-μm size fibers, similar to those from DMF alone [Fig. 4(a,b)]. Mixing 24% styrene, which was both a solvent and monomer of PS, with DMF created pitted fiber surface, but did not affect the spinning efficiency or the cylindrical fiber shape [Fig. 4(c)]. With further addition of DVB (5%) along with styrene (24%) in DMF, the fibers became smoother on the surfaces and smaller in diameters (0.9 μm) [Fig. 4(d)]. At a higher styrene content of 75%, larger fibers with similarly pitted surfaces were observed [Fig. 4(e)]. The observations made with added THF and styrene, i.e., increased irregularity and broader range of fiber sizes, are attributed to the low vapor pressure of these additives. The difference between the solubility parameters of aPS and the solvent was also deducted to be responsible for the bead-on-string morphology.[7]

These observations showed that the addition of a solvent (THF) generally improved uniformity and reduced size of the fibers, whereas the addition of nonsolvents (acetone, cyclohexane) enlarged fibers and created irregularities in their shapes. This fiber formation that can be sustained with the added monomer and crosslinker shows promising effects. Post-fiber formation polymerization and crosslinking can offer new ways to expand chemical structures or render solvent resistant to aPS fibers.

PSMA fiber formation

Single solvents

PSMA is readily soluble in acetone, THF, ethyl acetate, DMF, and DMSO. Electrospun of PSMA from these solvents yielded observable jets at 20–30%, 15–20%, 10–15%, 20–40%, and 15–25%, respectively (Table III). Acetone, THF, and ethyl acetate have low surface tensions that are favorable for electrospinning. However, their low boiling points and fast evaporations cause blockage of the capillary flow, lowering fiber generation efficiency. Consequently, few fibers were observed from electrospinning of PSMA in acetone, THF, or ethyl acetate solutions. The jets produced from 20% PSMA in DMF and 25% PSMA in DMSO were more continuous. The high dielectric constants, boiling points, and dipole moments of DMF and DMSO make them conductive to
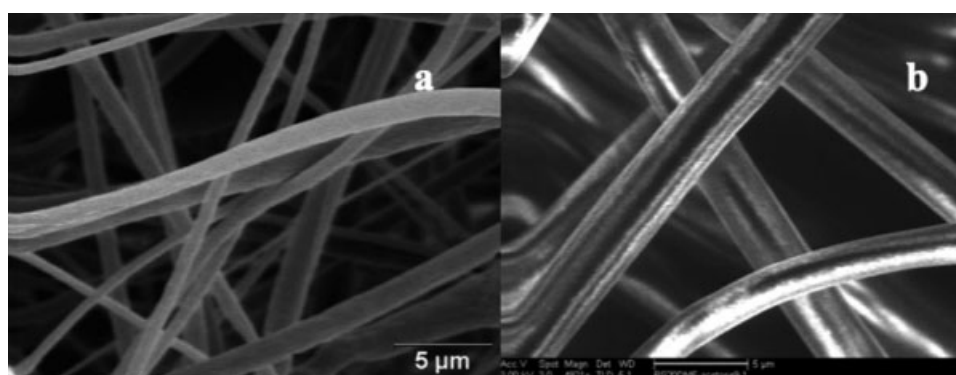

Figure 3 Acetone addition on PS fibers electrospun from 20% in DMF on different targets: (a) 12% acetone on water and (b) 30% acetone on Al foil.

TABLE III
Solubility and Electrospinning[a] of PSMA in Various Solvents at 25°C

Solvent	Max. solubility (wt %)	Electrospinning conditions			
		PSMA (wt %)	Voltage (kV)	Fiber/fibrous membrane	Fiber diameter (μm)
Acetone	50	20–30	8	Few	8.0 (20%)
		40–50	5–15	None	–
THF	40	15	8	Membrane	4.0
		20	8	Few	–
Ethyl acetate	30	10–15	5–15	Few	–
		20–30	5–15	None	–
DMF	50	10–15	5–15	None	–
		20	14	Membrane	2.0
DMSO	40	15	14	Few	–
		25	7	Membrane	0.6

[a] Distance to aluminum foil collector was 7 inches.

