Polymerized Ionic Liquids: Solution Properties and Electrospinning

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ABSTRACT: In this study, the solution properties and electrospinning of a polymerized ionic liquid was explored. Polymerized ionic liquids are synthesized from polymerizing ionic liquid monomers, where ionic liquids are of great interest due to their unique physiochemical properties. Compared to other polyelectrolyte solutions, this polymerized ionic liquid solution exhibits similar viscosity scaling relationships in the semidilute unentangled and semidilute entangled regimes. However, the electrospraying-electrospinning transition occurs at similar polymer solution concentrations compared to neutral polymers, where electrospinning produced beaded fibers and defect-free fibers at ~1.25 and ~2 times the entanglement concentration, respectively. Due to high solution conductivities, electrospinning produces fibers approximately an order of magnitude smaller than neutral polymers at equivalent normalized solution concentrations. In addition, a high ionic conductivity of the solid-state fiber mat was observed under dry conditions and even higher conductivities were observed for polyelectrolyte fiber mats produced from electrospinning polyelectrolyte−ionic liquid solutions, where both anion and cation are mobile species.

Introduction

Polymerized ionic liquids are macromolecules synthesized from polymerizing ionic liquid monomers and differ from conventional polyelectrolytes in that the cations and anions are usually organic and weakly coordinated. This results in polymers that have high ionic conductivities in the absence of water or even in organic solvents. Conventional polyelectrolytes in aqueous solutions exhibit unique viscoelastic behavior and consequently different electrospinning performance compared to neutral polymers due to electrostatic interactions between ionic groups.[1−5] Therefore, investigating the solution properties of polymerized ionic liquids in organic solvents is intriguing, specifically, whether polymerized ionic liquids in organic solvents exhibit similar properties to polyelectrolytes in aqueous solution.

Due to repulsive electrostatic interactions among ionic groups, polyelectrolytes show solution rheological properties remarkably different from neutral polymers. In the absence of salt, the chains of polyelectrolyte are locally rod-like and are set far apart from each other due to repulsive interactions. Consequently, polyelectrolytes have weaker scaling relationship between viscosity and concentration, where the specific viscosity (η_{sp}) scales with concentration as $\eta_{sp} \sim C^{0.5}$, $\eta_{sp} \sim C^{1.5}$, and $\eta_{sp} \sim C^{3.75}$ for semidilute unentangled, semidilute entangled, and concentrated regimes, respectively.[1,2] Specific viscosity is defined here as $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$, where η_0 is the zero shear rate viscosity of the polymer solution and η_s the is viscosity of solvent. The addition of inorganic salts to polyelectrolyte solutions screens the electrostatic interactions and the polymer chains become more coil-like. In the presence of high salt concentration, the rheological scaling relationship of polyelectrolytes behaves more like a neutral polymer, $\eta_{sp} \sim C^{1.25}$, at semidilute unentangled concentrations. A similar salt effect exists at the semidilute entangled concentrations. As the concentration reaches the concentrated regime, the electrostatic interactions are screened and polyelectrolyte behaves similar to neutral polymers even in the absence of salt.[1,2]

The solution properties of polyelectrolytes results in unique electrospinning properties. Electrospinning produces fibers in submicrometer sizes by applying electric force to polymer solutions or melts. The electric force extrudes polymer jets from a spinneret and stretches them from millimeter to submicrometer diameters through a whipping-like motion. In this spinning process, sufficient chain entanglement is required for fiber formation. It has been reported[3,4] that neutral polymers produce beaded electrospun fibers (electrospraying-electrospinning transition) at the entanglement concentration (C_e), while others[3] report salt-free polyelectrolyte solutions only form fibers above $8C_e$. Although some report electrospinning occurs at higher entanglement concentrations, it is also known that the repulsive electrostatic forces among polyelectrolyte chains promote fiber stretching during electrospinning, and therefore can produce smaller fiber sizes compared to neutral polymers.[3,4,6]

