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Ultra-fine polyelectrolyte fibers from electrospinning of poly(acrylic acid)

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Abstract

Ultra-fine polyelectrolyte fibers have been generated from electrospinning of poly(acrylic acid) in aqueous and DMF solutions. The fiber diameters ranged from 80 to 500 nm and increased with increasing solution concentrations and electrospinning voltages. The fibers generated from the aqueous solutions were more homogeneous in sizes, especially when NaCl or NaOH was added. Higher voltages in electrospinning of the aqueous solutions also resulted in fibers with larger heat capacity in the glass transition region, and higher dehydration temperatures. These polyelectrolyte fibers could be rendered water-insoluble by incorporating β-cyclodextrin (at 20 wt% of PAA) in the aqueous solution, then heat-induced crosslinking was performed at 140 °C for 20 min. The resulting hydrogel fibers showed strongly pH-responsive swelling behaviors.

Keywords: Nanofibers; Poly(acrylic acid); Electrospinning

1. Introduction

Fibers have been conventionally produced by mechanically extruding polymer solutions or melts through spinnerets then drawing to reduce diameters to tenths of μm, sizes similar to natural fibers. In recent decades, advanced fiber spinning technologies have enabled the manufacturing of micro-fibers whose diameters are typically a few μm in an economically feasible manner. Submicrometer or nanometer size fibers can be generated by electrospinning [1–5], in which high voltage is applied to the capillary droplet of polymer melts or solutions to overcome the liquid surface tension to form and draw the jet down to considerably finer fibers [6].

Fiber formation by electrospinning of polymer solutions has been extensively studied in terms of voltage, tip-to-collector distance, feeding rate of polymer solution [1,2,4] and the polymer solution properties [5,7]. In order to form fibers, polymers must possess sufficient chain entanglements that are both structural and concentration dependent. For any given polymer, solution concentrations have shown to have crucial effects on fiber formation and fiber size [8–11]. Fiber formation was observed at above certain concentrations, where the specific viscosity increased significantly [8]. Below such concentrations, droplets are produced due to a lack of molecular entanglement. These viscosity thresholds have been associated with entanglement concentrations. Another solution property critical to fiber formation in electrospinning is conductivity because the electric force is the main driving mechanism. Adding inorganic salts, such as sodium chloride (NaCl) to aqueous poly(ethylene oxide) (PEO) solutions [5], or NaCl, sodium phosphate and potassium phosphate to poly(D,L-lactic acid) (PDLA) in DMF [12] has been shown to significantly reduce the fiber sizes and the amount of beaded structures on the fibers.

Polyelectrolytes also carry charges in aqueous solutions. However, unlike the free moving small inorganic charge carriers, the close association of the charged polyelectrolytes and their counter ions is expected to exert different effects on the conformation of polyelectrolyte molecules, thus molecular entanglement and solution viscosity, both of which are critical for fiber formation. Furthermore, polyelectrolytes serve as excellent models for proteins so that studying their fiber formation helps to understand how to generate fibers from proteins that has not been possible with conventional methods. It is, therefore, of fundamental

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interest to understand the formation and properties of polyelectrolyte fibers from electrospinning.

This paper reports the generation of ultra-fine polyelectrolyte fibers from electrospinning of poly(acrylic acid) (PAA). The main focus was to understand how formation of fibers and the resulted fiber structure are affected by the conductivity of the solutions by using solvents with different dielectric constants, e.g. water and DMF. The effects of the solution concentration, solution viscosity, and the electrospinning voltage on the morphology, size and structure of the polyelectrolyte fibers were investigated. The conductivity of the aqueous solution was also adjusted by adding NaCl or neutralizing PAA carboxylic acid groups with sodium hydroxide (NaOH). These ultra-fine fibers were rendered insoluble by crosslinking with β-cyclodextrin.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA) (average $M_v \sim 450$ kDa) was obtained from Aldrich Chemical Company and β-cyclodextrin was from Acros Organics. NaOH and NaCl, both ACS reagent grade, were from Fisher Scientific. *N*,*N*-Dimethylformamide (DMF, 99.98%) was obtained from EM Science. All chemicals and solvents were used as received. The aqueous solutions were prepared with purified water (Millipore Milli-Q plus water purification system).