electrospinning. Comparisons among solvents show that viscosity is not the predominant parameter influencing PSMA fiber formation. For example, at 20% of PSMA, the DMF solution was fiber forming and THF was not, while their solution viscosities were not so dissimilar at 70.5 and 56.8 cp, respectively.
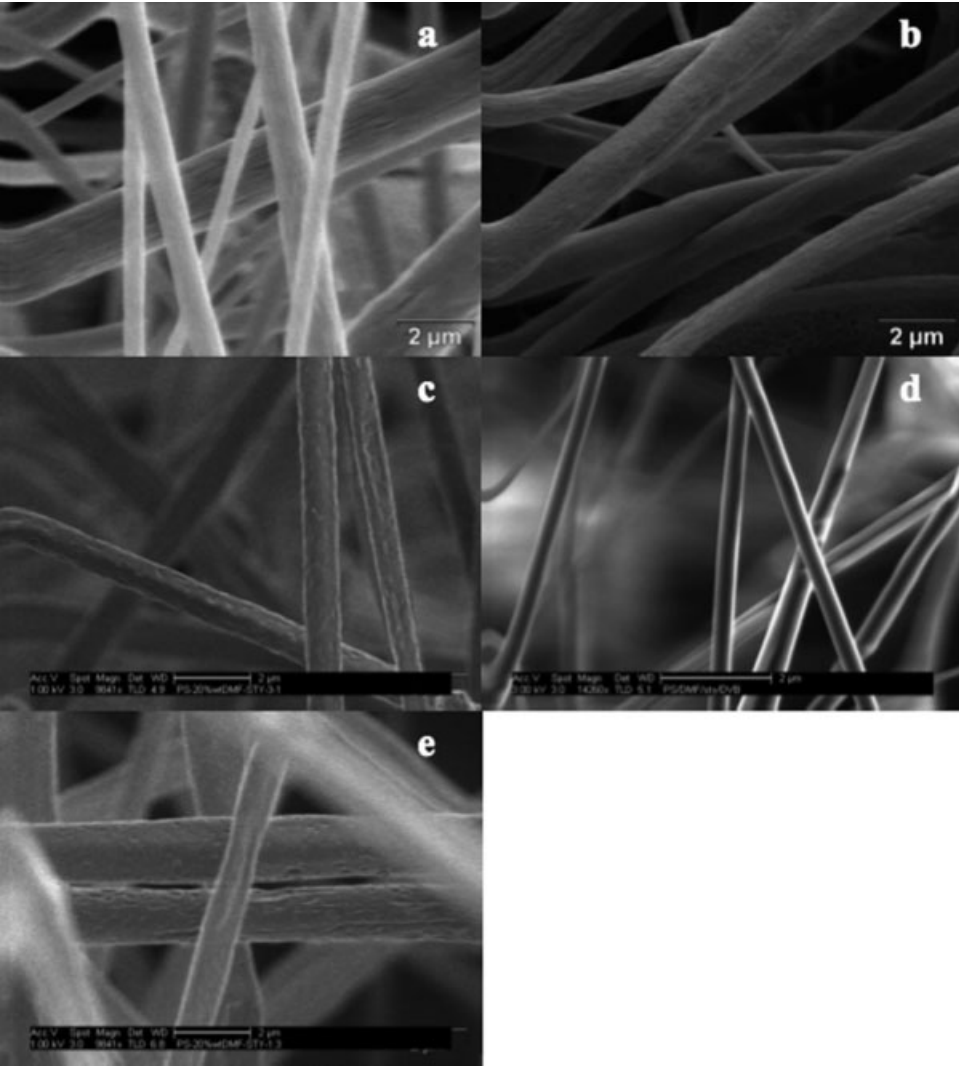