Owing to the outstanding physiochemical properties of ionic liquids, such as negligible vapor pressure, high conductivity, a wide electrochemical window, and good chemical and thermal stability, there has been a growing interest to develop polymerized ionic liquids for a variety of applications (e.g., solid-state electrochemical devices).[7−12] A number of these studies have focused on the synthesis and solid-state properties (e.g., conductivity) of polymerized ionic liquids. Currently, little is known about the solution properties of polymerized ionic liquids. In this work, the solution properties of a polymerized ionic liquid was examined. In addition, electrospinning of the polymerized ionic liquid solution was demonstrated, where the electrospinning performance was correlated to the solution behavior. To our knowledge, this is the first study to demonstrate electrospinning of a polymerized ionic liquid solution.

Experimental Section

Materials. 2-Bromoethanol (95%), methacryloyl chloride (97%, contains 200 ppm stabilizer monomethyl ether hydroquinone), triethylamine (≥99.5%), 1-butylimidazole (98%), sodium tetrafluoroborate (98%), *N*,*N*-dimethylformamide (DMF) (99%), (HPLC grade, ≥99.9%), acetonitrile (MeCN) (anhydrous, 99.8%), lithium bromide (LiBr) (99.995%, metals basis), 2-propanol (≥99.5%), azobisisobutyronitrile (AIBN) (97%), and poly(acrylic acid) (PAA) (M_v = 450 000) were purchased from Aldrich and used as received. Nafion (1100 EW, 5 wt % in a 3/1 volume ratio of 2-propanol/water) was purchased from Ion Power, Inc. (Liquion) and was used as received. EW refers to equivalent weight or grams of polymer divided by the equivalents of sulfonic acid. 1-Butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF_4) (puriss, 99%) was obtained from Solvent Innovation and used as received. Ultrapure deionized,

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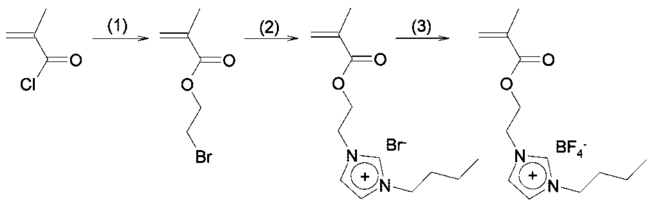
Scheme 1. Synthesis of Polymerizable Ionic Liquid MEBIm-BF_4

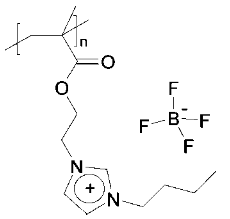


(1) 2-bromoethanol, triethylamine, dichloromethane, room temperature, 16 h

(2) 1-butylimidazole, 40 °C, 24 h

(3) $NaBF_4$, acetonitrile, room temperature, 48 h

Scheme 2. Structure of Polymerized Ionic Liquid Poly(MEBIm-BF_4)



reverse osmosis (RO) water (resistivity ~ 16 MΩ cm) was used as appropriate.

Synthesis. The polymerizable ionic liquid monomer 1-[2-methacryloyloxy)ethyl]-3-butylimidazolium tetrafluoroborate (MEBIm-BF_4) was synthesized by the method shown in Scheme 1.[11] Quarternization of 1-butylimidazole with 2-bromoethyl methacrylate produces imidazolium bromide. Anion-exchange of the bromide ion with tetrafluoroborate yielded the desired imidazolium tetrafluoroborate monomer. Halide residue in the final product was removed by extensive water washing and was examined by silver nitrate testing and elemental analysis.