2.2. Electrospinning

Homogeneous solutions of PAA were prepared in either water or DMF by adding PAA at 4, 5, 6, 8 and 10 wt% concentrations with gently magnetic stirring at ambient temperature for 8 h. NaCl and NaOH were added to aqueous solutions (8 wt% PAA) at 8 wt% of PAA and 10 mol% of acrylic acid, respectively. All solutions were prepared and used immediately for electrospinning. About 5 ml of solution was placed in a glass tube with a 0.4 mm inner-diameter tip, which was tilted downward at an angle between 0 and 30° depending on the solution viscosity (Fig. 1). A stainless steel electrode was immersed in the solution and connected to a power supply (Gamma High Voltage Supply, ES 30-0.1P). Aluminum foil was used as the collector and connected to the ground. The tip-to-collector distance was 25 cm. All electrospinning was conducted at room temperature for about 8 h.

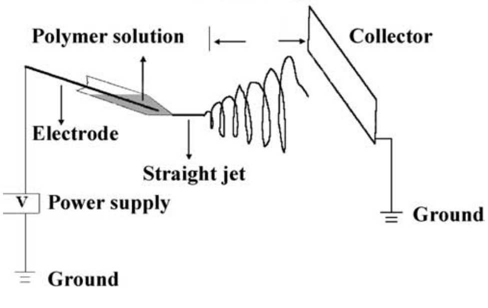

Fig. 1. Electrospinning set-up.

Crosslinking of PAA was attempted by adding β-cyclodextrin (20 wt% of PAA) in 10 wt% PAA aqueous solution followed by heating the electrospun membrane at 140 °C for 20 min.

2.3. Measurement and characterization

The viscosities of PAA solutions were measured according to ASTM D445 using a Cannon–Fenske viscometer (Cannon instrument company, USA). Conductivities and surface tensions for solutions were determined using a conductivity meter (YSI Model 35, Yellow Springs Instrument Co. Inc.) and a liquid tensiometer (K14, KRÜSS USA), respectively. The pH of the solutions was measured by PerpHect Meter (Model 310, ATI Orion Laboratory Products Group). The fiber and membrane morphology was observed with a scanning electron microscope (SEM) (XL30-SFEG, FEI/Philips) at 2 kV accelerating voltage without gold coating. Differential Scanning Calorimetry (DSC) analyses were conducted (DSC-60 Shimadzu, Japan) using ~5.0 mg samples at a 10 °C/min heating rate in nitrogen. The glass transition temperature (T_g) was recorded as the temperature at midpoint of the baseline shift. The overall pore volume of each fibrous membrane was estimated by its capacity (C_r, μl/mg) to retain a low surface tension and low viscosity liquid, i.e. hexadecane [13,14].

$$C_r = \frac{[(W_h - W_d)/\rho]}{W_d}$$

where W_d and W_h are the membrane mass before and after the immersion, respectively, and ρ is the density of hexadecane.

The swelling of the crosslinked fibrous membrane was done by immersing a 10 mg (W_0) of sample in 30 ml of buffer solution at 30 °C for 24 h and weigh (W_s). The swelling ratio (q) was calculated as:

$$q = \frac{(W_s - W_0)}{W_0} \quad (1)$$

The average of three measurements was reported.

3. Results and discussion

3.1. Properties of aqueous and DMF solutions

PAA is readily soluble in water and DMF, both at concentrations up to 20 wt% at ambient temperatures. Between the two, water has much higher dielectric constant and surface tension, but lower boiling temperature and slightly higher density and viscosity (Table 1). The ability of water molecules to hydrogen bond with each other results in extensive inter-molecular cohesive forces, and thus its very high surface tension. DMF has considerably weaker cohesive forces; therefore, a much lower surface tension.

