Electrospinning of Poly(vinyl pyrrolidone): Effects of Solvents on Electrospinnability for the Fabrication of Poly(p-phenylene vinylene) and TiO₂ Nanofibers

Surawut Chuangchote, Takashi Sagawa, Susumu Yoshikawa

Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

ABSTRACT: Seven different solvents (methanol, ethanol, 2-propanol, 1,2-dichloroethane, water, chloroform, and dichloromethane) were used to prepare electrospun poly (vinyl pyrrolidone) (PVP) fibers. The dielectric constant, viscosity, and surface tension of the solvents essentially affected the electrospinnability, morphological appearance, and size of the as-spun fibers. Small and uniform as-spun fibers could be fabricated from PVP solutions in solvents with a significantly high dielectric constant, low surface tension, and low viscosity. In three alcohol solutions (e.g., methanol, ethanol, and 2-propanol), the diameters of as-spun PVP fibers decreased with the dielectric constant, dipole moment, and density of the solvents increasing and with the viscosity of the solvents decreasing. Among these solvents, methanol was the best solvent, providing fibers with an optimal morphological appearance and a small fiber diameter. Mixing an unspinnable solvent with a sol-vent with a high dielectric constant, low surface tension, and low viscosity could increase the electrospinnability of the solution. The effects of solution properties and spinning conditions on the morphological appearance and diameter of electrospun PVP fibers were also carefully investigated. Under all investigated conditions for the electrospinning of a PVP solution in ethanol, the average diameters of the as-spun fibers ranged from 200 nm to 1.5 μm. Well-aligned PVP fibers were also produced with a rotating-drum collector technique. Lastly, PVP was used in the fabrication of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene] and TiO₂ fibers by acting as a polymer carrier or guide. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2777–2791, 2009

Key words: fibers; nanotechnology; solution properties; surfaces; viscosity

INTRODUCTION

One-dimensional nanomaterials have attracted interest and have been widely investigated for potential applications in mechanics, electronics, optoelectronics, and catalysis and for medical, biological, and environmental applications[1–4] because of several specific properties of nanomaterials (e.g., a high surface area to volume ratio, a very high aspect ratio, improved mechanical performance, relatively small pore sizes, and flexibility in surface functionalities).[5,6]

Over the past decade, there has been increasing interest in electrospinning. Electrospinning is a method for preparing continuous one-dimensional materials in the form of ultrafine fibers from a variety of materials, such as polymers, ceramics, inorganic complexes, and organic/inorganic hybrid composites, with diameters ranging from the microscale down to the nanoscale by the acceleration of a jet of a charged solution (or melt) in an electric field.

The electric field is generated between a syringe with a capillary tip and a grounded collector by a high-voltage power supply. Electrostatic charging at the tip of the nozzle results in the formation of the well-known Taylor cone, and then a single fluid jet is ejected from the apex.[7,8] As the jet accelerates, radial charge repulsion results in bending instability. The charged jet is thinned in the electric field and then solidified. These fibers are collected on the surface of a collector as highly impermeable, randomly deposited, and nonwoven mats.

So far, more than 40 different types of polymers have been fabricated into nanofibers by electrospinning.[4] Poly(vinyl pyrrolidone) (PVP) is an important synthetic polymer that consists of carbon, hydrogen, oxygen, and nitrogen in the repeating unit. It was first reported in a patent about 60 years ago, with good adhesion and complexation properties, low chemical toxicity, high hydrophilicity, excellent physiological compatibility, biocompatibility, and good solubility in water and various organic solvents.[9,10] It is, therefore, widely applied in many novel applications such as adhesives, paints, detergents, electronics, beverages, cosmetics, pharmaceuticals, and biological engineering materials.[10]

Correspondence to: S. Yoshikawa (s-yoshi@iae.kyoto-u.ac.jp).

The electrospinning of ultrafine PVP fibers was first reported by Bognitzki et al.[11] in 2001, and the successful fabrication of polylactide/PVP blend fibers was also reported at that time. Because of the various advantages of PVP mentioned previously and other specific benefits related to electrospinning (e.g., its ease of spinning, extractability, and ability to act as a non-ionogenic partner for the electrospinning of an ionogenic polymer), PVP is widely used in the fabrication of fibers via electrospinning with various other materials that are unspinnable or hardly spinnable by acting as a polymer carrier, a partner, or a guide. Metal oxides (e.g., TiO_2, ZnO, and SnO_2) and secondary metal-doped/metal oxide nanofibers can be prepared by the electrospinning of metal oxide precursors and PVP, which is followed by calcination at a high temperature to form the crystalline phase of metal oxides and get rid of PVP at the same time.[12–19] Some conductive polymers, hardly spinnable because of the limitations of suitable solvents and molecular weights, can also be successfully fabricated by direct blending with PVP[20–24] or through the use of separate spinning solutions with a coaxial two-capillary spinneret.[25,26] These reported conductive polymers include polyaniline,[20,21] poly(p-phenylene vinylene),[22] and its derivatives poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH–PPV)[23–25] and blended MEH–PPV/poly(3-hexylthiophene).[26] Biopolymers and other compounds for medical and biological applications (e.g., scaffolding, wound-dressing materials, and biosensors) have been reported to have been successfully fabricated in fiber form via blending with PVP.[11,27–31] Furthermore, PVP has also been mixed with small molecules and organic or inorganic compounds (e.g., functional organic molecules,[32] carbon black,[33] and metal oxide nanoparticles or nanorods[34–37]) to fabricate various kinds of composite fibers by electrospinning. Almost all the spinning solutions in these reported works were, however, prepared in ethanol; some were prepared in a mixed ethanol/water system; and only a few of them were prepared in water[31,33] and some organic solvents, including dichloromethane (DCM), N,N-dimethylformamide (DMF), and their mixtures,[10,35] 1,2-dichloroethane (DCE)/chlorobenzene (CB),[23] and CB/methanol.[24] The study of the fabrication of electrospun PVP fibers from solutions dissolved in other organic solvents and mixed solvents to discover ways of widening the utilization of PVP in the fabrication of electrospun fibers from other materials is, therefore, very interesting.

Generally, uniform fibers without any beads or droplets and small-diameter fibers are required for electrospinning. The morphological appearance and diameters of the electrospun fibers depend on a number of parameters, including the properties of the spinning solution [e.g., the type of polymer, con-formation of the polymer chain, composition of the polymer (in the case of polymer blends), viscosity (concentration) of the solution, and composition, conductivity, surface tension, and polarity of the solvent] and the electrospinning conditions [e.g., the applied electrical potential, distance between the capillary and collector (i.e., collection distance), and feed flow rate].[38–40] For the electrospinning of PVP, Yang et al.[10] reported the influence of solvents (including ethanol, DCM, DMF, and an ethanol/DMF mixture) on the formation of uniform PVP nanofibers in 2004. Li et al.[41] reported the application of patterned electrodes to change the alignment of PVP fibers in 2005. However, to the best of our knowledge, until now, no investigation about the electrospinning of PVP per se from solutions in various alcohols and other organic solvents and the influence of various spinning solution properties and electrospinning conditions has been reported. In this contribution, the electrospinning of PVP from solutions in various solvents, including methanol, ethanol, 2-propanol, DCE, water, chloroform, and DCM, was carried out to systematically study the effects of the solvents used and the composition of the solvents in a mixed solvent system on the morphological appearance and size of the as-spun products. Moreover, the effects of the molecular weight of PVP, solution concentration, applied electrical potential, and collection distance on the as-spun fibers and the potential to align PVP fibers in one direction were determined. Examples of the utilization of PVP in the fabrication of other electrospun fibers (e.g., conductive polymer and TiO_2 fibers) were also investigated and discussed.

EXPERIMENTAL

Materials

PVPs with weight-average molecular weight (M_w) values of 43,000 and 1,300,000 were supplied in powder form from Nacalai Tesque (Kyoto, Japan) and Aldrich (St. Louis, MO), respectively. The solvents were methanol, ethanol, 2-propanol, DCE, water, chloroform, DCM, toluene, CB, 1,2-dichlorobenzene (DCB), and tetrahydrofuran (THF). All of them were purchased from Wako (Osaka, Japan), except for DCB, which was purchased from Aldrich, and water, which was filtered in our laboratory. Some important properties of these solvents are summarized in Table I. A conductive polymer, MEH–PPV [number-average molecular weight (M_n) $\approx$ 40,000–70,000, $M_w/M_n \approx 5$], was purchased from Aldrich. For the preparation of the TiO_2 precursor, titanium(IV) butoxide (TiBu; reagent grade, 97%) and acetylacetone (ACA) were purchased from Aldrich and Nacalai Tesque, respectively.

<div align="center">

TABLE I
Some Properties of the Solvents

</div>

Solvent	Boiling point (°C)	Viscosity (mP s)	Surface tension (mN/m)	Density (g/cm^3)	Dipole moment (D)	Dielectric constant
Methanol	64.7	0.59	22.6	0.792	1.69	32.6
Ethanol	78.4	1.20	22.1	0.789	1.66	24.6
2-Propanol	82.3	2.07	23.0	0.785	1.66	19.9
DCE	83.5	0.84	31.6	1.239	2.94	10.2
Water	100.0	0.88	72.8	0.998	1.87	78.4
Chloroform	61.2	0.54	27.5	1.470	1.15	4.8
DCM	39.8	0.44	26.5	1.326	1.14	10.7
Toluene	110.6	0.59	28.5	0.867	0.31	2.4
CB	131.7	0.80	33.6	1.107	1.54	5.6
DCB	180.3	1.32	26.8	1.306	2.14	9.8
THF	66.0	0.48	26.4	0.875	1.75	7.6

Electrospinning of pure PVP

To study the effects of the molecular weight of PVP, the solution concentration, and the applied electrical potential, PVP solutions were prepared to attain concentrations of 40, 50, and 60% w/v and 6, 8, and 10% w/v from PVPs with M_w values of 43,000 and 1,300,000, respectively. In DCE solutions, to study the effects of the solution concentration, PVP (M_w = 1,300,000) solutions were prepared with concentrations in the range of 4–10% w/v. In other experiments, without another mention, only PVP with an M_w value of 1,300,000 was used, and the concentration of PVP was fixed at 8% w/v.