Polymerized ionic liquid poly(MEBIm-BF_4) was synthesized by a conventional free-radical polymerization (Scheme 2). Typically, to a 20 mL glass vial, monomer MEBIm-BF_4 (5 g), AIBN (5 mg), and DMF (5 g) were charged. The vial was sealed and purged with N_2 for 30 min and then immersed in an oil bath at 60 °C for 12 h. After polymerization, the mixture was diluted with 5 g of DMF and was poured into cold methanol to precipitate the polymer. The precipitation was repeated 3 times before drying under vacuum at 50 °C. The purity and structure of the final product were examined by ^{1}H NMR (UNITYINOVA 500 MHz, DMSO-d_6) and elemental analysis. More details regarding the synthesis and characterization of poly(MEBIm-BF_4) can be found elsewhere.[13]

Electrospinning. Polymer solutions of poly(MEBIm-BF_4) for electrospinning were prepared by dissolving the polymer in the appropriate solvent at room temperature and then sonicating for 30 min. Solvents that were studied include DMF, MeCN, and their cosolvents at various weight ratios. Nafion-PAA blend solution was prepared by mixing 5 wt % of PAA in 3/1 (vol/vol) 2-propanol/water with 5 wt % Nafion commercial solution at 3:2 weight ratios. This blend solution was then mixed with desired amount of BMIm-BF_4, which was then sonicated for 30 min before electrospinning.

The electrospinning apparatus used in this study consisted of a high voltage power supply (Glassman High Voltage Inc., Series EL), syringe pump, syringe, needle (i.d. 0.047 in.), and grounded collector (aluminum foil).[14] The needle was connected to the high voltage supply, which can generate positive DC voltages up to 50 kV. The spinning distance between the tip of needle and the collector was in the range of 10−15 cm. Positive voltage of 10−20 KV was applied to polymer solutions. The solution flow rates were controlled with syringe pump ranging from 0.1 to 1 mL/h. All electrospinning experiments were carried out at room temperature (~24 °C) and at relative humidities below 15%, which was maintained by supplying dry air to the enclosed electrospinning chamber.

Measurements. Molecular weight and polydispersity of poly(MEBIm-BF_4) was determined by a Waters GPC system equipped with a Styragel@HR 4 column, a 2410 RI detector, and a dual channel ($\lambda = 254$ and 270 nm) UV detector. Polymer was dissolved in HPLC grade DMF and 0.05 M of LiBr was added to reduce aggregation. Measurements were taken at a flow rate of 0.6 mL/min at 30 °C. Viscosity of polymer solutions was studied with a TA AR2000ex rheometer bearing smart SWAP temperature control at 25 ± 0.2 °C using a standard concentric cylinder geometry (approximately 19.6 mL sample volume). The stator inner radius was 14 mm and the rotor outer radius was 15 mm. The conductivity of polymer solutions was measured using a conductivity meter (accumet XL50) at ambient conditions. The conductivity meter was calibrated with standard solutions (84, 1413, and 15 000 μS). Three measurements were taken for each polymer solution sample and the average values were reported. Ionic conductivity of the solid-state electrospun fiber mats was measured between 10 Hz and 100 KHz using a Solartron AC impedance system (1260 impedance analyzer, 1287 electrochemical interface, Zplot software). Fiber mats (30 mm × 5 mm × thickness) were assembled in a cell with four parallel electrodes and placed in an environmental chamber (Tenney) at a fixed temperature 30 °C at a fixed relative humidity of 10%. An alternating current was applied to the outer electrodes, while resistance was measured between the two inner electrodes (10 mm apart). The real impedance or resistance (used to calculate ionic conductivity) was determined from the x-intercept of the imaginary versus real impedance data over a high frequency range. The morphology of electrospun fibers was observed using a scanning electron microscope (SEM) (Phillips/FEI XL30) after platinum coating (Denton Desk II Sputtering System, 40 mA, 30 s).

Results and Discussion

Solution Properties of Poly(MEBIm-BF_4). The polymerized ionic liquid poly(MEBIm-BF_4) synthesized by free-radical polymerization at an AIBN concentration of 0.1 wt % was a glassy solid at ambient conditions. The weight-average molecular weight determined by GPC in the presence of 0.05 M LiBr was 382 000 with a polydispersity 1.27. The polymer only dissolved in polar solvents (e.g., DMF, MeCN, and their cosolvents) and formed clear solutions in these solvents.