Figure 4 Cosolvent effects on PS fibers electropsun from 20 wt % in DMF: on copper mesh at (a) 20% THF and (b) 30% THF; and on Al foil at (c) 24% styrene, (d) 24% styrene and DVB (5 vol % of styrene), and (e) 74% styrene.
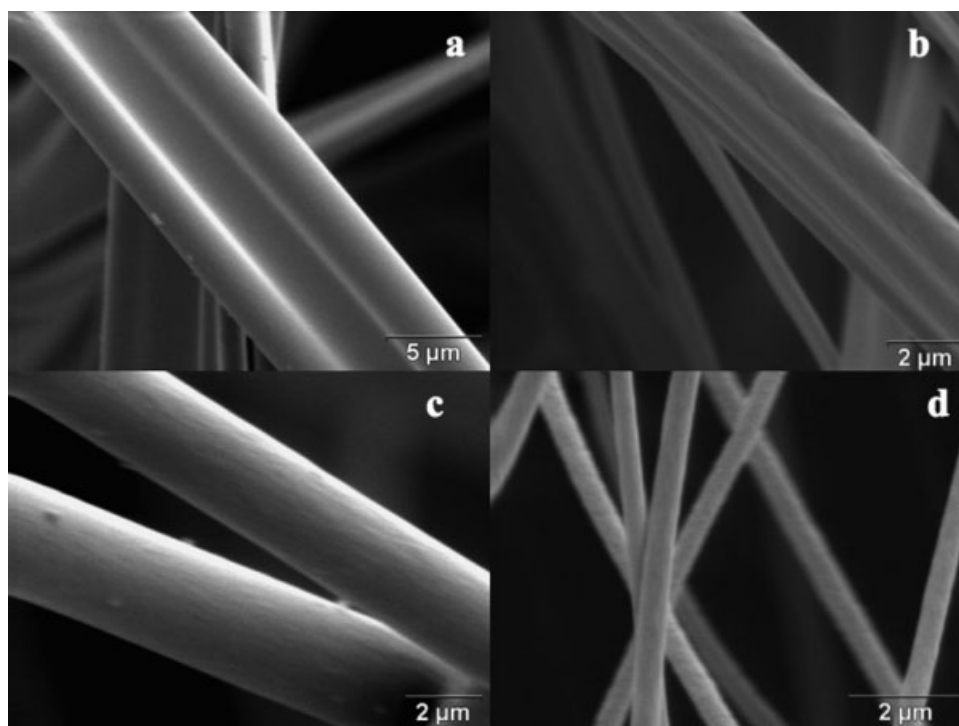
Figure 5 PSMA fibers electrospun from (collected on Al foil): (a) 15 wt % in THF; (b) 20 wt % in acetone; (c) 20 wt % in DMF; (d) 25 wt % in DMSO.

The PSMA fibers electrospun from more volatile solvents were rather large, i.e., diameters up to 4 μm from 20% in acetone (Table II) and about 8 μm from 15% in THF [Fig. 5(a)]. The irregular fiber shapes [Fig. 5(a,b)] were consistent with fiber collapse attributed to the fast solvent evaporation. The diameters of the fibers produced from DMF at 20 wt % were close to 4 μm, about half of those from THF [Fig. 5(b,c)]. While fibers from DMF kept cylindrical shapes and smooth surfaces, those from acetone were more varied in sizes and shapes. At an even higher concentration in DMSO (25%), the diameters of the fibers were further reduced to 0.6 μm [Fig. 5(d)], but again without any change on the surface morphology. As expected, solvents with high dielectric constants, such as DMF and DMSO, favor efficient fiber formation whereas the highly volatile THF produced very large fibers, but does not sustain continuous generation of fibers.

Although THF and DMF are solvents for both *a*PS and PSMA, THF has shown to be inefficient for continuous fiber generation because of its low viscosity, low dielectric constant, and high volatility. In DMF, there were greater PS–PS interactions, and PS at concentrations between 15 and 20% could be electrospun into fibers. The viscosity of DMF makes it conductive also to electrospun PSMA from DMF solutions. PSMA was, however, made into more continuous fibers at higher concentration, i.e., 20 wt % in comparison with *a*PS. Therefore, DMF was deter-

mined to be the most suitable solvent for both polymers and was used for the remaining of this study.