The electrospinning of these as-prepared solutions was carried out by the loading of each of the as-prepared solutions into a 3-mL plastic syringe. The nozzle was a blunt-end, stainless steel, gauge 22 needle (1.5 cm long). An aluminum sheet wrapped around a hard plastic backing plate was used as the collector. To study the alignment of the as-spun PVP fibers, an aluminum sheet wrapped around a rotating drum rotated at a speed of 3000 rpm was used as the collector instead. A gamma high-voltage research power supply was used to charge the solution across an electrode in solution. In a typical procedure, without another mention, as-prepared solutions were electrospun under an applied electrical potential of 15 kV over a fixed collection distance of 15 cm at room temperature ($\sim$ 18°C). The flow rate and the collection time were fixed for all experiments at 1 mL/h and 1 min, respectively. The samples were then dried overnight at 60°C in a vacuum oven before further characterization.

Electrospinning of a conductive polymer with PVP as a polymer carrier

Solutions of 7% w/v MEH–PVP/PVP (1 : 6 w/w) in mixed solvents of CB and methanol with CB/metha-

nol mixing ratios of 85 : 15, 80 : 20, and 75 : 25 v/v were prepared under vigorous stirring. The obtained solutions were sonicated for 10 min and heated to 40°C to exceed the dissolubility of MEH–PPV. The electrospinning of as-prepared solutions was carried out with the typical procedure described previously.

Fabrication of TiO$_2$ fibers with PVP as a polymer guide

For the preparation of the TiO$_2$ precursor, 5.45 g of TiBu was first introduced into equimolar ACA. The mixed solution was then gently stirred until intimate mixing to obtain a solution of the TiO$_2$ precursor. The TiO$_2$ precursor solution (0.6 g) was added to 1 mL of an 8% w/v PVP (M_w = 1,300,000) solution in ethanol. The resulting mixture was constantly stirred for 10 min. The as-prepared solution was called the spinning solution.

Electrospinning was carried out with the typical procedure described previously. The obtained fibers were left exposed to moisture for approximately 5 h to allow complete hydrolysis of TiBu and consequently subjected to calcination at a high temperature of 450°C for 3 h to remove residual PVP and impurities and increase the crystallinity of TiO$_2$.

Characterization

The morphological appearance of the as-spun fibers was examined with a JEOL (Tokyo, Japan) JSM-6500FE scanning electron microscope operating at an acceleration voltage of 10 kV. Diameters of the as-spun fibers were measured directly from scanning electron microscopy (SEM) images, with the average value being calculated from at least 50 measurements for each spinning condition. The crystalline phase of the TiO$_2$ fibers was identified with a Rigaku (Tokyo, Japan) Rint 2100 X-ray diffractometer.

RESULTS AND DISCUSSION

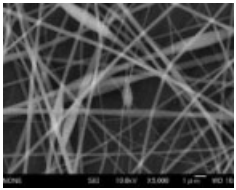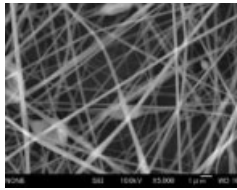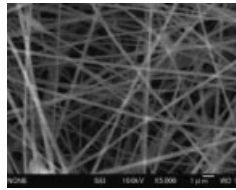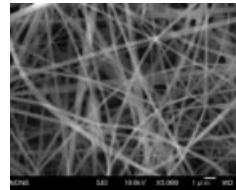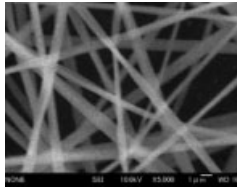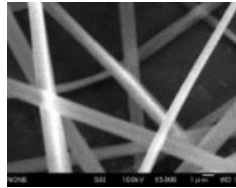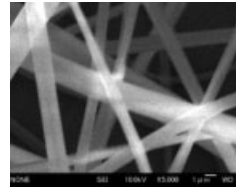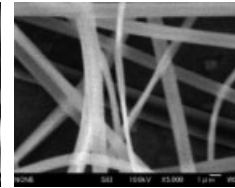### Electrospinning of PVP in single solvents
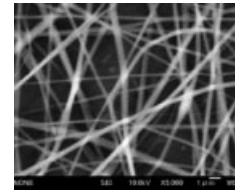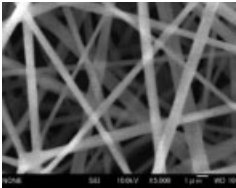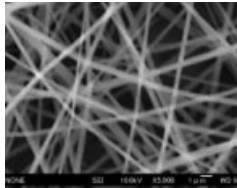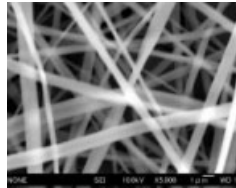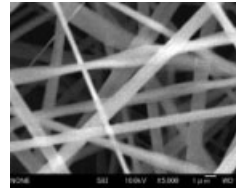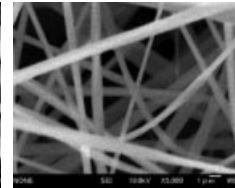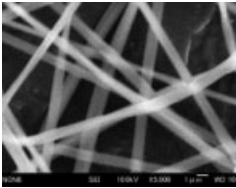
Many attempts to fabricate ultrafine fibers of PVP and its blends by the electrospinning of PVP solutions in ethanol have been reported. Before the electrospinning of PVP solutions in other solvents was carried out, the influences of various solution properties and electrospinning conditions were systematically investigated with ethanol as the solvent. To straightforwardly explain the reasons for the results, six types of forces involved in electrospinning should be mentioned,[6] including the gravitational or body force; the electrostatic force (the force exerted on charges carried within a jet segment when the jet is in an electrostatic field), which carries the charged jet from the needle to the collector; the Coulombic stretching force (the repulsion force between charges of mutual polarities), which tries to push apart adjacent charged species carried within the jet segment and is responsible for the thinning or stretching of the charged jet during its flight to the target; the viscoelastic force, which tries to prevent the charged jet from being stretched; the surface tension, which also acts against the stretching of the surface of the charged jet; and the drag force from the friction between the charged jet and the surrounding air.

Effects of the molecular weight of PVP, the solution concentration, and the applied electrical potential

Tables II and III show SEM images illustrating the morphological appearance of the as-spun fibers from 40–60 and 6–10% w/v PVP solutions in ethanol; the M_w values of PVP were 43,000 and 1,300,000, respectively. Quantitative results in terms of the average diameters of the as-spun fibers are summarized in Figure 1. The applied electrical potential varied in the range of 5–30 kV over a fixed collection distance of 15 cm. Ultrafine fibers with average diameters in the range of 200 nm to 1.5 μm could obviously be produced.
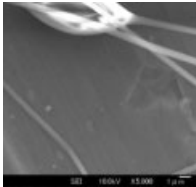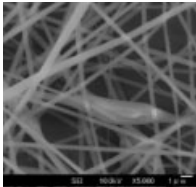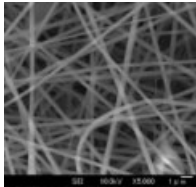
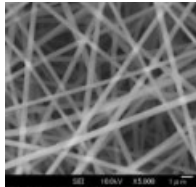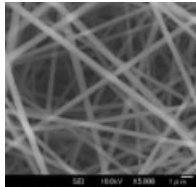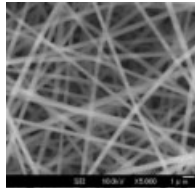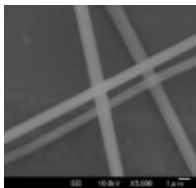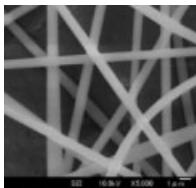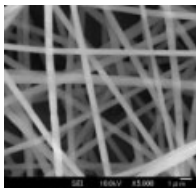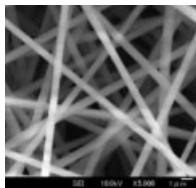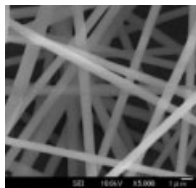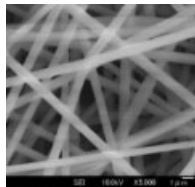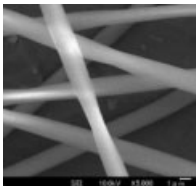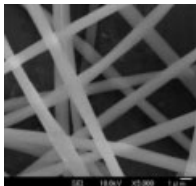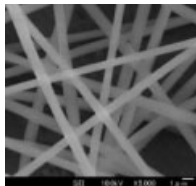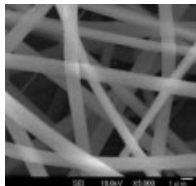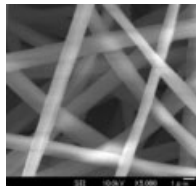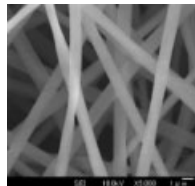In most of the reported works related to the electrospinning of PVP and its blends (or composites), PVP with an M_w value of 1,300,000 has been extremely investigated. Only a few have reported the use of PVP with an M_w value of 360,000[29,31] or 55,000.[35] Therefore, it was interesting to carry out the electrospinning of PVPs of very different molecular weights and study the effects on the electrospinning behavior. According to Tables I and II, for each molecular weight, a uniform fibrous structure was stabilized above a minimum concentration. This certain concentration of PVP with an M_w value of 43,000 was between 6 and 8% w/v, whereas that

TABLE II
SEM Images of the As-Spun Fibers from Solutions of 40, 50, and 60% w/v PVP (M_w = 43,000) in Ethanol

	Applied electrical potential (kV)				
	10	15	20	25	30
40% w/v					
50% w/v					
60% w/v					

The applied potentials for electrospinning were varied between 10 and 30 kV (in 5-kV increments) over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The scale bar in each image equals 1 μm.

