

Effects of Different Ionic Liquids on the Electrospinning of a Polyacrylonitrile Polymer Solution

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ABSTRACT: Additives have been proven to be useful in improving electrospinnability and controlling fiber morphology through the modification of solution properties, including the conductivity, viscosity, and surface tension. In this study, the effects of adding small amounts of four different types of ionic liquids [i.e., 1-butyl-3-methylimidazolium chloride (C_4MIMCl), 1-dodecyl-3-methylimidazolium chloride ($C_{12}MIMCl$), 1-ethyl-3-methylimidazolium bromide (C_2MIMBr), and 1-ethyl-3-methylimidazolium phosphate ($C_2MIM)_3PO_4$] on the solution properties, electrospinning process, and characteristics of polyacrylonitrile (PAN) were investigated. The results show that the solution conductivities significantly increased with the addition of different ionic liquids with concentrations varying from 0.1 to 1.0 wt %, and the tendency depended on the structures of the ionic liquids. $(C_2MIM)_3PO_4$ showed the highest conductivity value; this was followed by C_2MIMBr , C_4MIMCl , and $C_{12}MIMCl$. The ionic liquids formed visible crystals; this made the fiber surfaces rough, and some fiber segments underwent partial aggregation. A regular varying tendency between the minimum mean diameter of the PAN/ionic liquid fibers and the structure of the ionic liquid was found. The PAN/*N,N*-dimethylformamide (DMF)/ $(C_2MIM)_3PO_4$ solution showed the highest conductivity among the four systems with different ionic liquids added, and the thinnest minimum diameter of the PAN/ $(C_2MIM)_3PO_4$ fibers appeared with a relatively low ionic liquid concentration of 0.25 wt %, whereas the PAN/DMF/ $C_{12}MIMCl$ solution had the lowest conductivity, and the minimum mean diameter of PAN/ $C_{12}MIMCl$ fibers appeared at a relatively high ionic liquid concentration of 0.8 wt %. Although the conductivity of the PAN/DMF/ C_2MIMBr solution was higher than that of the PAN/DMF/ C_4MIMCl solution, the minimum mean diameters of the PAN/ C_2MIMBr and PAN/ C_4MIMCl fibers appeared at the same ionic liquid concentration of 0.5 wt % because of the similar ionic activities of C_2MIMBr and C_4MIMCl . © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2359–2368, 2013

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INTRODUCTION

Electrospinning has been recognized as an efficient method for fabricating polymer nanofibers. Various polymers have been successfully electrospun into ultrafine or nanometer fibers in recent years, mostly in solvent solutions and some in melt form.^{1–3} With smaller pores and higher surface areas than commonly used fibers, electrospun fibers have been successfully applied in nanocatalysis, tissue engineering scaffolds, protective clothing, filtration, biomedical applications, pharmaceutical applications, optical electronics, healthcare, biotechnology, defense and security, and environmental engineering.^{3–8}

In the electrospinning process, the parameters of polymer solutions influence the morphology of the obtained fibers and can be

divided into three categories: (1) solution properties, including viscosity, conductivity, and surface tension; (2) process parameters, including voltage, tip-to-collector distance, and feed or flow rate of the polymer solution; and (3) ambient parameters, including environmental temperature, relative humidity, and velocity of the surrounding air in the spinning chamber. Through proper manipulation of these parameters, we can obtain nanofibers with desired morphologies and diameters.^{9,10}

Additives such as inorganic salts,¹¹ cationic surfactants,¹² hyperbranched polymers,¹³ and organic salts¹⁴ have been proven to be useful for improving the electrospinnability and fiber morphology through the modification of one or two of the three solution properties: conductivity, viscosity, and surface tension. Qin et al.¹¹ used inorganic salts (LiCl, NaNO₃, NaCl, and

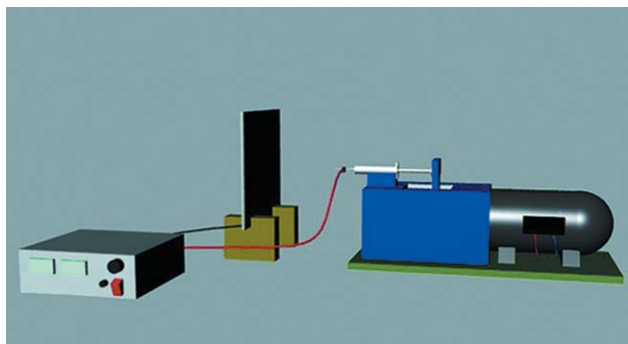


Figure 1. Diagram of the needle electrospinning setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CaCl₂) to change the properties of a polyacrylonitrile (PAN) solution and found that at different solution concentrations, the conductivities of the solutions increased compared to that of a no-salt system and varied with the type of salts. The conductivity tendency was LiCl > NaNO₃ > CaCl₂ > NaCl, but the viscosity and shearing strength of the electrospinning solutions were slightly affected. For the fiber diameters, the tendency was the same as that of the conductivities. Jun et al.¹⁴ reported that the addition of pyridinium formate (PF), an organic salt, into polymer solutions also increased the conductivities.

We used salts and surface-active agents for the modification of the ES fiber diameter, but in organic solvents, salts are not easy to dissolve; sometime, surface-active agents are not easy to handle, so room-temperature ionic liquids (RTILs) were considered because they could be used for both purposes. RTILs, which consist entirely of ions that exist in the liquid state around room temperature,^{15–17} show better compatibility and solubility in organic polymer solutions than inorganic salts. Meanwhile, RTILs possess unique properties, including a negligible vapor pressure, wide potential window, high thermal stability, and good conductivity.¹⁷ The use of RTILs instead of inorganic salts for the morphological control of electrospun nanofibers may be more desirable, also RTILs can be used as a good flame-retardant agents in polymer matrices,¹⁸ and others have used RTILs in the preparation of lithium-ion batteries.¹⁹ In our research, we also used RTILs to modify the phase separation in polymer blend systems.²⁰ However, few reports have been concerned with the effects of the addition of small amounts of ionic liquids to adjust the parameters of electrospinning solutions.²¹

We have tried this method with different ionic liquids in PAN, PVDF, PS, and PAN/PVDF, PVDF/PS blend systems separately and found some interesting results, including fiber diameters of less than 100 nm for PAN and a good conductivity and a kind of nanoflower structure in PVDF/PAN blends,²² combined or separated structures or fibers in PVDF/PS, PVDF/PAN that could be used for lithium-ion batteries, functional nanofiber mats, and high-performance PAN-based carbon fibers. In this work, four ionic liquids [1-butyl-3-methylimidazolium chloride (C₄MIMCl), 1-dodecyl-3-methylimidazolium chloride (C₁₂MIMCl), 1-ethyl-3-methylimidazolium bromide (C₂MIMBr), and 1-ethyl-3-methylimidazolium phosphate (C₂MIM)₃PO₄] were used separately in PAN electrospinning solutions with a solvent of *N,N*-dimethylformamide (DMF), and the properties of solutions and the morphologies of the PAN electrospun fibers were investigated.