Solvent mixtures

The effects of additions of solvents (THF) or nonsolvents (toluene, cyclohexane) to PSMA solutions and their resulted fiber structure and geometry (Table IV) were studied. The average fiber sizes decreased with increasing amounts of THF added [Fig. 6(a–c)]. The

TABLE IV
Solvent and Additive Effects on Fiber Formation of 20 wt % of PSMA Through Electrospinning (ES)

Solvents	Additives	Additives content (%)	Observation on ES
Acetone	Cyclohexane	6	No fibers
	Toluene	6	Membrane
THF	Methanol	6	Few fibers
	Cyclohexane	6, 11	Few fibers
	Water	6	Few fibers
	Toluene	6	Few fibers
Ethyl acetate	DMSO	10,[a] 25[a]	Few fibers
	DMSO	25,[b] 50[b]	No fibers
DMF	THF	32, 49, 65	Membrane
	Cyclohexane	6, 29	Membrane
	Toluene	6	Membrane

[a] PSMA concentration was 15 wt %.
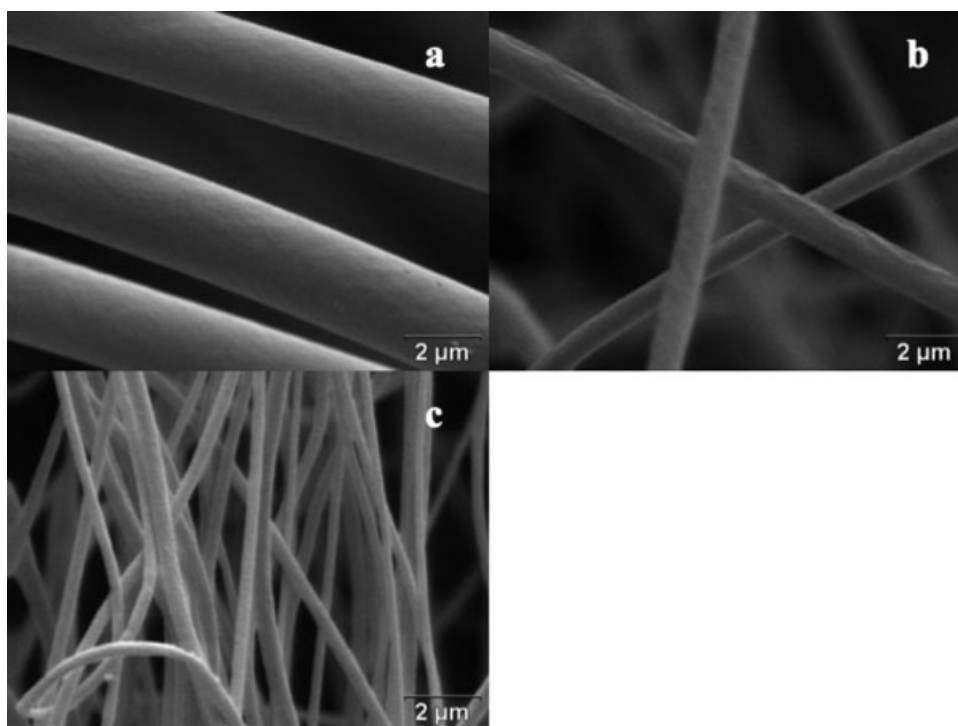[b] PSMA concentration was 25 wt %.

Figure 6 THF cosolvent on PSMA fibers electrospun from 20 wt % solution in DMF with (a) 32% THF, (b) 49% THF, and (c) 65% THF.