	Applied electrical potential (kV)					
	5	10	15	20	25	30
6% w/v						
8% w/v						
10% w/v						

The applied potentials for electrospinning were varied between 5 and 30 kV (in 5-kV increments) over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The scale bar in each image equals 1 μm.

with an M_w of 1,300,000 was between 40 and 50% w/v. At these concentrations, higher molecular weight PVP showed a little bit larger fiber diameter than lower molecular weight PVP (see Fig. 1). In other words, to obtain the same morphological appearance and same range of fiber diameters obtained with spinning solutions of higher molecular weight PVP (M_w = 1,300,000) at a concentration of 6–10% w/v, the concentration of the solution from lower molecular weight PVP (M_w = 43,000; ∼ 30 times lower) had to be increased to 40–60% w/v (∼ 6–7 times higher). The results from viscosity measurements (RC-100 viscometer controller, Toki Sangyo Co., Ltd., Tokyo, Japan) showed that the same range of solution viscosities with both molecular weights was the cause of this. In particular, the viscosities of PVP (M_w = 43,000) solutions at 40, 50, and 60% w/v were 200, 418, and 636 mPa s, respectively, whereas those of PVP (M_w = 1,300,000) solutions at 6, 8, and 10% w/v were 93, 221, and 425 mPa s, respectively.

To obtain uniform ejection of the charged jet in electrospinning, a solution with an appropriate concentration or viscosity is required to be exceeded as extensive molecular entanglements are prerequisites for the formation of a stable and continuous charged jet. If the concentration of the solution is too low, a continuous stream of the charged jet cannot be formed, as the charged jet experiences instability leading to the formation of droplets; this is called electrospraying.[42] Conversely, if the solution concentration is too great, a prohibition of continuous flow of the polymer liquid from the nozzle tip will be achieved.[6] As a result, there is a processing window in terms of the concentration or viscosity range within which the polymer solutions are electrospinnable and beyond which discrete droplets are likely to occur.[6,43] For this work, regardless of the molecular weight and applied electrical potential, electrospinning of the solution with the lowest concentration (6 and 40% w/v for PVPs with M_w values of 1,300,000 and 43,000, respectively) resulted only in the formation of beaded fibers because of the low viscosity of the solution; hence, the low viscoelastic force was not enough to prevent Coulombic-repulsion-caused partial breakup of the charged jet. A further increase in the solution concentration resulted in the formation of uniform fibers because of the increased viscosity; hence, the increased viscoelastic force was enough to completely prevent the partial breakup of the charged jet and allowed the Coulombic stress to elongate the charged jet.[6] Increasing the solution concentration of PVP caused the fiber diameters to increase monotonically with a broader distribution. This is in general accordance with the literature.[10] For the fiber diameter, according
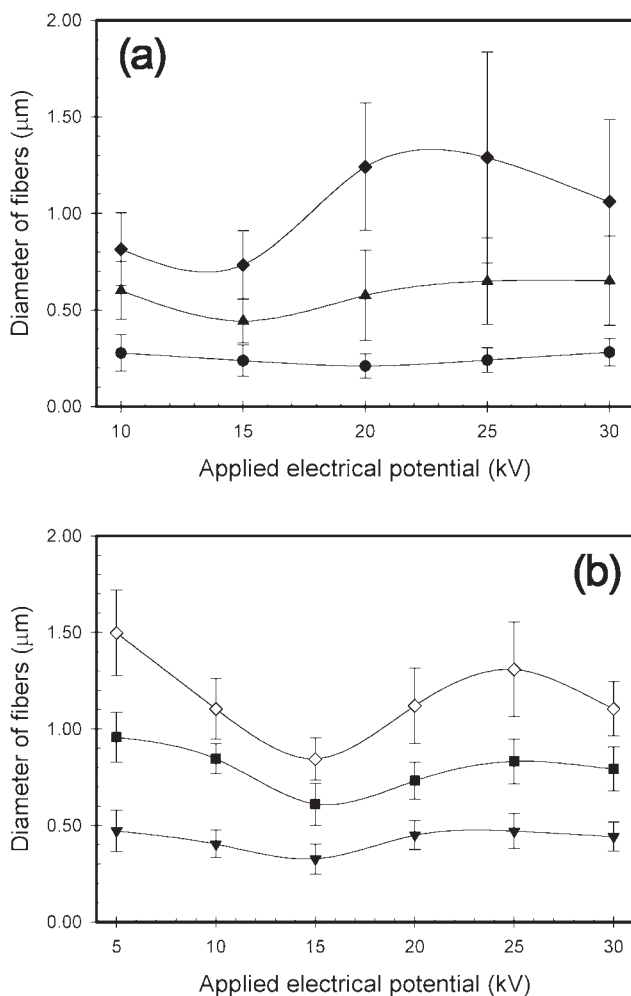
Figure 1 Average diameters of the as-spun fibers from (●) 40, (▲) 50, (◆) 60, (▼) 6, (■) 8, and (◇) 10% w/v PVP solutions in ethanol. The M_w values of PVP were (a) 43,000 and (b) 1,300,000. The electrical potential in electrospinning was applied in the ranges of 10–30 and 5–30 kV for solutions of PVP with M_w values of 43,000 and 1,300,000, respectively, over a fixed collection distance of 15 cm. The feed flow rate was 1 mL/h.

to Figure 1, regardless of the applied electrical potential investigated, at the lowest concentration investigated (6 and 40% w/v for PVPs with M_w values of 1,300,000 and 43,000, respectively), the average diameter of the as-spun fibers ranged between 326 and 472 and between 210 and 281 nm for PVPs with M_w values of 1,300,000 and 43,000, respectively. However, at the highest concentration investigated (10 and 60% w/v for PVPs with M_w values of 1,300,000 and 43,000, respectively), it ranged between 734 nm and 1.29 µm and between 844 nm and 1.50 µm for PVPs with M_w values of 1,300,000 and 43,000, respectively. Yang et al.[10] reported that the average diameters of as-spun fibers from PVP ($M_w = 1,300,000$) ethanol solutions increased from 120 to 250, 400, 750, and 1500 nm with the PVP concentration increasing from 2 to 4, 6, 8, and 10%,

respectively [for an electrostatic field strength (EFS) of 8 kV/12 cm].[10] Obviously, for PVP with an M_w value of 1,300,000, our results were in line with those of this previous report. Interestingly, flat and twisted (ribbon-like) fibers could be observed at a high solution concentration (see Tables II and III) as a result of a broader distribution of the fiber diameters at a higher concentration. Moreover, it was observed that, at a higher concentration, the electrospinning of lower molecular weight PVP resulted in more flat and twisted fiber structures than the electrospinning of high-molecular-weight PVP. This may be due to the fact that a charged jet from the low-molecular-weight PVP could be stretched during bending instability more than that from the high-molecular-weight PVP.

For any given molecular weight and solution concentration, increasing the applied electrical potential caused the number of the as-spun fibers (or beaded fibers) per unit of area to increase. Increasing the applied electrical potential also caused the number of beads per unit of area to decrease or disappear; this was an indication of the increased stretching force exerted on a jet segment (see Tables II and III). According to Figure 1, for any given molecular weight and solution concentration, the average diameters of the as-spun PVP fibers as well as their variations were generally found to decrease with an initial increase in the applied electrical potential, reach a minimum value at about 15 kV, then increase with a further increase in the applied electrical potential, reach a maximum value, and decrease again at the highest applied electrical potential (at 30 kV). The increase in the applied electrical potential should cause the number of charges carried within a jet segment to increase and hence an increase in both the electrostatic and Coulombic repulsion forces. The increased Coulombic repulsion force should cause the diameters of the as-spun fibers to decrease (because of increased stretching force exerted on the jet segment), whereas the increased electrostatic force should cause the diameters of the as-spun fibers to increase (because of both the increase in the speed of the jet segment and the increase in the mass flow rate, the phenomena that cause the onset of bending instability to occur closer to the screen collector).[6] On the basis of this statement, the observed decrease in the fiber diameters with the initial increase in the applied electrical potential could be due to a contribution from the increase in the Coulombic repulsion force, whereas the observed increase in the fiber diameters with a further increase in the applied electrical potential could be due to a contribution from the increase in the electrostatic force, and the decrease in the fiber diameter again at the highest applied electrical potential could be due to a contribution from the increase in the Coulombic repulsion

force, which was too high to overcome the electro-static force. For reported works related to the electrospinning of pristine PVP, there has been no report on the effects of the applied electrical potential; however, there are various conflicting results reported in the literature for the electrospinning of other polymers and also PVP blends and composites.[12,22,29,32,40] Competing effects of two forces should be the reason for these conflicting results. In the case of the electrospinning of another polymer, poly(vinyl alcohol) (PVA), the average diameter of the as-spun PVA fibers as well as their variation was also reported to decrease with the initial increase in the applied electrical potential, reach a minimum value, and increase with a further increase in the applied electrical potential to 25 kV.[7] In accordance with this, we obtained similar results, except for the last decrease in the diameter at the maximum applied electrical potential, because a higher applied electrical potential (30 kV) was also investigated.

The effects of the solution concentration in another organic solvent (i.e., DCE), not just in ethanol solutions, were also investigated and are shown in Figure 2 (M_w of PVP = 1,300,000). The results showed the same trend in comparison with the electrospinning of PVP solutions in ethanol; that is, increasing the solution concentration of PVP caused a change in the morphological appearance from beaded fibers to uniform fibers at a certain concentration (6–8%

w/v) and caused the fiber diameters to increase monotonically with a broader distribution. The electrospinnability became more difficult with the concentration increasing to 10% w/v [see Fig. 2(d)], and at a higher concentration over 10% w/v, the electrospinning was inhibitive because of the high viscosity. As shown in Figures 1(b) and 2(e), even with the same concentration and applied electrical potential, electrospun PVP fibers from DCE solutions showed significantly larger average diameters than those from ethanol solutions (e.g., 610 nm and 2.11 μm, respectively, at the concentration of 8% w/v and at the applied electrical potential of 15 kV).