EXPERIMENTAL

Materials

PAN, with a weight-average molecular weight of 80,000, was purchased from Shanghai Jinshan Petrochemical Co., Ltd.

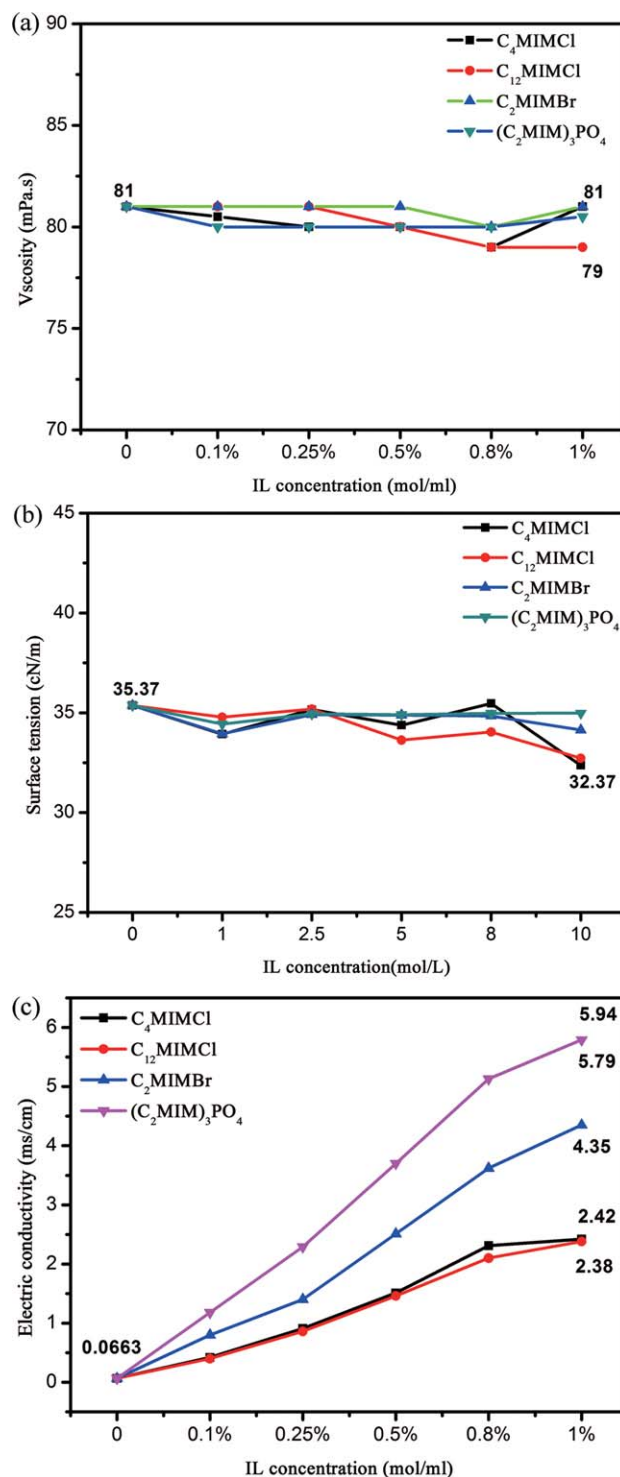


Figure 2. Properties of PAN/DMF/ionic liquid solutions with a concentration of 6 wt % and different ionic liquid additives ranging from 0.1 to 1.0 wt %: (a) viscosity, (b) surface tension, and (c) conductivity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

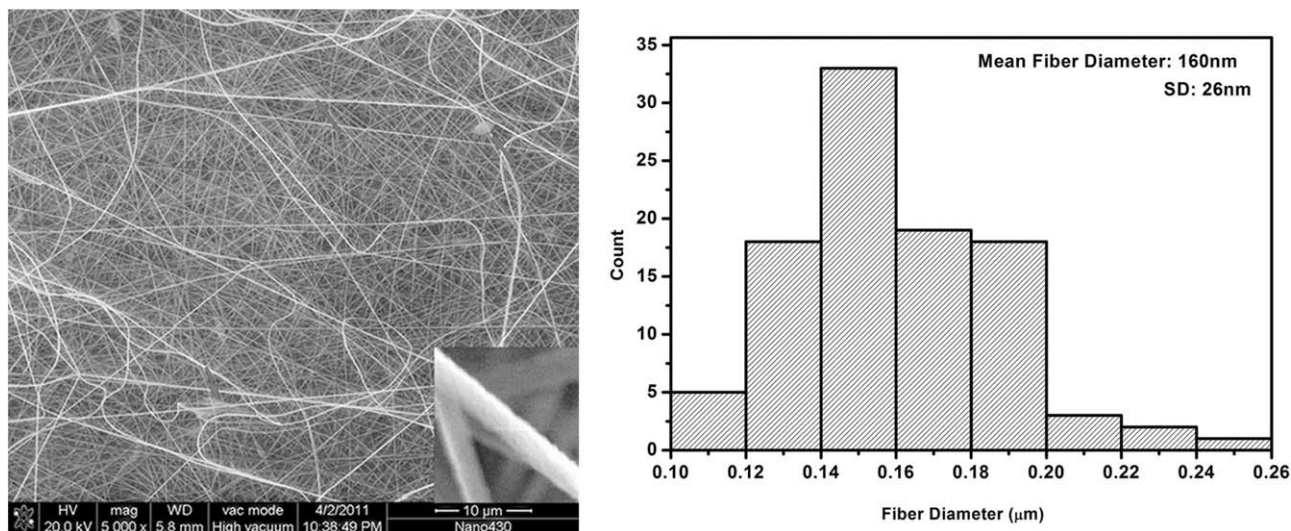


Figure 3. Morphology and distribution of the diameter of the electrospun PAN fibers.