The high dielectric constant of water and partial ionizaiton of the carboxylic acid groups on PAA cause the aqueous solutions to be much more conductive than DMF solutions (Table 2). The aqueous PAA solutions had significantly lowered surface tensions (low to mid-40's) than water (72.8 mN/m), whereas the surface tensions of the DMF solutions were slightly higher than DMF (35.2 mN/m) by 2–3 mN/m (Table 2). While neither was concentration dependent, the aqueous solutions had consistently higher surface tensions than the DMF solutions. These surface tension differences can be explained by the different PAA-solvent interactions. PAA molecules consist of highly polar carboxylic side groups (–COOH) on a non-polar hydrocarbon backbone. In aqueous solutions, the abundant polar side groups form hydrogen bonds with water and impede the inter-molecular cohesive forces among water molecules, lowering its surface tension. The hydrophobic hydrocarbon backbones of PAA tend to orient toward the surface of the solution to minimize the surface tension. Adding the more polar PAA to DMF enhances the cohesive forces at the solution surface, resulting in an increased surface tension of the solution.

In the PAA concentration range studied, the viscosities of both aqueous and DMF solutions increased with increasing polymer concentrations as expected (Table 2). The concentration-dependence of solution viscosity was higher for the DMF solutions than the aqueous solutions. This may be due to the more expanded conformation of PAA in the aqueous media caused by the electrostatic repulsion between partially charged PAA molecules. The molecular entanglement among PAA in DMF is expected to be higher.

3.2. Fiber formation

In electrospinning of polymer solutions, the fiber formation process can be characterized by the formation and thinning of the liquid jet to the solidification and deposition of fibers on the collecting target. The applied voltage first overcomes the liquid surface tension to form a jet, which then bend, and spiral into a larger looping path as the jet thins into finer fibers and solidifies [6].

Both solutions in the 4–10 wt% concentration range could be electrospun to generate fibers. Fiber formation from the aqueous solutions was continuous at all concentrations, but could only be sustained in DMF at up to 6 wt% of PAA. The highly viscous 8 and 10% DMF solutions caused tip blockage and interrupted the fiber formation process about every 10 min. At the highest soluble concentration of 20 wt%, no jet could be observed from either solution. The fiber collection rates from the aqueous solutions were higher and increased with increasing concentrations of both solutions. The dry fiber mass collected was 50, 65, and 80 mg/h from the 5, 8, and 10 wt% aqueous solutions, respectively. The rate at which fibers were generated from the 5 wt% PAA/DMF solution was much lower (30 mg/h). Viscosity appears to be the determining factor for continuous fiber formation. Fiber formation is continuous when the solution viscosity was lower than 704 cP for aqueous solution and 1439 cP for DMF solution.

Formation of jet and thus fibers is driven and sustained by the applied voltage. The voltage required to initiate jet from and sustain the electrospinning of 5% PAA/DMF solution was between 5.0 and 9.5 kV. At voltage exceeding 9.5 kV, the jet became unstable and broke into drops. The voltage needed to sustain continuous electrospinning of aqueous PAA solutions was between 6.5 and 16.0 kV. The higher working voltage required for electrospinning of aqueous solutions might be due to their higher surface tensions and/or possibly higher feeding rate due to their lower viscosities.

Fig. 2 shows SEM images of PAA fibers electrospun from aqueous (13.5 kV) and DMF (5.0 kV) solutions at three different concentrations. Fig. 3 shows SEM images of PAA fibers electrospun at the same concentration (8 wt%) and voltage (9.5 kV). The average fiber sizes increased with increasing solution concentrations from both solution series (Table 2). In general, higher concentrations also lead to more homogeneous fiber sizes (Fig. 2). At any given concentration, the fibers generated from aqueous solutions were much more homogenous in their sizes than those from DMF solutions (Figs. 2 and 3).

Larger fibers were also observed at higher voltages for both aqueous (Fig. 2(b): 280 nm and Fig. 3(a): 200 nm) and DMF solutions (Fig. 3(b): 370 nm and Fig. 2(c): 160 nm). In our setup, the solution feeding rate is expected to be proportional to the electric potential applied. Therefore, larger fiber sizes associated with higher voltages were due to

Table 1
Physical properties of water [22] and DMF [23]

Solvent	Density (g/cm^3)	T_b (°C at 760 mm Hg)	Viscosity (centipoise)	Surface tension (mN/m)	Dielectric constant
Water[a]	0.998	100	1.002	72.8	80.2
DMF [b]	0.950	153	0.802	35.2	26.6

[a] 20 °C.
[b] 25 °C.