Effects of the solvents

Among the 11 solvents used, that is, methanol, ethanol, 2-propanol, DCE, water, chloroform, DCM, toluene, CB, DCB, and THF, it was found that toluene, CB, DCB, and THF were not able to dissolve PVP to form a clear solution at room temperature ($\sim 18°C$). Interestingly, solvents that were able to dissolve PVP and were able to fabricate fibers by electrospinning have quite high dipole moments and low boiling points ($\leq 100°C$). Moreover, their dielectric constants are higher than those of the solvents that were not able to dissolve PVP, and those values are higher than 10, except for chloroform (see Table I). To study the effects of the solvents, 8% w/v PVP (M_w =
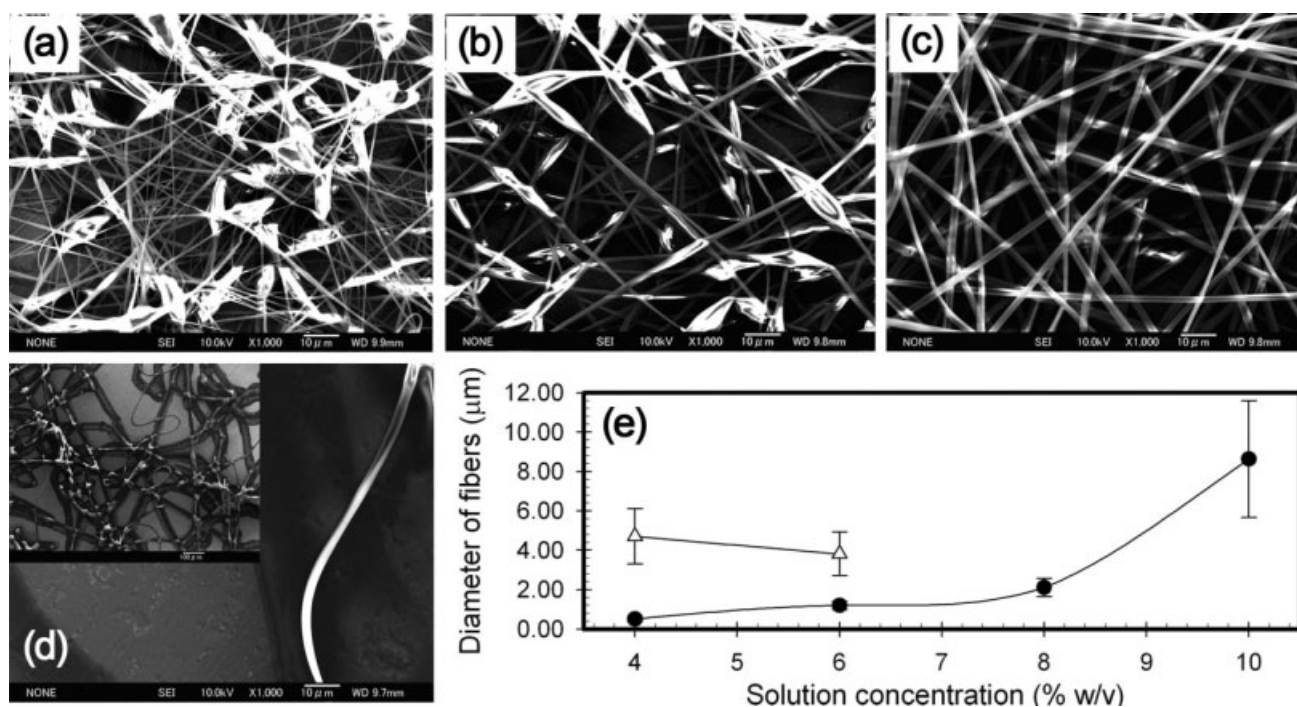
Figure 2 (a–d) SEM images and (e) quantitative results in terms of the average diameters of ($\triangle$) beads and ($\bullet$) as-spun fibers from solutions of (a) 4, (b) 6, (c) 8, and (d) 10% w/v PVP (M_w = 1,300,000) in DCE. The applied potential for electrospinning was 15 kV over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The scale bar in each image equals 1 μm, except for the inset in part d, for which it equals 100 μm.

1,300,000) in methanol, ethanol, 2-propanol, DCE, water, chloroform, and DCM was electrospun with a fixed electrical potential, collection distance, and feed flow rate of 15 kV, 15 cm, and 1 mL/h, respectively. The obtained results are shown in Figure 3. According to Figure 3(a–c), smooth fibers without the presence of beads were obtained from the electrospinning of all three PVP alcohol solutions. At a high magnification, it was revealed that the cross-sectional geometry was quite round because of the low boiling point of the solvent used. The charged jets could be dry enough before being collected on a grounded target.

In three alcohol solutions (methanol, ethanol, and 2-propanol), the three solvents are a good system to determine the effect of a solvent on the morphological appearance and fiber diameter. Because all of them have the same functional (hydroxyl) group, the type of molecular interaction between the solvent and the polymer can be observed for comparison. According to the properties of the three alcohols, if the type of alcohol solvent is changed from 2-propanol to ethanol or methanol, the dielectric constant will be remarkably increased from 19.9 to 24.6 and 32.6, respectively; the dipole moment will be quite constant (constant at 1.66 D and increasing to 1.69 D). The solvent density will increase from 0.785 to 0.789 and 0.792 g/cm^3, respectively; the surface tension will be quite constant (decreasing from 23.0 to 22.1 mN/m and increasing to 22.6 mN/m). The viscosity will be remarkably reduced from 2.07 to 1.20 and 0.59 mP s, respectively; the boiling point will be reduced from 82.3 to 78.4 and 64.7°C, respectively (see Table I). The diameter of as-spun fibers from a PVP solution in 2-propanol was larger than that from an ethanol solution, which was also larger than that from a methanol solution; that is, the average diameters of as-spun fibers from solutions in 2-propanol, ethanol, and methanol were 1250, 638, and 274 nm, respectively. Obviously, it can be concluded that the diameters of as-spun PVP fibers decreased with the dielectric constant, dipole moment, and density of the solvents increasing and with the viscosity and boiling point of the solvents decreasing.

When we consider each property of the solvents, we find that a greater dielectric constant is responsible for the observed smaller diameters of the obtained PVP fibers because a greater dielectric constant leads to greater Coulombic repulsion force (which is responsible for the stretching of the charged jet) and electrostatic force (which is responsible for carrying the charged jet to the collector).[6] Lee et al.[44] found the dielectric constant to be one of the key factors in the electrospinning process. The dielectric constant is related to the dipole moment and generally reflects the polarity of the molecules; that is, methanol has greater polarity than ethanol and 2-propanol. For the density of solvents, Wannatong et al.[45] reported that the fiber diameter of polystyrene fibers decreased with the density of the solvents increasing, and this corresponds with our results. The effects of the viscosity of the solvent are directly related to the visco-elastic force. This force tries to prevent the charged jet
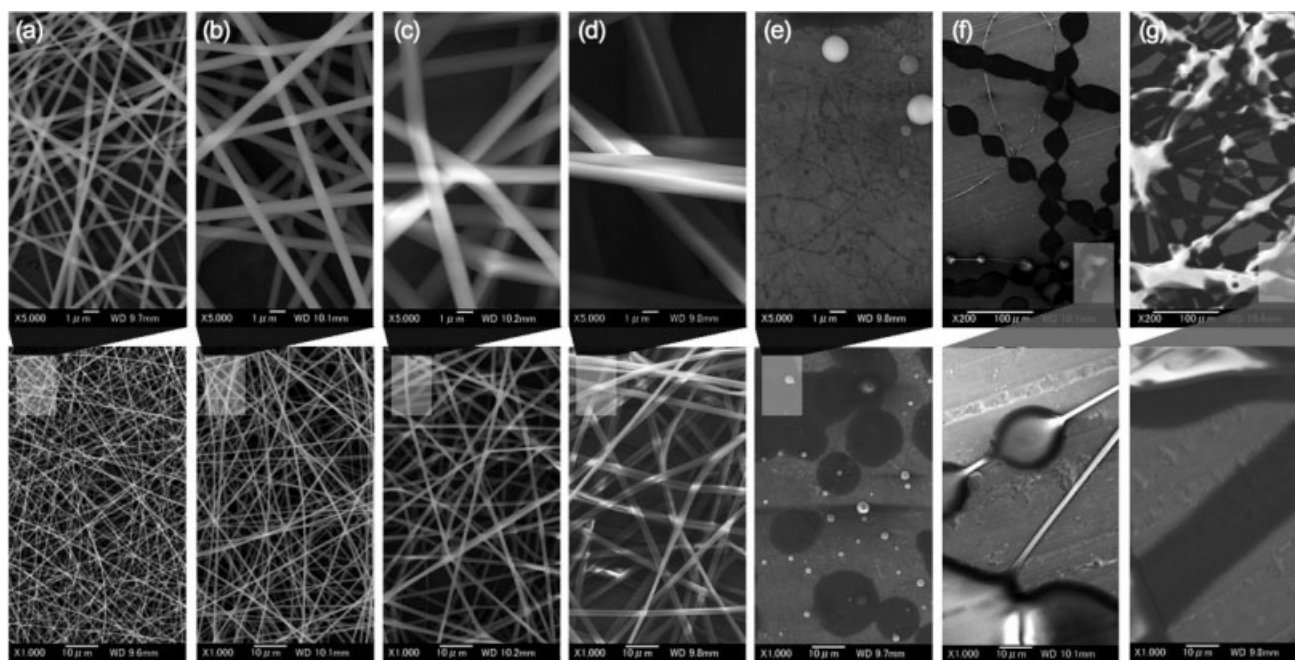
Figure 3 SEM images of the as-spun fibers from 8% w/v PVP (M_w = 1,300,000) solutions in various solvents: (a) methanol, (b) ethanol, (c) 2-propanol, (d) DCE, (e) water, (f) chloroform, and (g) DCM. The applied potential for electrospinning was 15 kV over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The scale bar in each image in the second row equals 10 μm, whereas those in the first row equal (a–e) 1 or (f,g) 100 μm.

from being stretched, as discussed previously; as a result, the diameter of PVP fibers was found to decrease with the viscosity of the solvent decreasing. On the contrary, it has been reported in the literature that the observed fiber diameter decreases with an increase in the boiling point of the solvents,[45] and this is inconsistent with our results. The reason for the conflicting observations is the large difference in the ranges of boiling points of the investigated solvents, which were 65–203°C (a 138°C difference) and 65–82°C (an approximately 17°C difference) for the reference[45] and our experiment, respectively. Therefore, for the three alcohols investigated, other properties of the solvent, that is, the dielectric constant, dipole moment, density, and viscosity, as described previously, played more important roles in the diameter changes of as-spun PVP fibers than the slight change in the boiling point.