DMF and phosphoric acid were purchased from Shanghai Rich Joint Chemical Reagent Co., Ltd. 1-Chlorobutane, 1-methylimidazole, chlorododecane, and bromoethane were purchased from Aladdin Reagent Co., Ltd. The ionic liquids [C_4MIMCl , $C_{12}MIMCl$, C_2MIMBr , and $(C_2MIM)_3PO_4$] were synthesized according to procedures described in previously published articles.^{23–26}

Preparation of the Solutions and Electrospinning

As-spun solutions were prepared by the dissolution of PAN in DMF solvent and stirred for 3 h at 60°C. Then various ionic liquids [C_4MIMCl , $C_{12}MIMCl$, C_2MIMBr , or $(C_2MIM)_3PO_4$] were dissolved in 6 wt % PAN/DMF solutions to attain ionic liquid concentrations in the range 0.1–1.0 wt %. The mixtures were stirred at 60°C until they were clear and transparent to form spinning solutions. The PAN solutions were placed in a 1-mL syringe fitted with a metallic needle (0.6 mm in diameter). The electrospinning voltage was fixed at 8 kV, the tip-to-collector distance was 10 cm, and the feeding rate was 0.5 mL/h. Electrospinning was carried out at a relative humidity of 30% and an ambient temperature of 25°C. The experimental setup for the needle electrospinning was positioned horizontally, as shown in Figure 1.

Measurement and Characterization

The solution viscosities were measured on a NDJ-79 rotational viscometer (Machinery and Electrical Equipment Factory of Tongji University) with a constant speed of 750 rpm at 25°C.

The surface tensions were measured on an OCA-20-LHT surface tensiometer (Dataphysics, Germany). The solution temperature was 25°C.

The conductivities of the solutions were measured on a CyberScan PC510 conductivity meter (EUTECH, Singapore). A standard solution was used to calibrate the meter before each measurement. The solution temperature was 25°C.

The fiber morphologies were observed with a Nano430 scanning electron microscope. We prepared the specimens for scanning

electron microscopy (SEM) observation by cutting an Al sheet covered with the as-spun fibers and carefully affixing the cut section onto an SEM stub. Each sample was coated with gold with 5-nm Au/Pd before SEM observation.

RESULTS AND DISCUSSION

Effect of the Ionic Liquids on the Solution Properties

Ionic liquids are salts consisting of organic cations and organic or inorganic anions. For the four ionic liquids [C_4MIMCl , $C_{12}MIMCl$, C_2MIMBr , and $(C_2MIM)_3PO_4$], we considered two aspects. One was the influence of the length of the organic chain of the ionic liquids; the other was the properties of the inorganic anions. The properties of the PAN/DMF solution with ionic liquid concentrations ranging from 0.1 to 1.0 wt % are shown in Figure 2.

In the PAN/DMF solution, the ionic liquids showed little effect on the viscosity and the surface tension of the solution regardless of the various structures of the ionic liquids. The viscosity fluctuated between 79 and 81 mPa s, with the biggest decline being 2 mPa s when 1.0 wt % $C_{12}MIMCl$ was used. Meanwhile, the surface tension was found to range between 32.37 and 35.37 cN/m, with biggest decline being 3 cN/m when 1.0 wt % $C_{12}MIMCl$ was used.

However, a small amount of ionic liquid resulted in a marked increase in the conductivity of the PAN/DMF solutions. The conductivity reflects the ability of free ions to carry a charge; it mainly depends on the concentrations of free ions. Ionic liquids can ionize to free ions in DMF. Because of the strong polarity of PAN, the $-C\equiv N$ functional groups had a strong attraction to halogen anions, and this resulted in the reduction of free ions in the solution. As the anion size increased, the association interaction became weaker, and the quantity of free ions in the solution increased; this created a higher conductivity. So, the conductivity of the solutions with ionic liquids changed from high to low in the following order: $(C_2MIM)_3PO_4$, C_2MIMBr , C_4MIMCl , and $C_{12}MIMCl$.