fiber diameters reduced very slightly with 32% THF [Fig. 6(a)], and then significantly lowered to about 1 μm at 49% [Fig. 6(b)], and yet further to about 500 nm at 65% [Fig. 6(c)]. With either THF or ethyl acetate becoming the majority, the efficiency of fiber generation decreased, and only few fibers were collected.
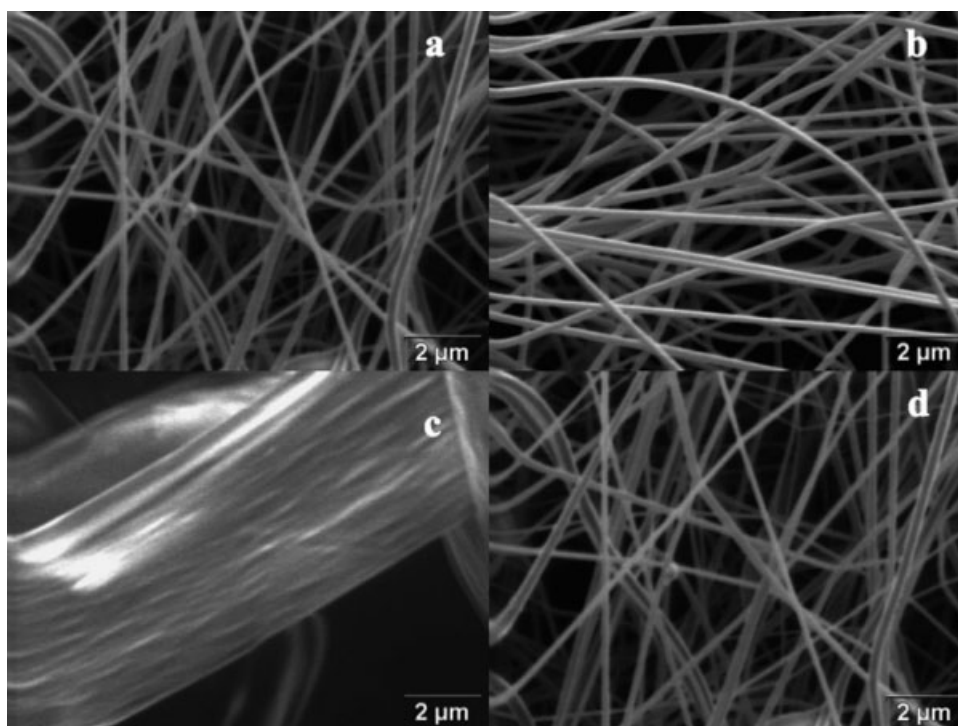

Figure 7 Nonsolvent additive (6 wt % of solvent) on PSMA fibers electrospun from 20 wt % solution: (a) toluene in DMF; (b) cyclohexane in DMF; (c) water in THF; and (d) cyclohexane in acetone.
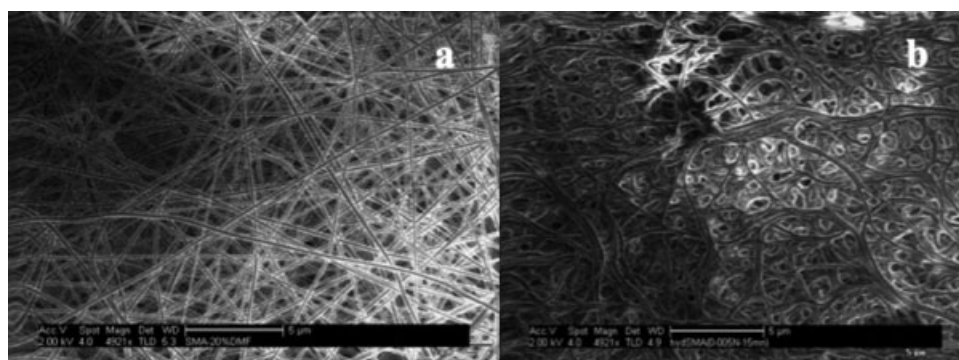
Figure 8 PSMA fibers (20 wt % in DMF, collected on Al foil): (a) as-spun; (b) after immersion in aqueous NaOH (0.005N, 15 min) solution [rinsing with HCl (0.005N) and water].

This instability of the jet was likely due to the fast evaporation of solvents during electrospinning.

Adding small amount (6%) of nonsolvents, i.e., toluene or cyclohexane to DMF [Fig. 7(a,b)] and cyclohexane to acetone [Fig. 7(d)], also led to significantly smaller fibers. The PSMA fibers electrospun from DMF with toluene [Fig. 7(a)] or cyclohexane [Fig. 7(b)] and from acetone with cyclohexane [Fig. 7(d)] were similar in appearance and had diameters around 200–300 nm. In comparison with the THF/ DMF mixtures, the reduction in fiber sizes from the addition of these nonsolvents was much greater than that of a solvent like THF and at much lower solvent contents. The exception was those electrospun from THF with 6% water where large (5 µm in diameter) and flat fibers were observed [Fig. 7(c)].