As remarked previously, an 8% w/v PVP solution in DCE could be electrospun to form uniform fibers with quite large diameters (or widths; ~ 1.25 µm). In comparison with alcohols, the fact that DCE has a much lower dielectric constant and a significantly high surface tension may be responsible for the larger fiber diameter. The role of the dielectric constant has been already discussed. For surface tension, it acts against the stretching of the surface of the charged jet. The size of the charged jets from a high surface tension solution could not be reduced much during bending instability as a result of the large diameter of the obtained as-spun fibers. Moreover, the cross-sectional geometry of the as-spun fibers was c-shaped [see Fig. 3(d)], and this could be a result of the collapse of the fibers upon the evaporation of the solvent.

An 8% w/v PVP aqueous solution was spun out to form ultrafine fibers (~ 33 nm in diameter) with spherical beads or globs of PVP [1.35 µm in diameter; see Fig. 3(e)]. It is believed that the very high surface tension of water made the droplets of the solutions form spherical beads during drying, whereas the very high dielectric constant led to the formation of ultrafine fibers with a very small diameter. To obtain uniform electrospun fibers, a reduction of the surface tension in aqueous solutions should be carried out. One easy way is the mixing of water with a solvent that has a lower surface tension. Fong et al.[38] reported that increasing the ethanol composition in a poly(ethylene oxide) (PEO) solution in a mixture of water and ethanol could reduce the surface tension of obtained solutions, and the electrospinning of those solutions resulted in uniform as-spun PEO fibers. The electrospinning of some materials from solutions in a mixture of water and ethanol with PVP as the polymer carrier has also been reported.[13,25,26,29,30,34]

Electrospinning of an 8% w/v PVP solution in chloroform resulted in bead-on-string structures with flat beads [see Fig. 3(f)]. The average diameters of the fibers and beads were 1.45 and 31.9 µm, respectively. However, ribbon-like fibers with flat beads could be observed from the electrospinning of an 8% w/v PVP solution in DCM [see Fig. 3(g)]. The average width of the fibers and the average diameter of the beads were 15.7 and 34.9 µm, respectively. As-spun PVP fibers from DCM solutions appeared to be wet as they were fused to adjacent fibers at touching points. Fong et al.[38] attributed the formation of beads to the low viscosity and high surface tension of the solutions and the high boiling point of the solvent (low evaporation rate). In other words, when we consider the aforementioned forces, the formation of beads could be ascribed to the viscoelastic and surface tension forces. In this case, chloroform and DCM have low boiling points. Therefore, a bead structure is most likely a result of higher surface tension in comparison with that of alcohols. Another possible reason is that there was not enough viscoelastic force in the PVP solutions at the concentration of 8% w/v because chloroform and DCM have low viscosities (see Table I). This concentration is too low to exceed molecular entanglements, which are prerequisites for the formation of a stable and continuous charged jet. The composition of the solvent in the charged jets was high, and the even evaporation rate was not low, but the charged jets could not be dry enough before being collected on a grounded collector. In this sense, some parts of the damp fibers would be flat during very rapid deposition.

Effects of the collection distance

Figure 4 shows SEM images of electrospun fibers prepared under conditions with several collection distances. The 8% w/v PVA solutions in 2-propanol and in chloroform were electrospun under a fixed applied electrical potential of 15 kV. The collection distances for the electrospinning of PVP solutions in 2-propanol and chloroform were 9.5 and 15 cm and 15, 20, and 25 cm, respectively. As shown in Figure 4(a), from the electrospinning of the PVP solution in 2-propanol at the collection distance of 9.5 cm, nonsmooth, wet-like fibers with a large diameter (~ 3.25 µm) were obtained, and the adjacent fibers appeared to fuse to one another at touching points; this was an indication of the incomplete drying of the jet before deposition on the collector. A further increase in the collection distance to 15 cm resulted in the formation of smooth fibers with a much smaller diameter (~ 1.25), which indicated that the jets were stretched and dried enough before deposition on the collector. From this observation, it can be deduced that an insufficient collection distance in the electrospinning of 8% PVP solutions in chloroform may be another cause of the formation of flat bead structures, as
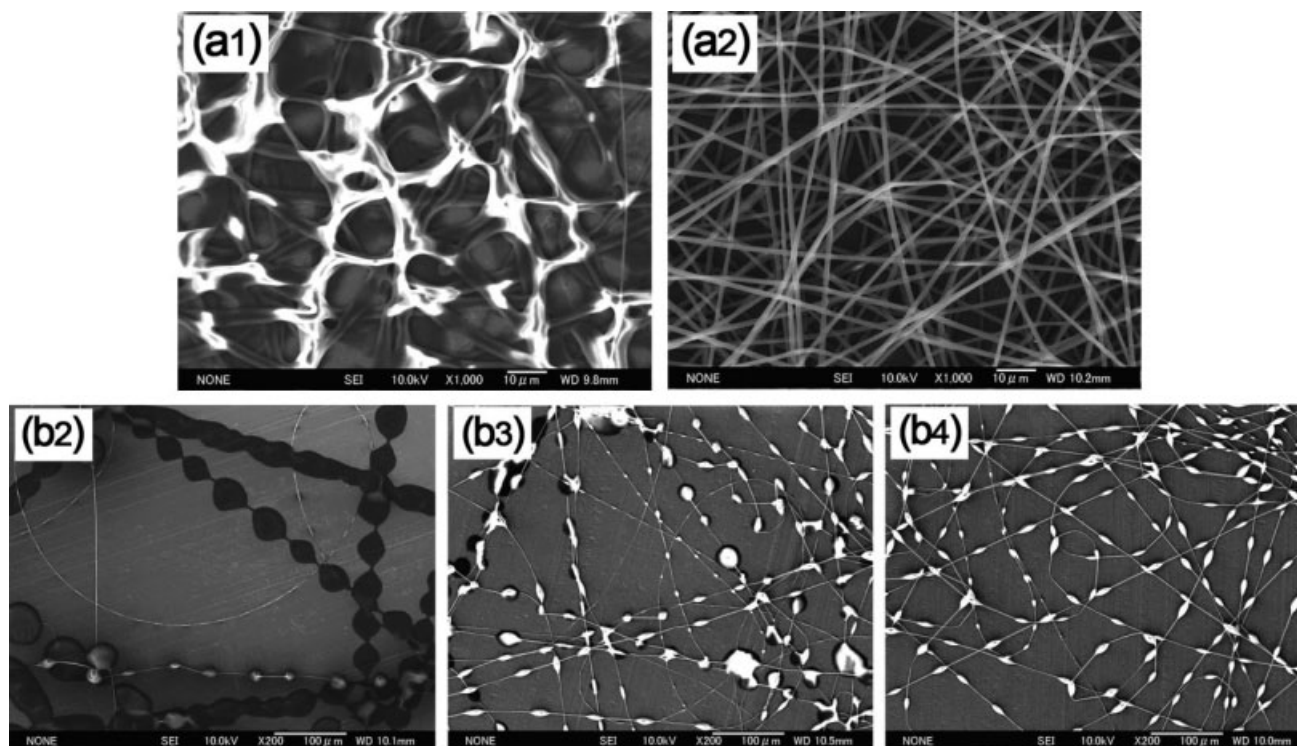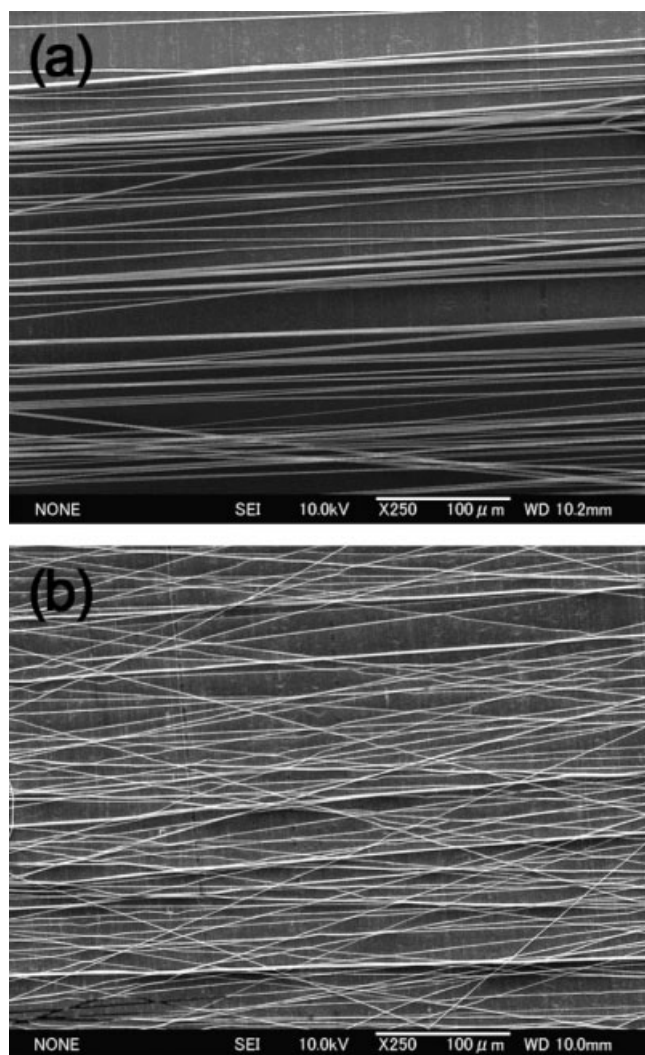
Figure 4 SEM images of the as-spun fibers from 8% w/v PVP (M_w = 1,300,000) solutions in (a) 2-propanol (scale bar = 10 μm) and (b) chloroform (scale bar = 100 μm). The applied potential for electrospinning was 15 kV. Suffixes 1–4 represent collection distances of 9.5, 15, 20, and 25 cm, respectively. The feed flow rate was 1 mL/h. The scale bar in each image equals 10 μm.

described previously. Therefore, the electrospinning of PVP solutions in chloroform at various collection distances was also carried out. As shown in Figure 4(b), the shapes of beads in beaded fibers were found to change from flat to spindle-like. The diameters of the as-spun fibers and beads were found to decrease with the collection distance decreasing. Specifically, the diameter of as-spun fibers decreased from about 1.45 to 1.12 and 1.04 μm with the collection distance increasing from 15 to 20 and 25 cm, respectively. The observed decrease in the diameters of the fibers and beads with the collection distance increasing must be a result of the increase in the total path trajectory of the jet, which allowed more stretching of the jet during its flight to the collector.