Table 2
PAA solution properties, electrospinning voltage, and fiber sizes

PAA concentration (wt%)	Solution				Electrospinning	
	Viscosity (centipoise)	Surface tension (mN/m)	Conductivity (mS)	pH (mS)	Voltage (kV)	Average diameter (Nm)
Aqueous						
5	32	43.23	2.28	2.19	13.5	90
8	247	44.49	2.15	2.30	13.5	280
10	704	42.78	2.01	2.30	13.5	550
8 (NaOH)[a]	443	45.47	3.68	4.01	13.5	290
8 (NaCl)[b]	237	44.05	15.68	2.20	13.5	276
DMF						
5	131	37.09	0.07	5.29	5.0	60
8	1439	38.15	0.07	5.48	5.0	160
10	3913	38.56	0.06	5.56	5.0	330

[a] Neutralized with sodium hydroxide at neutralization degree of 10%.
[b] Addition of sodium chloride at 8 wt% of PAA.

the higher solution feeding rates. The same observation was made on a similar set up for electrospinning of an acrylic copolymer [15]. It should be noted, however, in the case of a constant feeding rate (2 ml/h), higher voltage has been reported to result in smaller fiber diameters from poly(L-lactide-*co*-α-caprolactone) [P(LLA-CL)] [16].

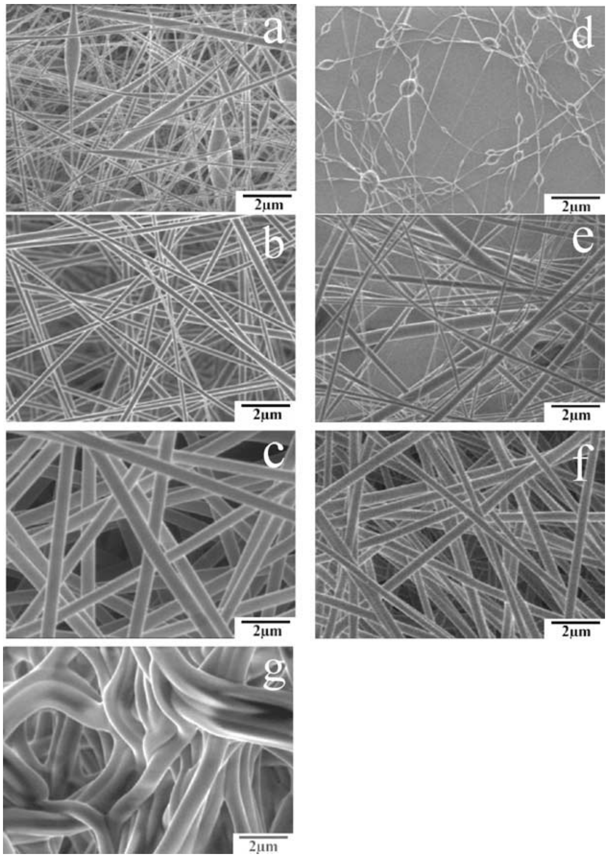

Fig. 2. SEM of PAA fibers (bar = 2 μm) electrospun from: (a) 5 wt%, (b) 8 wt%, (c) 10 wt% aqueous solutions at 13.5 kV; and (d) 5 wt%, (e) 8 wt%, (f) 10 wt% DMF solutions at 5.0 kV; (g) PAA/β-cyclodextrin electrospun fibers after being cured at 140 °C for 20 min and water treatment for 24 h.