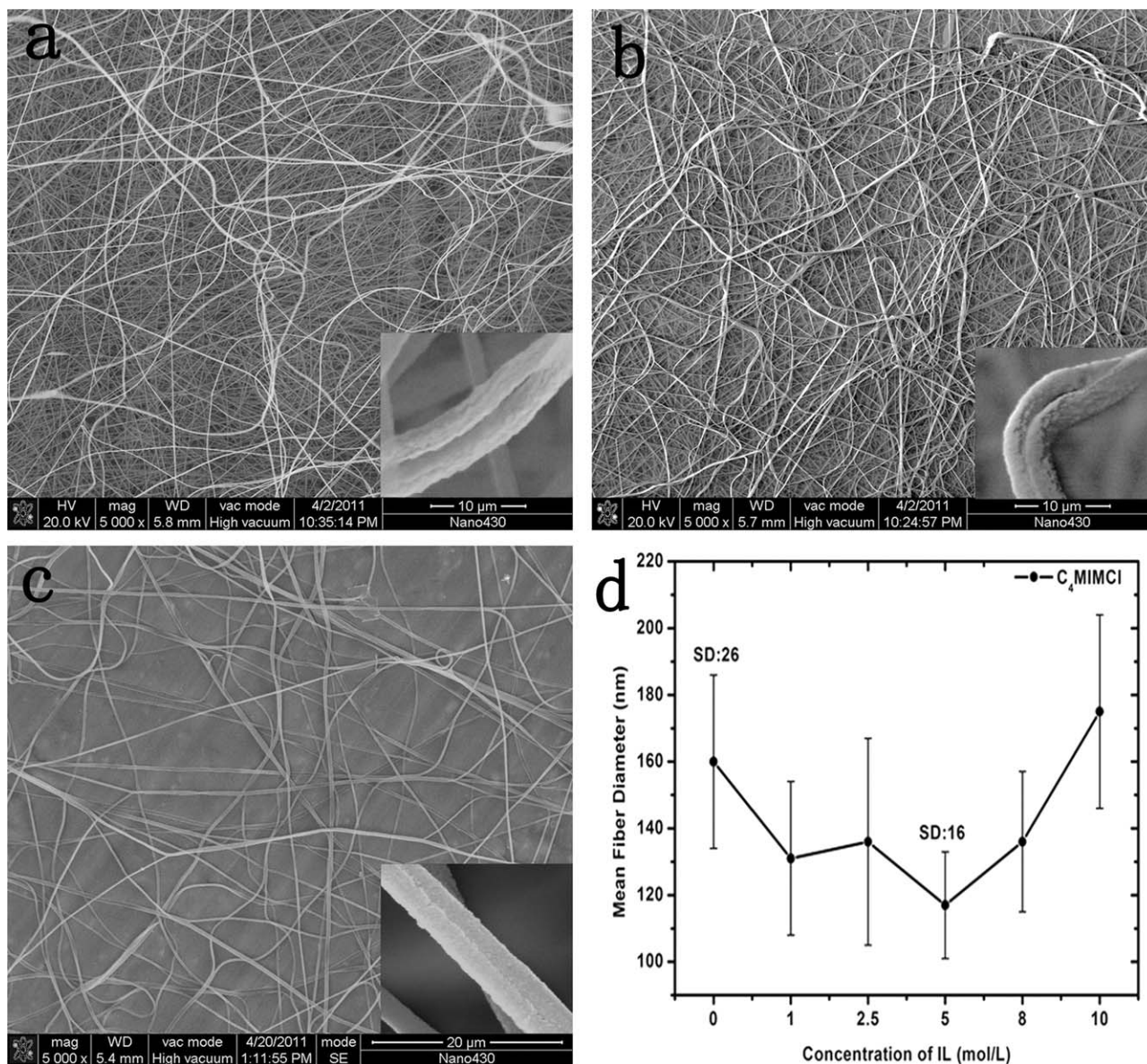


Figure 4. Impact of the C_4MIMCl concentration on the morphology and diameter of the electrospun PAN/ C_4MIMCl fibers: (a) 0.1, (b) 0.5, and (c) 1.0 wt % and (d) mean diameter of the PAN/ C_4MIMCl fibers.

Effect of the Ionic Liquids on the Morphology of the Electrospun PAN Fibers

Figure 3 shows the SEM micrograph of the pure 6 wt % PAN fibers with a few beads. The fibers were relatively uniform with a diameter of 160 nm with a standard deviation (SD) of 26 nm. All of the fibers had clearly smooth surfaces without flat strip structures; this indicated that much of the DMF evaporated before the fiber was deposited onto the collector.

Figure 4 shows the SEM micrographs of the morphology and diameter distribution of the electrospun PAN fibers with C_4MIMCl . Compared to that of the pure PAN fibers, the surfaces of the PAN/ C_4MIMCl fibers were rough (see the enlarged micrograph in the lower right corner). The observed particles on the surface of the PAN/ C_4MIMCl fibers may have been small crystals of C_4MIMCl , similar to the KCl crystals on the surface

of the poly(vinyl alcohol) (PVA) fibers.²⁷ The ionic liquid C_4MIMCl showed good solubility in the PAN/DMF solution and an insignificant vapor pressure. With DMF evaporating quickly from the polymer solution jet and forming fibers in the electrospinning process, the ionic liquid crystallized on-site on the basis of lattice exclusion theory; C_4MIMCl crystals formed on the surface of the fibers, and this made the surface rough. The formation tendency of the C_4MIMCl crystals was clearly evident in the PAN/ C_4MIMCl fibers at higher C_4MIMCl contents.

Meanwhile, the PAN/ C_4MIMCl fibers appeared to form aggregate structures. These features were most likely the result of separate fibers that collided and underwent various degrees of fusion before deposition on the collector. The PAN/ C_4MIMCl fibers containing 0.1 wt % C_4MIMCl showed little fiber-fusion

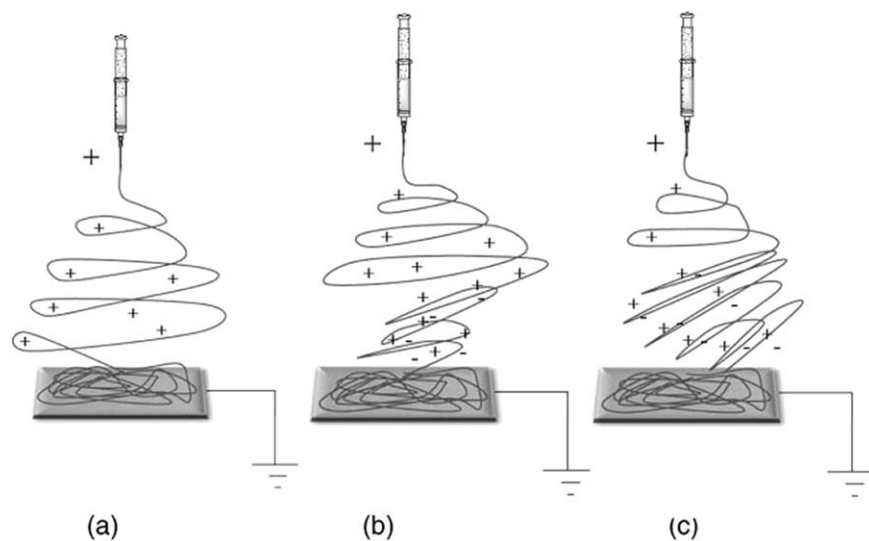


Figure 5. Mechanism of the fiber aggregation in the electrospinning process.