Alignment of the electrospun PVP fibers

One characteristic feature of electrospun fibers that has received much interest recently is the possibility of aligning fibers in one direction. For the preparation of aligned PVP fibers, Li et al. reported aligned arrays of pure PVP fibers via the collection of as-spun fibers with patterned electrodes[10] and aligned ceramic fibers fabricated with PVP as a polymer guide and with two parallel pieces of electrodes as a collector.[13] In this work, a rotating-drum collector technique was applied to align electrospun fibers.

Figure 5 illustrates the effects of the applied potential on the alignment of the as-spun PVP fibers in the machine direction. These fibers were fabricated from a 10% w/v PVP solution in ethanol. The applied potential was varied from 5 to 25 kV over a collection distance of 1 cm. The rotational speed of the collector was also fixed at 3000 rpm. Clearly, the alignment in the machine direction of the as-spun fibers from the electrostatic potential of 5 kV was much better than that of the fibers from the applied potential of 15 kV. This can be explained on the basis of the relationships between the three major forces (i.e., the body, electrostatic, and drag forces). At a lower applied electrical potential (e.g., 5 kV), the lateral speed at the points of contact between the depositing charged jets and the collector screen was fit to the approaching speed of the charged jets, and this finally resulted in well-aligned as-spun fibers. At a higher applied electrical potential (e.g., 15 kV), the approaching speed of the charged jets was much greater than the lateral speed at the points of contact between the depositing charged jets and the collector screen, and this resulted in partial alignment of the charged jets on the collector screen.[45] At a given applied electrical potential, it was observed that a change in the collector from an aluminum sheet wrapped around a hard plastic plate to a rotting drum did not affect the diameters of the as-spun fibers.

Figure 5 SEM images of aligned as-spun fibers from solutions of 10% w/v PVP ($M_w = 1,300,000$) in ethanol. The collector was a rotating drum rotated at a speed of 3000 rpm. The applied potential for electrospinning was varied as (a) 5 and (b) 15 kV over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The scale bar equals 100 μm.

Electrospinning of PVP in mixed solvents

As mentioned previously, some organic solvents that have low dielectric constants and surface tension (e.g., toluene, CB, DCB, and THF) were not able to dissolve PVP to form clear solutions at room temperature; thus, as-spun fibers from PVP solutions in those solvents could not be fabricated. However, those solvents may be good solvents for dissolving various organic compounds. To fabricate those organic compounds in a fiber form with PVP as a polymer carrier or guide, a mixed solvent system had to be used. We selected CB as a solvent model because it has a very low dielectric constant and high surface tension. Last year, the successful fabrication of ultrafine fibers from PVP/MEH–PPV blended solutions in a mixture of CB and DCE (50 : 50 v/v) was

reported.[23] Unfortunately, with our best trial, the mixed CB/DCE solvent could not dissolve PVP to form a clear solution at room temperature. Among all the solvents investigated, the electrospinning of PVP in a methanol solution resulted in the smallest diameter fibers; thus, we tried to add methanol to 8% w/v PVP solutions in a mixed solvent of CB and DCE (50 : 50 v/v) as the third solvent. Surprisingly, the solution became clear. Therefore, the electrospinning of PVP solutions in a mixture of methanol, CB, and DCE was systematically carried out.

Figure 6(a) shows SEM images of the as-spun fibers from 8% w/v PVP solutions in a mixture of methanol, CB, and DCE with various contents (100, 250, and 500 μL) of methanol added to 1 mL of 8% w/v PVP ($M_w = 1,300,000$) solutions in the mixed solvent of CB and DCE (50 : 50 v/v). The results suggest that the addition of methanol to PVP solutions in the mixed solvent of CB and DCE helped to improve the electrospinnability of the resulting solutions. At the lowest content of methanol (i.e., 100 μL), electrospun PVP fibers could be fabricated with a rough surface morphological appearance and a large diameter (i.e., 6.18 μm). Evidently, with the content of methanol increasing to 250 μL, uniform as-spun fibers with a smooth surface and a smaller diameter (i.e., 1.451 μL) were obtained. However, as-spun fibers (diameter ~ 697 nm) with some parts of a capsular structure were found with the content of methanol increasing up to 500 μL. This was a direct result of the extremely greater dielectric constant, lower viscosity, and lower surface tension of methanol in comparison with those of CB and DCE (see Table I). The capsular structure of as-spun fibers from a 500 μL methanol-added solution may be due to the greater contents of solvents with different boiling points as a result of the collapse of some parts of the fibers upon the evaporation of the high-boiling-point solvent after the deposition of a collector. Instead of a mixture of CB with DCE and methanol, a direct mixture of CB with methanol or ethanol (solvents that also have high dielectric constants and low surface tension) was also found to be usable as a suitable solvent for the fabrication of as-spun fibers. For example, as shown in Figure 6(b), the electrospinning of 8% w/v PVP solutions in mixed solvents of CB and ethanol (50 : 50 v/v) resulted in uniform fibers with an average diameter of 0.671 μm. The electrospinning of PVP solutions in mixed solvents of CB and methanol is discussed in the next section.

Fabrication of electrospun conductive polymer fibers with PVP as a polymer carrier

MEH–PPV was chosen to be the model for the fabrication of conductive polymer fibers with PVP because it is not a water-soluble polymer that can be
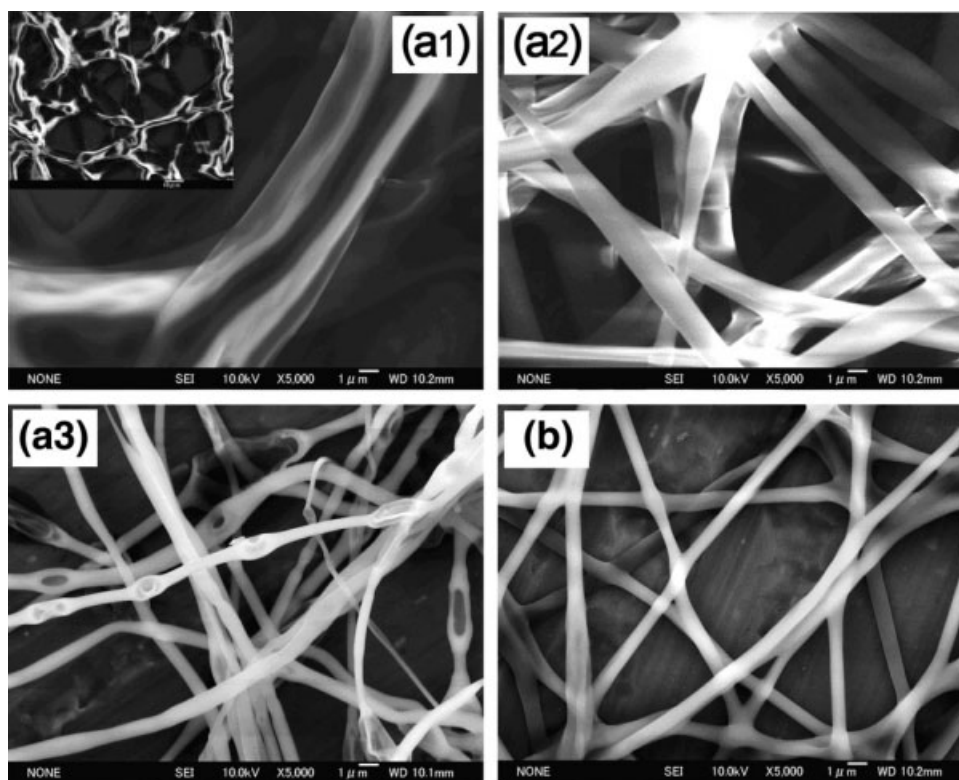
Figure 6 SEM images of the as-spun fibers from 8% w/v PVP (M_w = 1,300,000) solutions in mixed solvents of (a) methanol, CB, and DCE (CB/DCE = 50 : 50 v/v with various contents of methanol) or (b) CB and ethanol (50 : 50 v/v). Suffixes 1–3 represent 100, 250, and 500 μL, respectively, of methanol added to 1 mL of an 8% w/v PVP (M_w = 1,300,000) solution in a mixed solvent of CB and DCE (50 : 50 v/v). The applied potential for electrospinning was 15 kV over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The scale bar in each image equals 1 μm, except for the inset in part a1, for which it equals 10 μm.

dissolved in only a limited number of organic solvents. Therefore, the electrospinning of a pure MEH–PPV solution resulted in the formation of only many beads on fibers.[46] To fabricate uniform electrospun MEH–PPV fibers, the blending of MEH–PPV with a polymer carrier that is easily spinnable and extractable before electrospinning is one promising technique.[24]

CB is a good solvent for MEH–PPV, whereas the electrospinning of PVP solutions in methanol resulted in uniform fibers with the smallest diameter, as reported previously. Therefore, a mixture of CB and methanol was chosen as the solvent for electrospinning. Both MEH–PPV and PVP were able to be dissolved in the mixed solvent of CB and methanol in a limited range. Before the study of the electrospinning of MEH–PPV/PVP solutions, the electrospinning of PVP solutions in the mixed solvent of CB and methanol was carried out.