Figure 1 shows the concentration dependence of specific viscosity (η_{sp}) in various organic solvents between 0.15−20 wt % concentrations. Specific viscosity is defined as $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$, where η_0 is zero shear rate viscosity of polymer solution and η_s is viscosity of solvent. In Figure 1, the data is regressed into two regimes, a semidilute unentangled and a semidilute entangled regime. In the semidilute unentangled regime, a scaling behavior of $\eta_{sp} \sim C^{0.5}$ was observed, which is similar to the theoretical predictions for polyelectrolytes without salt. As the concentration increased to the semidilute entangled regime, the polymerized ionic liquid showed a concentration dependence of $\eta_{sp} \sim C^{1.5}$, which is also similar to theoretical predictions for salt-free polyelectrolytes.

The key result as it applies to electrospinning is the entanglement concentration (C_e) - the transition point between the semidilute unentangled regime and semidilute entangled regime or the concentration at which polymer chain entanglement initiates. Figure 1 shows an entanglement concentration of 2, 4, and 5 wt % for this polymerized ionic liquid in DMF, 3/1 MeCN/DMF, and MeCN, respectively.

Electrospinning of Poly(MEBIm-BF_4) Solutions. This study was performed on poly(MEBIm-BF_4) solutions in DMF, MeCN, and their cosolvents. A smooth and a steady polymer jet was observed from electrospinning in DMF. In comparison, the spinneret was blocked frequently during the electrospinning of the MeCN solution. This was ascribed to the high volatility of