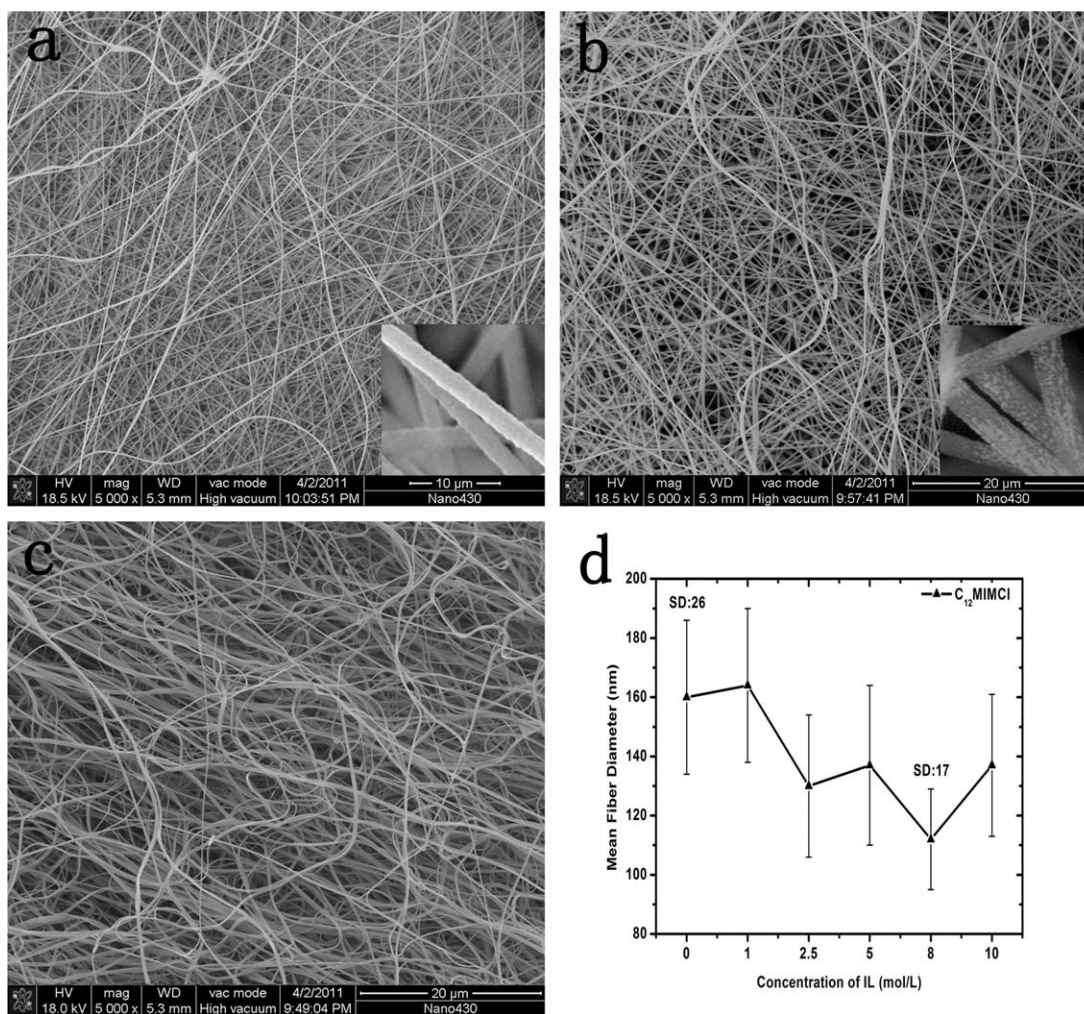


Figure 6. Impact of the $C_{12}MIMCl$ concentration on the morphology and diameter of the electrospun PAN/ $C_{12}MIMCl$ fibers: (a) 0.1, (b) 0.5, and (c) 1.0 wt % and (d) mean diameter of the PAN/ $C_{12}MIMCl$ fibers.

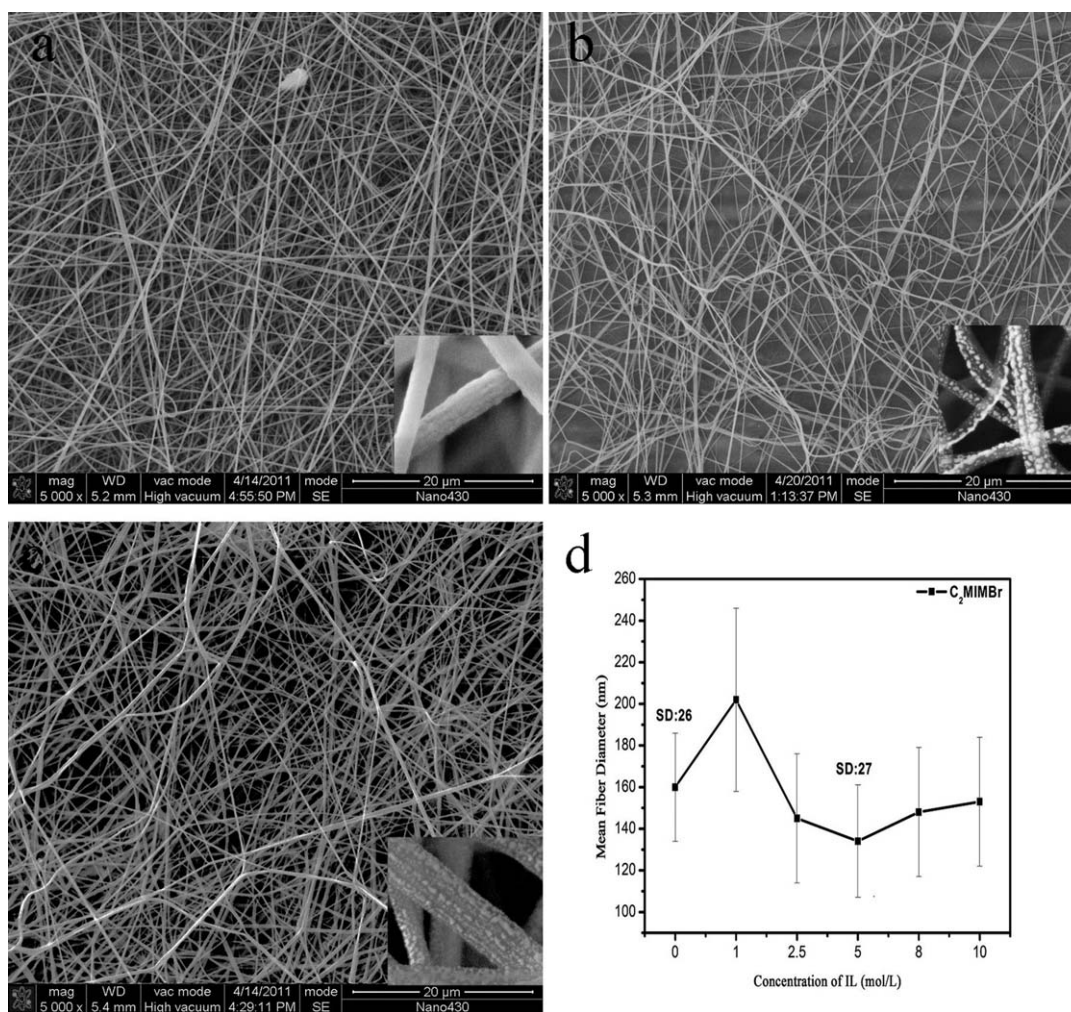


Figure 7. Impact of the C₂MIMBr concentration on the morphology and diameter of the electrospun PAN/C₂MIMBr fibers: (a) 0.1, (b) 0.5, and (c) 1.0 wt % and (d) mean diameter of the PAN/C₂MIMBr fibers.

tendency, whereas the micrograph of the fibers containing 1.0 wt % C₄MIMCl showed extensive aggregation, and the fibers were intertwined into a bundle structure, then bonded into larger fibers.