Figure 7(a) shows SEM images of the as-spun fibers from 7% w/v PVP solutions in mixed solvents of CB and methanol with mixing ratios in the range of 75 : 25–80 : 20. Obviously, ultrafine, uniform PVP fibers could be fabricated. The diameter of the as-spun PVP fibers was found to decrease from 3.08 to

1.89 and 1.45 μm with the content of methanol increasing (i.e., CB/methanol = 85 : 15, 80 : 20, and 75 : 25 v/v, respectively). This was attributed again to the extremely greater dielectric constant, significantly lower viscosity, and significantly lower surface tension of methanol in comparison with CB (see Table I). At the highest content of methanol (i.e., CB/methanol = 75 : 25 v/v), a small-wrinkle surface could be observed because of the collapse of the surface upon the evaporation of CB after the deposition of a collector. For a fixed applied electrical potential of 15 kV, only the density of the as-spun fibers was found to decrease, and a more twisted structure was found to increase with increasing collection distance, whereas it did not affect the diameter of the as-spun fibers (not shown here).

Figure 7(b) shows SEM images of the as-spun fibers from 7% w/v MEH–PPV/PVP (1 : 6 w/w) solutions in mixed solvents of CB and methanol with mixing ratios in the range of 75 : 25–80 : 20. Following the same trend found for the electrospinning of pure PVP, with an increasing content of methanol (i.e., CB/methanol = 85 : 15, 80 : 20, and 75 : 25 v/v), the diameter of the as-spun PVP fibers was found to decrease from 1.55 to 1.44 μm and 936 nm,
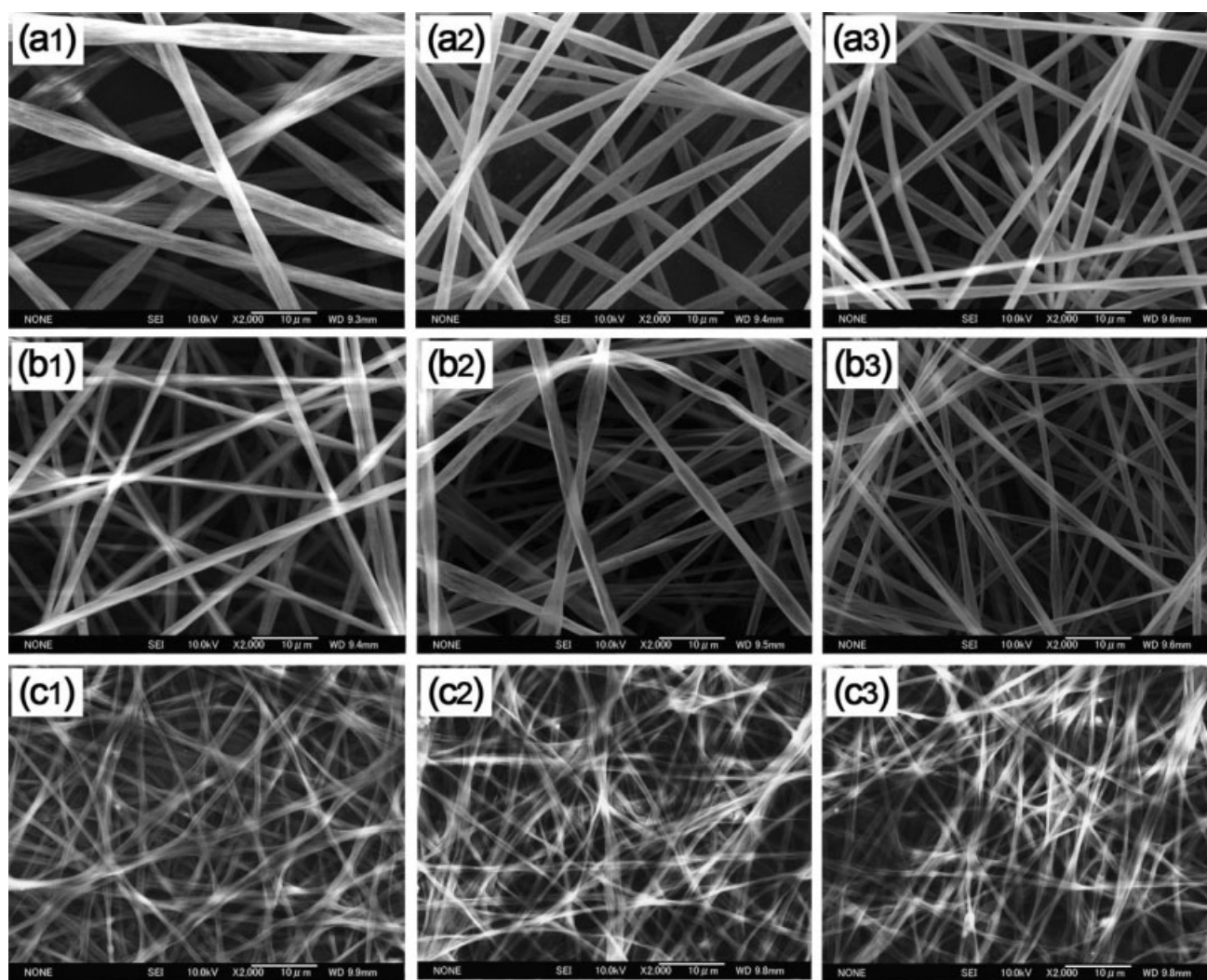
Figure 7 SEM images (scale bar = 10 μm) of (a,b) as-spun fibers from (a) 7% w/v PVP (M_w = 1,300,000) solutions and (b) 7% w/v MEH–PPV/PVP (1 : 6 w/w) solutions in mixed solvents of CB and methanol with various mixing ratios, respectively, and (c) MEH–PPV fibers after the removal of PVP from MEH–PPV/PVP electrospun fibers. Suffixes 1–3 represent CB/methanol mixing ratios of 85 : 15, 80 : 20, and 75 : 25 v/v, respectively. The applied potential for electrospinning was 15 kV over a collection distance of 15 cm. The feed flow rate was 1 mL/h.

respectively. The removal of PVP from the as-spun MEH–PPV/PVP fibers could be carried out with Soxhlet extraction. MEH–PPV fibers obtained after the removal of PVP are shown in Figure 7(c). The complete removal of PVP was confirmed with UV–vis spectroscopy. After the removal of PVP, pure MEH–PPV fibers showed an aligned, wrinkled, surface-ribbon-like structure with a smaller diameter than the MEH–PPV/PVP fibers before extraction. Because the main objective of this section is to show the usefulness of the study of the effects of solvents and the potential to use PVP as a polymer carrier in a mixed solvent system for the fabrication of MEH–PPV fibers, the issues regarding the effects of the solution properties, spinning conditions, and addition of an organic salt to spinning solutions on the morphological appearance, fiber diameter, crystallinity, and optical properties of obtained as-spun MEH–

PPV/PVP fibers were reported in another contribution[24,47] and will be reported further elsewhere.

Fabrication of TiO$_2$ fibers with PVP as a polymer guide

To the best of our knowledge, all reported works related to the fabrication of fibers of TiO$_2$ and other metal oxides with PVP as a polymer guide used ethanol as the solvent.[12–19] According to our results, the electrospinning of PVP solutions in methanol resulted in a smaller fiber diameter than electrospinning in ethanol. Therefore, methanol might be a promising candidate for the fabrication of ultrafine TiO$_2$ fibers with PVP as a polymer guide.

Figure 8 shows SEM images of the as-spun PVP/ TiO$_2$ precursor and calcined TiO$_2$ fibers from the
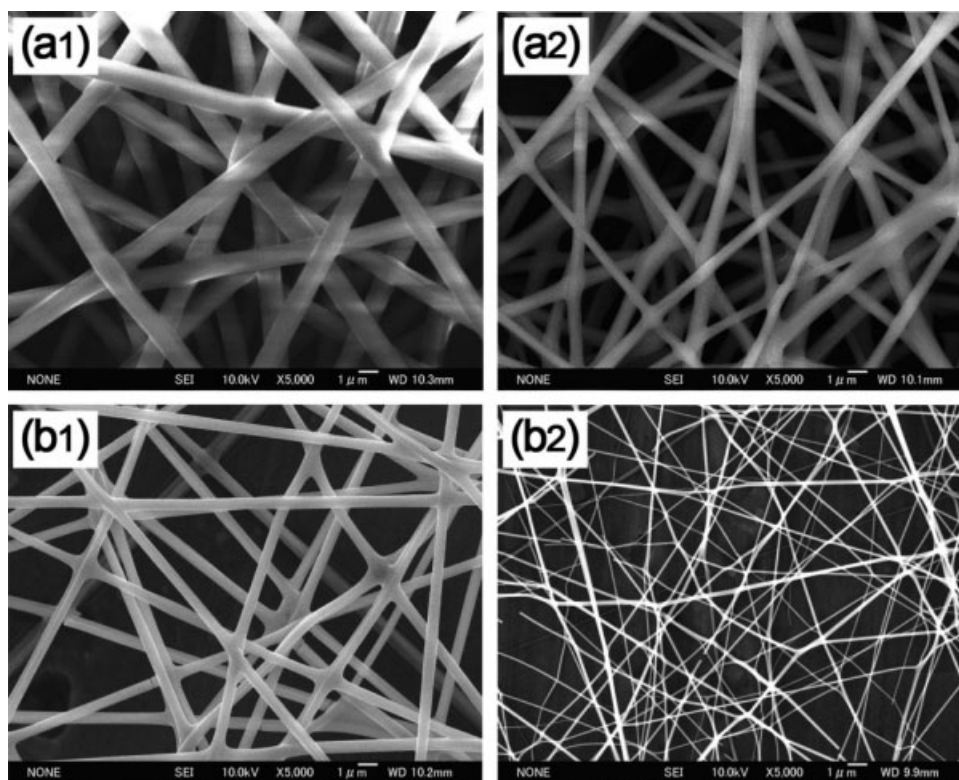
Figure 8 SEM images (scale bar = 1 μm) of (a) the as-spun PVP/TiO$_2$ precursor and (b) calcined TiO$_2$ fibers from the electrospinning of 8% w/v PVP (M_w = 1,300,000) solutions in ethanol and methanol (suffixes 1 and 2, respectively) with the TiO$_2$ precursor. The amount of the TiO$_2$ precursor was 0.6 in 1-mL PVP solutions. The applied potential for electrospinning was 15 kV over a collection distance of 15 cm. The feed flow rate was 1 mL/h. The average diameters of the fibers were (a1) 1107, (a2) 654, (b1) 545, and (b2) 201 nm, respectively.