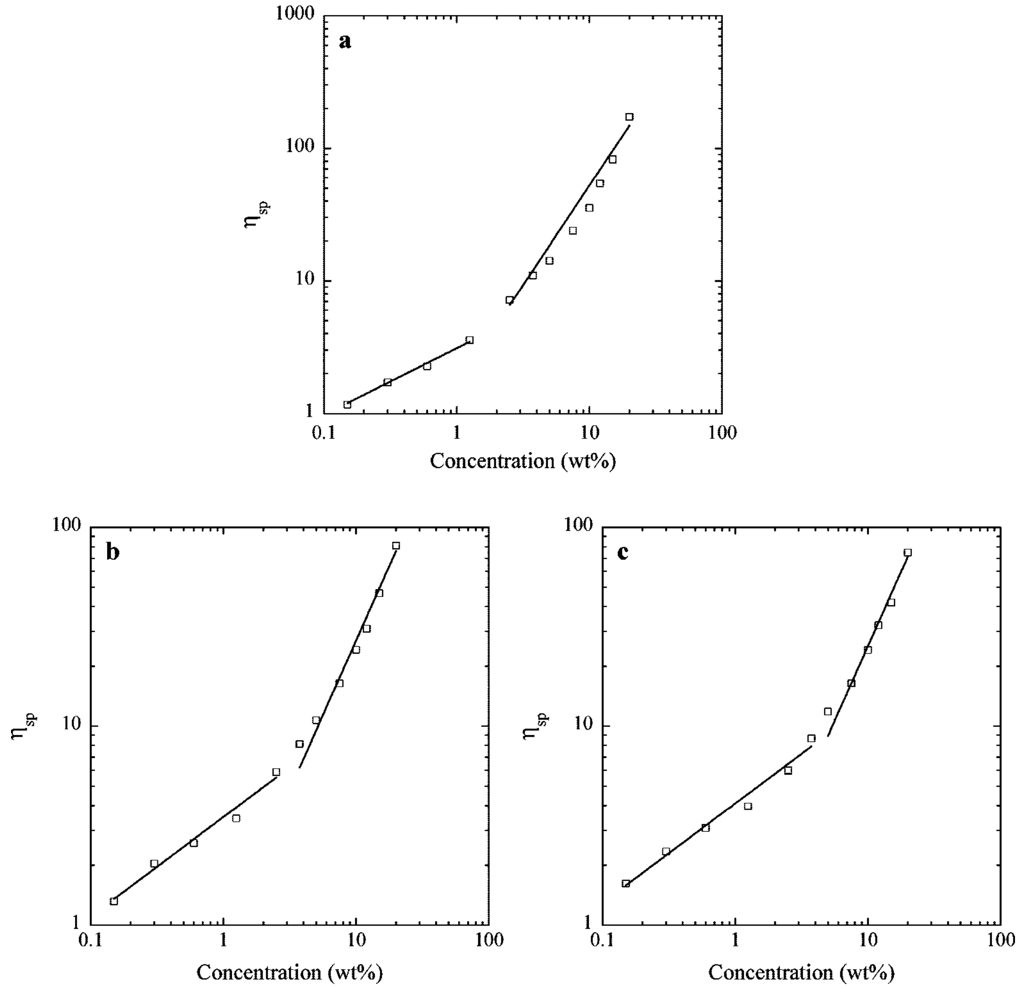


Figure 1. Concentration dependence of specific viscosity of poly(MEBIm-BF_4) in (a) DMF, (b) 3/1 MeCN/DMF, and (c) MeCN. Slopes of semidilute unentangled and semidilute entangled regimes are 0.5 and 1.5, respectively.

the solvent. Similar blockage was observed with a cosolvent of 9/1 MeCN/DMF. Increasing the content of the high boiling point solvent DMF to 3/1 and 1/1 MeCN/DMF resulted in smoother electrospinning. Steady polymer jets were obtained at ~14 kV and 10 cm spin distance at a flow rate of 0.1 mL/h. The electrospun fibers were collected on aluminum foil and their morphology is shown in Figure 2. Despite a steady polymer jet, only beads were collected from DMF solution. Beaded fibers were observed from the 1/1 MeCN/DMF cosolvent. A further increase in MeCN content in the solution (3/1 MeCN/DMF) produced defect free fibers.

With a constant polymer concentration, the electrospinning performance indicates a remarkable solvent effect on solution properties. Table 1 lists some of the physical properties of DMF and MeCN. Both solvents have a similar solubility parameter and dielectric constant, suggesting similar thermodynamic favorability to the polymer and a similar dipole moment in the electric field. However, DMF exhibits a higher viscosity and surface tension. Thus, the formation of beads might be caused by the high surface tension and viscosity that tend to break the continuous polymer jet and retract into spheres.

The micrographs also show an interconnected branched structure for the polymerized ionic liquid electrospun fiber. Other investigators[16] have observed a similar branched structure with electrospun cellulose fiber from an ionic liquid solvent and this was ascribed to the high viscosity and nonvolatility of the ionic liquid. In the polymer form of ionic liquid, the fiber thinning may be an indication of charge interaction (e.g., repulsion) along the polymer backbone or among different polymer chains, which could stretch the fibers to smaller sizes.

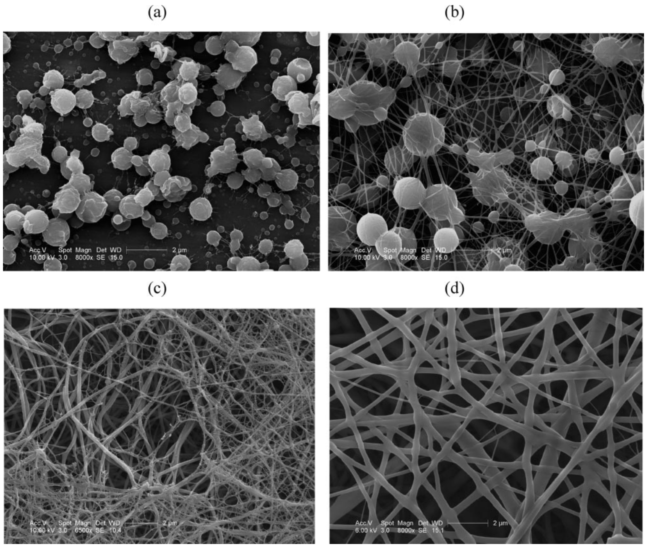


Figure 2. Solvent effect on the electrospinning of poly(MEBIm-BF_4) (10 wt % solution): (a) DMF; (b) 1/1 MeCN/DMF; (c) 3/1 MeCN/DMF; (d) MeCN.