A possible mechanism of fiber aggregation is shown in Figure 5, as reported in an earlier article.²¹ In the electrospinning process of the PAN/DMF solution with no conductive additives, the positively charged fibers moved in a normal way to the grounded collector and repelled one another, as shown in Figure 5(a), because of the repulsion theory of similar charge. Figure 5(b,c) shows a possible mechanism to account for the fiber attraction, which lead to fiber aggregation. The conductive additive C₄MIMCl offered excess charge to the solution jet. A negative charge was drawn back through the positively charged jet, so these fiber segments contained excess negative charges. Those segments closer to the needle with excess positive charges were drawn first toward the negatively charged fiber segments before hitting the collector, and then the aggregate fibers formed. With increasing concentration of C₄MIMCl, the fiber fusion tendency also became more extensive because backbuilding began to

occur closer to the needle and before all of the solvent evaporated. C₄MIMCl, being a liquid, may also have led to some degree of fusion. The backbuilding of charge and fiber aggregation climbed nearly to the needle, and this effect involving fibers closer to the needle is represented in Figure 5(c).

The diameters of PAN/C₄MIMCl fibers with different C₄MIMCl contents are given in Figure 4. The mean fiber diameter first decreased to a minimum value of 117 nm with 0.5 wt % C₄MIMCl in a vibrational manner and then increased as the C₄MIMCl increased further. So the most significant decrease was with the addition of 0.5 wt % C₄MIMCl, and the fiber distribution was more uniform. The solution properties are important factors that influence fiber diameter when the spinning process and environmental parameters stay the same. As the viscosity and surface tension rarely changed with the addition of ionic liquid, the increase in the conductivity of the spinning solution, however, could either increase or decrease the diameters of the fibers.²⁸ The addition of a small amount of ionic liquid could significantly increase the conductivity, which increased the coulombic repulsion of mutual charges present within the jet

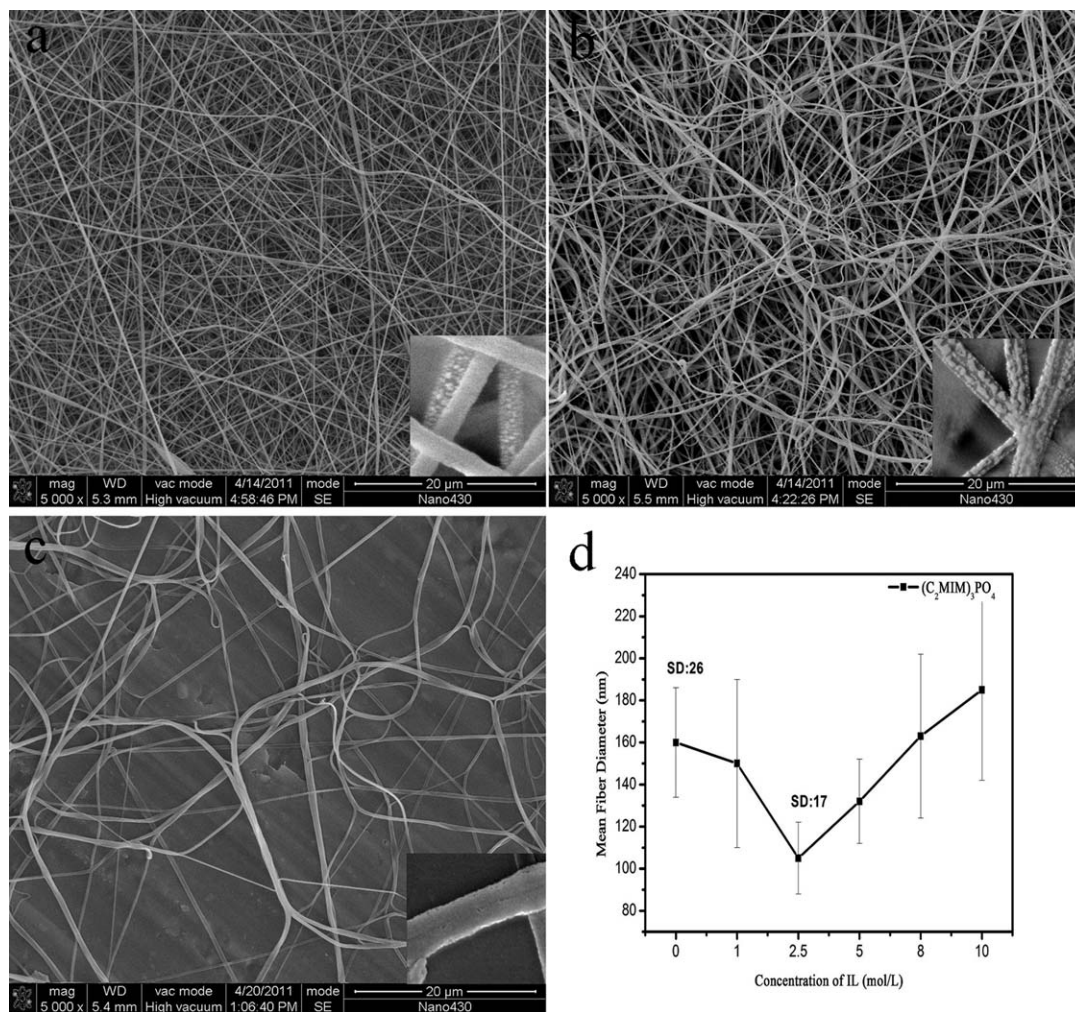


Figure 8. Impact of the $(C_2MIM)_3PO_4$ concentration on the morphology and diameter of the electrospun PAN/ $(C_2MIM)_3PO_4$ fibers: (a) 0.1, (b) 0.5, and (c) 1.0 wt % and (d) mean diameter of the PAN/ $(C_2MIM)_3PO_4$ fibers.

segment,^{29,30} this resulted in a smaller fiber diameter. The ionic liquid could have been plasticizing the fiber and providing additional fiber stretching; this could have also decreased the fiber diameter. So the fiber diameter decreased at first. The increase in the electrostatic force due to the further increase in the conductivity with more ionic liquid tended to delay the onset of the bending instability³¹ and thus shorten the fiber stretching process, producing larger fibers. The aggregation is also a factor of fiber diameter increase.

Figure 6 shows the SEM micrographs of the morphology and diameter distribution of the electrospun PAN/ $C_{12}MIMCl$ fibers. These PAN/ $C_{12}MIMCl$ fibers showed features similar to those of the PAN/ C_4MIMCl fibers. $C_{12}MIMCl$ formed visible crystals, which made the fiber surface rough, and some fiber segments underwent partial aggregation (a possible mechanism is described in Figure 5). The fiber diameter first decreased to a minimum value of 117 nm with 0.8 wt % $C_{12}MIMCl$ in a vibrational manner and then increased as the $C_{12}MIMCl$ content increased further. So the most significant decrease occurred with the addition of 0.8 wt % $C_{12}MIMCl$, and the fiber distribution was more uniform (SD decreased to 17).