3.3. Morphology of fibrous membrane

In addition to fibers, distinct beaded structures (Fig. 2(d)) and enlarged segments (Fig. 2(a)) along the fibers were observed at 6 wt% or lower concentrations for both solution systems. Greater numbers of beads were found from DMF (Fig. 2(d)) than aqueous solutions (Fig. 2(a)). From DMF, the beads along the fibers were also closer to each other and spherical in shape (Fig. 2 (d)). The beads generated from the aqueous solutions were more elongated and spindle-like (Fig. 2(a)). This is consistent with the higher electrospinning voltage (Table 2), which exerted a stronger drawing force on the solution jet. The concentration dependence of PAA solution viscosity became greater between 6 and 8 wt% for both solution series, but more obvious for DMF solutions (Fig. 4). This may indicate that significant molecular entanglement in PAA solutions happens above this concentration range. It is also consistent with the observation that beaded structures were only observed at the 6 wt% or lower concentrations.

Fibers generated from the aqueous solutions were more loosely packed than those from the DMF solutions, showing larger inter-fiber pores (Fig. 3). This is expected of the larger repulsion between the surface charges on fibers from aqueous solutions. The overall pore volume of these fibrous membranes was estimated by their capacity to retain a low surface tension and low viscosity wetting liquid, i.e. hexadecane. The retention of hexadecane in the fibrous

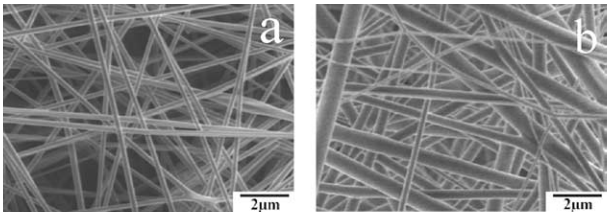

Fig. 3. SEM of fibers (bar = 2 μm) electrospun (9.5 kV) from 8 wt% PAA (a) aqueous and (b) DMF solution.

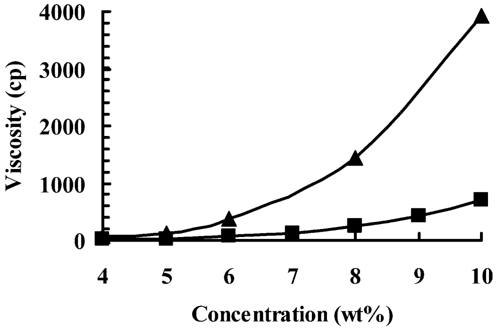

Fig. 4. Dependence of PAA solution viscosity on concentration.

membrane from PAA aqueous solution was 3.95 μl/mg, which was more than twice of that electrospun from DMF solution (1.73 μl/mg).

3.4. Effects of conductivity in aqueous solution

The conductivity of the aqueous solutions was altered by either adding NaCl or neutralizing PAA with NaOH. NaCl added to 8 wt% PAA aqueous solution at 8 wt% of the PAA significantly increased the solution conductivity from 2.15 to 15.68 mS (Table 2). Although NaCl added to polyethylene oxide (1–10 wt% of PEO) solutions has been shown to reduce fiber size by 10–40% [5], our data did not show any effect of NaCl. NaCl increases the ion concentration, consequently the conductivity of PAA aqueous solution. The ions also shield the electrostatic repulsion between the partially charged PAA molecules, making PAA molecules more compacted [17], increasing molecular entanglement. The conductivity in the solution tends to reduce the fiber sizes [5] but the increased entanglement among PAA molecules balance out the conductivity effect, causing no net change in fiber size. The fiber sizes, however, did become more homogeneous with the addition of NaCl as shown in Fig. 5(b).

Neutralization of PAA with NaOH enhanced the ionization of the carboxyl groups and was reflected by the increased solution pH and viscosity (Table 2). At a 10% neutralization degree, based on the NaOH to AA molar ratio, for 8 wt% PAA aqueous solution, the solution conductivity increased from 2.15 to 3.68 mS. The increased viscosity of the neutralized PAA aqueous solution, which is expected to favor larger fiber sizes, counteracts the opposing effect of the increased conductivity, leading to no change in fiber size. The increased conductivity also made the fiber sizes more homogeneous (Fig. 5(a)).