Figure 3 shows the electrospun fibers from various concentrations of poly(MEBIm-BF_4) in cosolvent 3/1 MeCN/DMF. At 2.5 wt %, a concentration below the entanglement concentration

Table 1. Physical Properties of Solvents[15]

solvent	T_b (°C)	η (cp) at 25 °C	δ (cal/cm^3)$^{1/2}$	ε at 20 °C	γ (dyn/cm) at 20 °C
DMF	153	0.82	12.1	36.7	35
MeCN	81.6	0.38	11.9	37.5	29.1

(C_e = 4 wt %), only droplets were obtained (Figure 3a). Beaded fibers were observed at 5 wt % (~1.25C_e) (Figure 3b) and defect-free fibers were formed at 8 wt % (~2C_e) (Figure 3d). Others have observed that for neutral polymers, beaded fibers are formed from electrospinning of the polymer solution at the entanglement concentration (C_e) (i.e., electrospraying-electrospinning transition).[4] In contrast, others have shown that strong polyelectrolytes form fibers at higher concentrations (e.g., at 8C_e for poly(2-(dimethyl amino)ethyl methacrylate hydrochloride)).[3] Therefore, the concentration of polymerized ionic liquid needed for fiber formation in this study is similar to a neutral polymer, but lower than other polyelectrolytes. McKee et al.[3] attributed the higher concentration required for electrospinning to the relatively large conductivities of the polyelectrolyte solution.

The concentration effect on the fiber diameter of poly(MEBIm-BF$_4$) can be summarized in Figure 4. By normalizing concentration with C_e, the effect of chain length and branching architecture can be removed. The solid line indicates the relationship that was recently developed for neutral polymers with either linear or branched structures, $D = 0.18(C/C_e)^{2.7}$, where D is the average fiber diameter in micrometers.[4] Figure 4 shows that poly(MEBIm-BF$_4$) produces fibers about an order of magnitude smaller in size at equivalent relative concentrations. A similar fiber thinning phenomenon for polyelectrolytes in aqueous solutions has been observed and was attributed to the dissociation of ionic groups that resulted in a higher conductivity and greater charge repulsion during electrospinning.[3,6]

Conductivity of poly(MEBIm-BF$_4$) in organic solvents was measured at various concentrations. The polymer in MeCN has a conductivity on the order of magnitude of 10^{-4} S/cm at a concentration of 1.25 wt % (Figure 5a). It increases almost linearly with concentration and reaches a value close to 10^{-2} S/cm at 20 wt %. Conductivity of the polymer in DMF was ~60−70% of the value in MeCN. This may be due to the higher viscosity of the DMF solution, which restricts the mobility of the ions. It was noted that the conductivity of the polymerized ionic liquid in organic solvents was comparable to polyelectrolytes in aqueous solutions, e.g., poly(acrylic acid) (PAA) in water has a conductivity of 1.56 mS at 5 wt %.[6] Nevertheless, the presence of organic solvent usually significantly depresses the conductivity of a polyelectrolyte due to the suppressed ionization, e.g., PAA in DMF has a conductivity of 0.07 mS at 5 wt %.[6] The high conductivity of poly(MEBIm-BF$_4$) contributes to thinner electrospun fibers.