Figure 7 shows the SEM micrographs of the fibers from the C_2MIMBr -containing PAN solutions. These fibers show the same features and trends seen in the PAN/ C_4MIMCl and PAN/ $C_{12}MIMCl$ fibers. For example, they had a rough surface and some fiber aggregations, and the fiber diameter first decreased and then increased in a vibrational manner. The minimum mean fiber diameter was 134 nm with the addition of 0.5 wt % C_2MIMBr , but the diameter distribution was wider than that of the PAN/ C_4MIMCl and PAN/ $C_{12}MIMCl$ fibers (SD increased to 27). A possible explanation is as follows: the C_2MIMBr -containing solution had a higher conductivity than the C_4MIMCl - and $C_{12}MIMCl$ -containing solutions. The higher conductivity caused instability in the electrospinning and resulted in a relatively diverse diameter distribution.

Figure 8 shows images of the PAN/ $(C_2MIM)_3PO_4$ fibers. Those fibers showed the same rough surface and fiber aggregation seen in the previous three kinds of ionic liquids. The minimum mean fiber diameter was 105 nm, and SD was 17 with the addition of 0.25 wt % $(C_2MIM)_3PO_4$. The PAN/ $(C_2MIM)_3PO_4$ fibers had a much smaller minimum mean fiber diameter than the previous three PAN/ionic liquid systems because of the

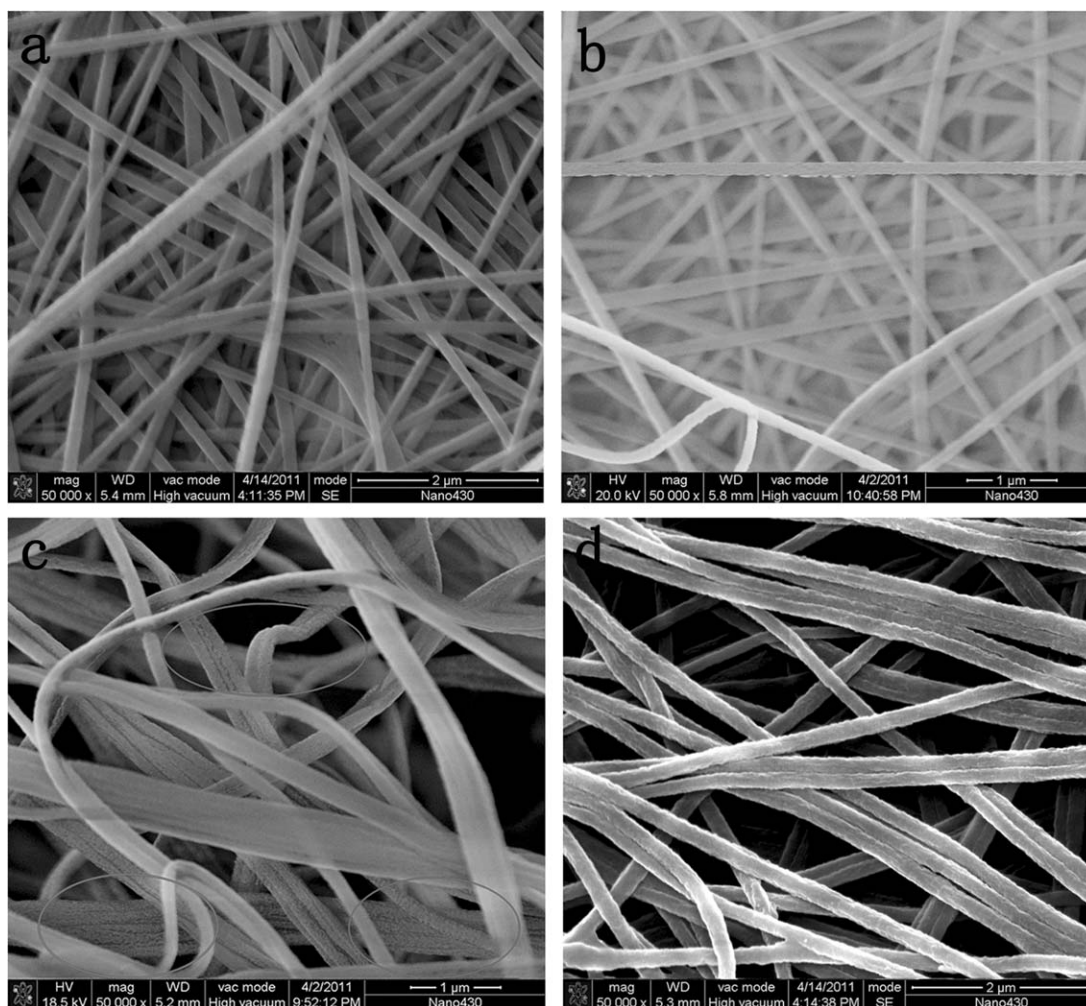


Figure 9. Morphology of the electrospun PAN fibers and PAN/C₁₂MIMCl composite fibers before and after immersion in distilled water: (a) PAN fibers before immersion, (b) PAN fibers after immersion, (c) PAN/C₁₂MIMCl composite fibers before immersion, and (d) PAN/C₁₂MIMCl composite fibers after immersion.

higher conductivity of the PAN/DMF/(C₂MIM)₃PO₄ solution; this resulted in a greater stretching effect on the jet during electrospinning.

The four ionic liquids used [C₄MIMCl, C₁₂MIMCl, C₂MIMBr, and (C₂MIM)₃PO₄] were all water-soluble. The PAN/ionic liquid composite fibers were immersed in distilled water to wash off all of the ionic liquids, and we then compared them with their original ones, respectively. The morphologies of the pure PAN fibers and PAN/ionic liquid composite fibers before and after water washing are shown in Figure 9. The pure PAN fibers after immersion in water retained surfaces as smooth as the original unwashed PAN fibers, whereas the surfaces of the PAN/ionic liquid composite fibers changed from rough to smooth after water washing. Figure 9(c) shows plenty of particle distribution in the composite fibers, which caused the rough surfaces. However, the particles disappeared, and the surfaces became smooth after immersion in water, as shown in Figure 9(d). The Fourier transform infrared spectra of the PAN/ionic liquid composite fibers before and after water washing are shown in Figure

10. The $\text{—C}\equiv\text{N}$ group had an infrared absorption at 2242 cm^{-1} . The absorption peaks at 1577, 1170, 751, 650, and 623 cm^{-1} were related to imidazole,^{32–34} whereas those peaks all became weak after water washing. This confirmed that the particles on the surfaces of the PAN/ionic liquid composite fibers were undoubtedly ionic liquids.