electrospinning of 8% w/v PVP solutions in ethanol and methanol with the TiO$_2$ precursor. In comparison with pure PVP, at the same PVP concentration and spinning conditions, the electrospinning of PVP/TiO$_2$ precursor solutions resulted in larger diameter fibers [cf. Fig. 3(a,b) with Fig. 8(a1,a2)]. The increase in the viscosity caused by the addition of the TiO$_2$ precursor may be responsible for the observed larger diameters of the obtained fibers. Following the same trend found for the electrospinning of pure PVP, as-spun fibers from solutions in methanol showed a smaller diameter than those from ethanol solutions. After calcination at 450°C for 3 h, the obtained fibers from the electrospinning of methanol still showed lower diameter fibers than those from ethanol solutions (201 and 545 nm, respectively). X-ray diffraction patterns of calcined TiO$_2$ fibers indicated the formation of a high anatase phase in the obtained fibers (not shown here). In conclusion, methanol has shown the potential to be used as a suitable solvent instead of ethanol, which has been frequently reported,[12–19] for the fabrication of ultrafine TiO$_2$ fibers by electrospinning with PVP as a polymer guide.

CONCLUSIONS

The effects of solution properties and spinning conditions, including the molecular weight of PVP, solution concentration, applied electrical potential, and collection distance, on the morphological appearance and diameter of electrospun PVP fibers were investigated. At the lowest concentration of the solutions studied, beaded fibers were observed. A uniform fibrous structure was stabilized (with a change from beaded fibers to more uniform fibers) above a minimum concentration, which was related to the molecular weight of PVP. A solution from the lower molecular weight PVP (M_w = 43,000) needed a higher concentration to stabilize uniform fibers than that from the higher molecular weight PVP (M_w = 1,300,000; 40–50 and 6–8% w/v, respectively). Interestingly, flat and twisted (ribbon-like) fibers could be observed at a high solution concentration. The average diameters of the as-spun PVP fibers were in the range of 200 nm to 1.5 μm. The average diameters increased with the solution concentration increasing but decreased with the collection distance increasing. Furthermore, the average diameters

decreased with the initial increase in the applied electrical potential, reached a minimum value, then increased with a further increase in the applied electrical potential, reached a maximal value, and decreased again at the highest applied electrical potential. The effects of the solvents, including methanol, ethanol, 2-propanol, DCE, water, chloroform, and DCM, were also investigated, whereas toluene, CB, DCB, and THF were not able to dissolve PVP to form a clear solution. The properties of the solvents, especially the dielectric constant, viscosity, and surface tension, played very important roles in the electrospinnability, morphological appearance, and size of the as-spun fibers. Small and uniform as-spun fibers could be fabricated from PVP solutions in solvents with a significantly high dielectric constant, low surface tension, and low viscosity. In three alcohol solutions investigated, the diameters of the as-spun PVP fibers decreased with the dielectric constant, dipole moment, and density of the solvents increasing and with the viscosity of the solvents decreasing. Among the solvents investigated, under the same spinning conditions, methanol was the best solvent for the fabrication of the smallest as-spun PVP fibers. Mixing a unspinnable solvent with a solvent that has a high dielectric constant, low surface tension, and low viscosity (e.g., methanol or ethanol) could increase the electrospinnability of the obtained solution. Therefore, the electrospinning of PVP solutions in mixed solvents of methanol, CB, and DCE, CB and ethanol, or CB and methanol resulted in uniform ultrafine fibers. Additionally, we were able to fabricate aligned arrays of pure PVP fibers by using a rotating-drum collector technique in electrospinning. Finally, PVP was used in the fabrication of MEH–PPV and TiO_2 fibers by acting as a polymer carrier or guide.

References

1. Pan, Z. W.; Dai, Z. R.; Wang, Z. L. Science 2001, 291, 1947.
2. Iijima, S. Nature 1991, 354, 56.
3. Li, D.; Xia, Y. Adv Mater 2004, 16, 1151.
4. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. Compos Sci Technol 2003, 63, 2223.
5. Hohman, M. M.; Shin, M.; Rutledge, G.; Brenner, M. P. Phys Fluids 2001, 13, 2201.
6. Hohman, M. M.; Shin, M.; Rutledge, G.; Brenner, M. P. Phys Fluids 2001, 13, 2221.
7. Chuangchote, S.; Sirivat, A.; Supaphol, P. Nanotechnology 2007, 18, 145705.
8. Supaphol, P.; Chuangchote, S. J Appl Polym Sci 2008, 108, 969.
9. Encyclopedia of Polymer Science and Engineering, 2nd ed.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley-Interscience: New York, 1985; Vol.17.
10. Yang, Q.; Li, Z.; Hong, Y.; Zhao, Y.; Qiu, S.; Wang, C.; Wei, Y. J Polym Sci Part B: Polym Phys 2004, 42, 3721.
11. Bognitzki, M.; Frese, T.; Steinhart, M.; Greiner, A.; Wendorff, J. H.; Schaper, A.; Hellwing, M. Polym Eng Sci 2001, 41, 982.
12. Li, D.; Xia, Y. Nano Lett 2003, 3, 555.
13. Li, D.; Wang, Y.; Xia, Y. Nano Lett 2003, 3, 1167.
14. Azad, A.-M.; Matthews, T.; Swary, J. Mater Sci Eng B 2005, 123, 252.
15. Lee, S.-H.; Tekmen, C.; Sigmund, W. M. Mater Sci Eng A 2005, 398, 77.
16. Nuansing, W.; Ninmuang, S.; Jarernboon, W.; Maensiri, S.; Seraphin, S. Mater Sci Eng B 2006, 131, 147.
17. Bender, E. T.; Katta, P.; Chase, G. G.; Ramsier, R. D. Surf Interface Anal 2006, 38, 1252.
18. Watthanaarun, J.; Supaphol, P.; Pavarajarn, V. J Nanosci Nanotechnol 2007, 7, 2443.
19. Lee, S.-J.; Cho, N.-I.; Lee, D. Y. J Eur Ceram Soc 2007, 27, 3651.
20. Bishop, A.; Gouma, P. Rev Adv Mater Sci 2005, 10, 209.
21. Bishop-Haynes, A.; Gouma, P. Mater Manuf Process 2007, 22, 764.
22. Xin, Y.; Huang, Z. H.; Yan, E. Y.; Zhang, W.; Zhao, Q. Appl Phys Lett 2006, 89, 053101.
23. Zhao, Q.; Huang, Z.; Wang, C.; Zhao, Q.; Sun, H.; Wang, D. Mater Lett 2007, 61, 2159.
24. Chuangchote, S.; Sagawa, T.; Yoshikawa, S. Jpn J Appl Phys 2008, 47, 787.
25. Li, D.; Babel, A.; Jenekhe, S. A.; Xia, Y. Adv Mater 2004, 16, 2062.
26. Babel, A.; Li, D.; Xia, Y.; Jenekhe, S. A. Macromolecules 2005, 38, 4705.
27. Lee, S.-W.; Belcher, A. M. Nano Lett 2004, 4, 387.
28. Sawicka, K.; Gouma, P.; Simon, S. Sens Actuators B 2005, 108, 585.
29. Ignatova, M.; Manolova, N.; Rashkov, I. Eur Polym J 2007, 43, 1609.
30. Yao, C.; Li, X.; Song, T. J Biomater Sci Polym Ed 2007, 18, 731.
31. Ignatova, M.; Manolova, N.; Rashkov, I. Eur Polym J 2007, 43, 1112.
32. Jin, Y.; Lu, X.; Wang, C. J Appl Polym Sci 2006, 102, 6017.
33. Kessick, R.; Tepper, G. Sens Actuators B 2006, 117, 205.
34. Lu, X.; Zhao, Y.; Wang, C.; Wei, Y. Macromol Rapid Commun 2005, 26, 1325.
35. Jin, W.-J.; Lee, H. K.; Jeong, E. H.; Park, W. H.; Youk, J. H. Macromol Rapid Commun 2005, 26, 1903.
36. Lu, X.; Zhang, W.; Zhao, Q.; Wang, L.; Wang, C. e-Polymers 2006, No. 033.
37. Li, X.; Wang, C.; Li, Y.; Chu, H. B.; Li, L. J. Solid State Phenom 2007, 121, 109.
38. Fong, H.; Chun, I.; Reneker, D. H. Polymer 1999, 40, 4585.
39. Deitzel, J. M.; Kleinmeyer, J. D.; Hirvonen, J. K.; Beck Tan, N. C. Polymer 2001, 42, 8163.
40. Zhang, C.; Yuan, X.; Wu, L.; Han, Y.; Sheng, J. Eur Polym J 2005, 41, 423.
41. Li, D.; Ouyang, G.; McCann, J. T.; Xia, Y. Nano Lett 2005, 5, 943.
42. Pantano, C.; Gañán-Calvo, A. M.; Barrero, A. J Aerosol Sci 1994, 25, 1065.
43. Lee, K. H.; Kim, H. Y.; Bang, H. J.; Jung, Y. H.; Lee, S. G. Polymer 2003, 44, 4029.
44. Lee, K. H.; Kim, H. Y.; Khil, M. S.; Ra, Y. M.; Lee, D. R. Polymer 2003, 44, 1287.
45. Wannatong, L.; Sirivat, A.; Supaphol, P. Polym Int 2004, 53, 1851.
46. Madhugiri, S.; Dalton, A.; Gutierrez, J.; Ferraris, J. P.; Balkus, K. J., Jr. J Am Chem Soc 2003, 125, 14531.
47. Chuangchote, S.; Sagawa, T.; Yoshikawa, S. Macromol Symp 2008, 264, 80.