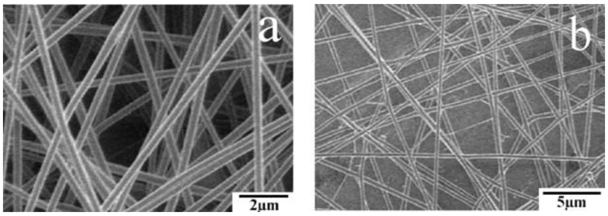

Fig. 5. The morphology of fibers electrospun (13.5 kV) from 8 wt% PAA aqueous solution: (a) neutralized with sodium hydroxide (bar = 2 μm), and (b) with NaCl (8 wt% of PAA) (bar = 5 μm).

3.5. Heat capacity change and dehydration of PAA fibers

The DSC thermograms of all electrospun PAA fibers showed large endothermic peaks below 100 °C from the evaporation of absorbed moisture, glass transitions at 129 °C, and broad endothermic peaks between 150 and 300 °C from the dehydration between the carboxyl groups (Fig. 6). The heat capacity increase and dehydration temperature were higher for fibers from the aqueous solution (Fig. 6(b)) as well as at higher voltage (Fig. 6(b)–(d)).

Heat capacity is a thermodynamic property directly associated with the intensity of long-range segmental motions of non-crystalline polymer main-chains [18]. Therefore, the heat capacity data suggest larger free volume in the fibers can be generated from aqueous media as well as by increasing the electrospinning voltage. The lower dehydration temperature of PAA fibers from aqueous solutions at lower voltages could be related to the reduced free volume, facilitating dehydration.

On the other hand, NaCl addition lowered the magnitude of the heat capacity and dehydration temperature (Fig. 6(e)). This is because the addition of NaCl to the PAA aqueous solution shielded the electrostatic repulsion between the partially ionized PAA molecules, and reduced the free volume inside the fibers.

3.6. PAA hydrogel fibers by crosslinking with β-cyclodextrin

These ultra-fine PAA fibrous membranes dissolve in water instantaneously. In order to retain their unique ultra-fine fibrous structure, crosslinking of PAA was attempted. First, heat-induced inter-molecular crosslinking of PAA molecules by anhydride formation was examined. Heating the fibrous membrane at 140 °C for 20 min did not change its solubility in water.

Another approach was adding β-cyclodextrin as a crosslinker (at 20 wt% of PAA) in aqueous PAA solution.

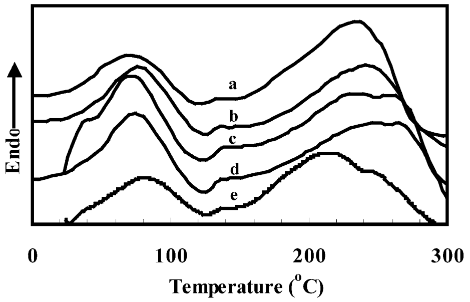

Fig. 6. DSC of PAA fibrous membrane electrospun from 8 wt% (a) DMF at 9.5 kV; aqueous solution at (b) 9.5 kV, (c) 12.0 kV, (d) 13.5 kV, (e) aqueous with NaCl (8 wt% of PAA) at 13.5 kV.

The molar ratio between the carboxylic acid groups of PAA and hydroxyl groups of β-cyclodextrin was 3.5. The electrospun fibrous membranes were heated at 140 °C for 20 min. The mechanism for the crosslinking reaction was shown in Fig. 7. During heating, glutaric anhydride type rings could form first by the dehydration of carboxylic acid groups of PAA (Fig. 7(a)), and these six-member cyclic anhydride rings further react with the hydroxyl groups from β-cyclodextrin by esterification to form the ester bonds and become water insoluble (Fig. 7(b)) [19,20]. The β-cyclodextrin added and heat-crosslinked fibrous membranes not only retained their fibrous structure after prolonged immersion (24 h) in water (Fig. 2(g)), but also showed the pH-responsive swelling behaviors in pH buffer solutions. Their swelling ratios increased from 2 to 17 with pH of buffer solutions increasing from 2 to 7, and most significantly around the pH close to the pKa of PAA, 4.5 (Fig. 8). With the increasing pH in the buffer solutions especially around the pKa of PAA, more and more carboxylic acid groups of PAA ionize and carry negative charges. Due to the dissociation of carboxylic acid groups of PAA the osmotic pressure inside the fibers is higher than that in the surrounding solution, which causes the influx of surrounding solution into the fibers, and thus makes the fibers swell. The repulsion among the partially ionized PAA molecules may also give more room for water molecules to diffuse into the fibers [21].