The comparisons between aPS and PSMA show that the addition of a solvent, such as THF, generally improves the fiber uniformity and reduces the fiber sizes for both polymers. The effects of nonsolvents, however, were different between aPS and PSMA. The addition of nonsolvents significantly reduced PSMA fiber diameters to 200 to 300 nm, which created larger and irregularly shaped aPS fibers.

Hydrolysis of PSMA fibers

The electrospun PSMA membranes were stable enough to tolerate extended immersions in alkaline solutions. The fibers kept their diameters around 300

TABLE V
Maximum Hexadecane-Retention Capacity (C_m) of PSMA Fibers (20 wt % in DMF) After Hydrolysis with 0.005N NaOH Aqueous Solution for 15 min

Hydrolysis time (min)	C_m (µL /mg)
0	24.6
2.3	5.0
5	4.2

nm after 15 min of hydrolysis in a 0.005N NaOH aqueous solution (Fig. 8). The fibers, however, became relaxed and packed. A significant decrease in overall pore volume, as indicated by the maximum liquid retention values (Table V), after only 2.3 min is consistent with the fact that hydrolyzed PSMA fibers are much more densely packed.

Wetting of both PS and PSMA fibers

The electrospun PS membranes showed water contact angles (θ) at around 90° as expected from their hydrophobic character. The hydrophobicity of the membranes electrospun with various solvents or non-solvent additives did not change, also as expected. The electrospun PSMA membranes (from 20 wt % PSMA in DMF) had similar water contact angle values as the aPS membranes. This shows that the styrene moieties dominate on the PSMA fiber surfaces, minimizing the surface tension. There was, however, a tendency of the aPS membranes to bend along on the water surface during the wetting analysis. This observation was a result of the hydrophobic nature and the thinness of the membranes of aPS. However, this was not observed on the PSMA fibrous membranes, suggesting the latter being slightly less hydrophobic.

CONCLUSIONS

aPS was soluble to 60% in DMF, 55% in THF, 50% in toluene, and 40% in styrene. Alternating copolymer PSMA, on the other hand, was soluble in acetone and DMF, both at 50%, followed by the 40% solubility in THF and DMSO and 30% in ethyl acetate. This is consistent with the fact that PSMA is more polar than aPS, and thus soluble in more polar solvents. While DMF and THF are solvents for both polymers, aPS has a higher solubility than PSMA in these solvents with 60% in DMF and 55% in THF for aPS and 50% and 40% for PSMA.

Electrospinning of *a*PS from DMF produced uniformly sized fibers with diameters around 2 µm. PSMA fibers produced from 20% DMF and 25% DMSO solutions had cylindrical shapes and smooth surfaces, with average diameters of 4 and 0.6 µm, respectively. Electrospinning from the more volatile solvents led to much larger and irregularly shaped fibers, such as those with up to 8 µm diameters from 20% in acetone and about 4 µm diameters from 15% THF. As expected, solvents with high dielectric constants, such as DMF and DMSO, facilitated electrospinning of both PSMA and *a*PS and favored efficient fiber formation. In contrast, the highly volatile solvents, like THF, produced very large fibers, but did not sustain continuous generation of fibers. Fibers collected on Al foil, water, and copper mesh showed that the target types did not affect the fiber morphology, as long as the targets were conductive. Adding a solvent, such as THF, to either PSMA or *a*PS generally improved uniformity and reduced size of the fibers. The effects of nonsolvents, however, were different between *a*PS and PSMA. With the addition of nonsolvents, the PSMA fiber diameters were significantly reduced to 200–300 nm, whereas the PS fibers became larger and more irregularly shaped. Both electrospun fibrous membranes exhibited 90° water contact angles with PSMA that appeared to be slightly less hydrophobic. The ability to incorporate the monomer and crosslinking DVB in *a*PS fibers as well as hydrolyze PSMA fibers with diluted NaOH solutions demonstrated potential for post-electrospinning reactions and modification of these ultrafine fibers for reactive support materials.

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