Effect of the Ionic Liquids on the Fiber Diameters

Figure 11 shows the relationships between the electrospun PAN/ionic liquid fiber diameter and the ionic liquid content. The diameters of all types of PAN/ionic liquid fibers first decreased and then increased in a vibrational manner as the content of the ionic liquid increased. The possible reason was described previously. There existed a regularity between the minimum mean diameter of the PAN/ionic liquid fibers and the structure of the ionic liquid.

The diameters of the PAN/((C₂MIM)₃PO₄) fibers decreased quickly at first, and the minimum mean diameter appeared at a relatively low ionic concentration of 0.25 wt %. Because the

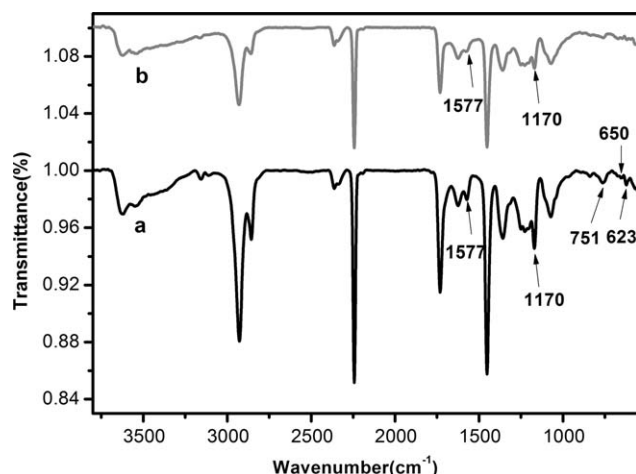


Figure 10. Fourier transform infrared spectra of the PAN/C₁₂MIMCl composite fibers (a) before and (b) after water washing.

PAN/DMF/(C₂MIM)₃PO₄ solution had a relatively high conductivity, the stretching effects on the PAN/(C₂MIM)₃PO₄ fibers were the strongest among the four PAN/ionic liquid fibers. As the (C₂MIM)₃PO₄ content increased further, the fiber diameters increased faster than those of the other PAN/ionic liquid fibers because of the large size of (C₂MIM)₃PO₄ distributed on the fiber surfaces. The PAN/DMF/C₁₂MIMCl solution showed a relatively low conductivity, and the minimum mean diameter of the PAN/C₁₂MIMCl fibers appeared at a relatively high ionic liquid concentration of 0.8 wt %. Although the conductivity of the PAN/DMF/C₂MIMBr solution was higher than that of the PAN/DMF/C₄MIMCl solution and C₂MIM⁺, with a shorter carbon chain, had a stronger mobility than C₄MIM⁺, the Br⁻, with its larger size, was more difficult to move than Cl⁻. According to the relationships of the ionic activity in the spinning solution and fiber diameters described elsewhere,^{11,27} the

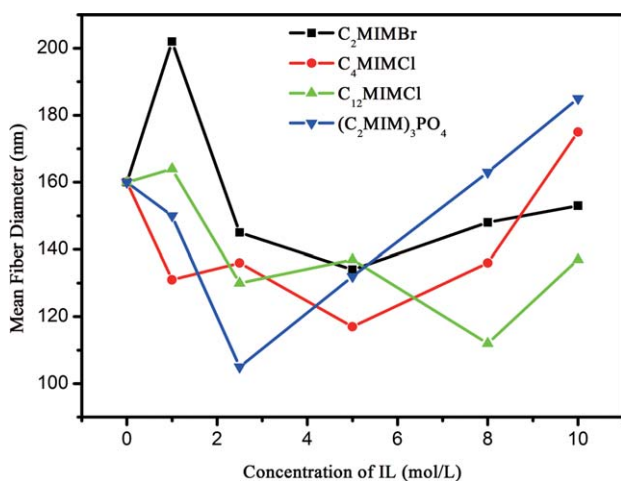


Figure 11. Relationship of the mean diameter of the electrospun PAN/ionic liquid fibers and concentration of the ionic liquid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

larger the ionic activity is, the smaller the fiber diameters will be. The minimum mean diameters of the PAN/C₂MIMBr and PAN/C₄MIMCl fibers appeared at the same ionic liquid concentration of 0.5 wt % because of the similar ionic activities of C₂MIMBr and C₄MIMCl.

CONCLUSIONS

Ionic liquids can be used to control the diameter and morphology of electrospun PAN nanofibers. The addition of different ionic liquids, including C₄MIMCl, C₁₂MIMCl, C₂MIMBr, and (C₂MIM)₃PO₄, with concentrations ranging between 0.1 and 1.0 wt %, did not much affect the viscosity and surface tension of the PAN polymer solutions. However, the conductivity significantly increased compared to the original PAN/DMF solution, and the conductivity decreased in the following order: (C₂MIM)₃PO₄, C₂MIMBr, C₄MIMCl, C₁₂MIMCl. However, these values were all higher than that of the solution without ionic liquids. Ionic liquids added to the spinning solution formed visible crystals and made the fiber surfaces rough, and some fiber segments underwent partial aggregation. The diameters of the PAN/ionic liquid fibers first decreased and then increased in a vibrational manner as the content of ionic liquid increased. There existed a regularity between the minimum mean diameter of the PAN/ionic liquid fibers and the structure of the ionic liquid: the PAN/DMF/(C₂MIM)₃PO₄ solution had a relatively high conductivity, and the minimum mean diameter of the PAN/(C₂MIM)₃PO₄ fibers appeared at a relatively low ionic liquid concentration of 0.25 wt %. However, the PAN/DMF/C₁₂MIMCl solution had a relatively low conductivity, and the minimum mean diameter of the PAN/C₁₂MIMCl fibers appeared at a relatively high ionic liquid concentration of 0.8 wt %. Although the conductivity of the PAN/DMF/C₂MIMBr solution was higher than that of the PAN/DMF/C₄MIMCl solution, the minimum mean diameters of the PAN/C₂MIMBr fibers and PAN/C₄MIMCl fibers appeared at the same ionic liquid concentration of 0.5 wt % because of the similar ionic activities of C₂MIMBr and C₄MIMCl.

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