Investigation of other crosslinking compounds is also underway in order to improve the crosslinking efficiency and increase the swelling ratio of the crosslinked PAA fibers, and will be reported in the near future.

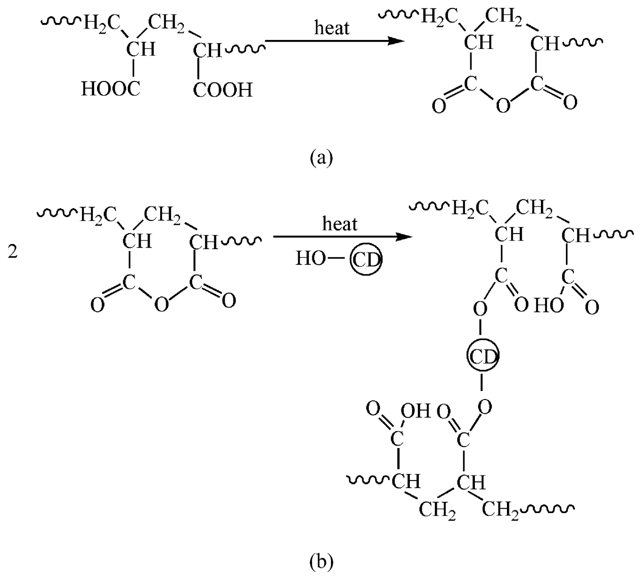

Fig. 7. pH-responsive swelling behavior of heat cured (140 °C, 20 min). PAA/β-cyclodextrin fibrous membranes.

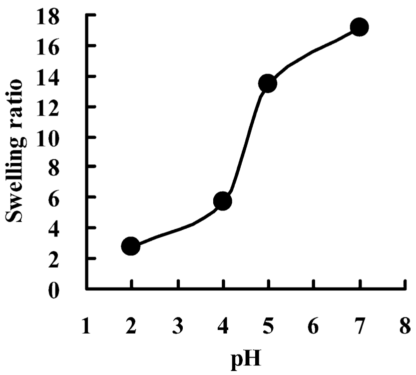

Fig. 8. Mechanism for the crosslinking reaction between PAA and β-cyclodextrin: (a) formation of six-member cyclic anhydride rings by dehydration of carboxylic acid groups of PAA; (b) formation of ester bonds between the cyclic anhydride and β-cyclodextrin.

4. Conclusions

PAA is readily soluble in water and DMF up to 20 wt% and has been electrospun into fibers from either solution at 4–10 wt% concentrations. The aqueous PAA solutions had lower viscosities and could support continuous fiber formation whereas only the 6 wt% or lower concentrations of PAA/DMF solutions could.

Fiber sizes were strongly dependent on the concentrations and voltages in both solution series and averaged from 80 to 500 nm. Thinner fibers were generated at lower concentrations as well as lower voltage. Fibers generated from the aqueous solutions were more uniform in sizes and the homogeneity of fiber sizes could be further improved by raising solution concentrations, adding NaCl, or neutralizing carboxylic acid groups of PAA with NaOH. Adding NaCl or neutralizing PAA with NaOH, however, did not affect the average fiber size. Both inter-fiber pore sizes and the overall pore volume of the fibrous membranes from the aqueous solutions were higher than those from DMF solutions at the same concentration and electrospinning voltage. Higher free volume, shown by increased heat capacity and dehydration temperature, in the fibers was found to increase with increasing voltage. NaCl addition had opposite effect.

Ultra-fine PAA fibers could be rendered insoluble in water by crosslinking with the addition of β-cyclodextrin in the aqueous solution at 20 wt% of PAA followed by heating at 140 °C for 20 min. The crosslinked PAA electrospun fibers showed a swelling ratio in the range from 2 to 17 when the pH of buffer solutions increased from 2 to 7.

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