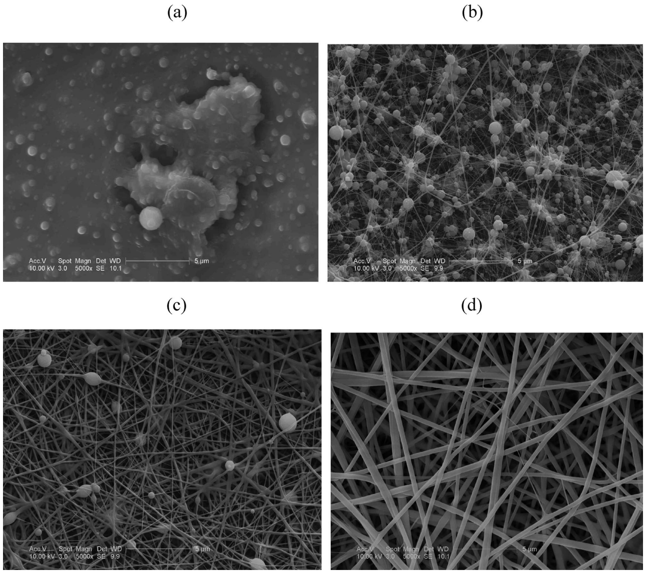


Figure 3. Concentration effect on the electrospinning of poly(MEBIm-BF$_4$) in 3/1 MeCN/DMF. Polymer concentrations: (a) 2.5, (b) 5, (c) 6, and (d) 8 wt %.

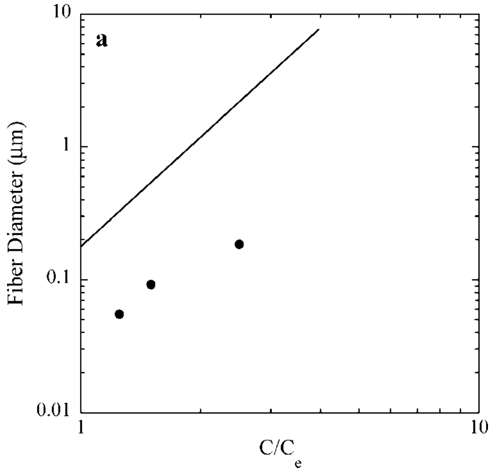


Figure 4. Concentration effect on the fiber diameter of poly(MEBIm-BF$_4$). Solid line represents fiber diameter estimated for electrospun neutral polymers.

Figure 5b shows the concentration dependence of the product of viscosity and conductivity, where the values differ at higher concentrations but are similar at low polymer concentrations. This data appears to concur with Walden's Rule, where the product of viscosity and ionic conductivity at infinite dilution is constant independent of the solvent.

Specifically, in comparison to the study by McKee et al.[3] on a strong polyelectrolyte (poly(2-(dimethyl amino)ethyl methacrylate hydrochloride), conductivities were higher than the ones reported here for the polymerized ionic liquid. Additionally, the fiber diameters are significantly smaller at equivalent relative concentrations and their electrospinning-electrospraying transition occurs at higher entanglement concentrations compared to this study. It is well-known that higher conductivities leads to smaller electrospun fiber sizes, but it is not conclusive at this point if conductivity is the sole reason for dictating the relationship between electrospinnability and entanglement concentration. More experimental studies will be needed to determine this relationship.

Effect of Ionic Liquid on Electrospinning. Owing to the high conductivity, adding small molecule electrolytes to polymer solutions has shown to facilitate the electrospinning process and significantly reduce electrospun fiber sizes.[6,17] To investigate the effect of small molecule ionic liquid on electrospinning, BMIm-BF$_4$ was added to a Nafion−PAA blend solution. Our previous work[14] has demonstrated the success of electrospinning Nafion in an 2-propanol/water cosolvent with the aid of a linear polyelectrolyte, PAA. In the organic−water cosolvent, conductivity of the polyelectrolyte blend was highly suppressed. Addition of ionic liquid was expected to increase the conductivity and consequently further improve the spinning performance. As expected, electrospinning of Nafion−PAA became smoother with the presence of ionic liquid BMIm-BF$_4$. During electrospinning, a smooth and steady polymer jet was observed with no spinneret blockage. Thick and detachable fiber mats were obtained within hours.

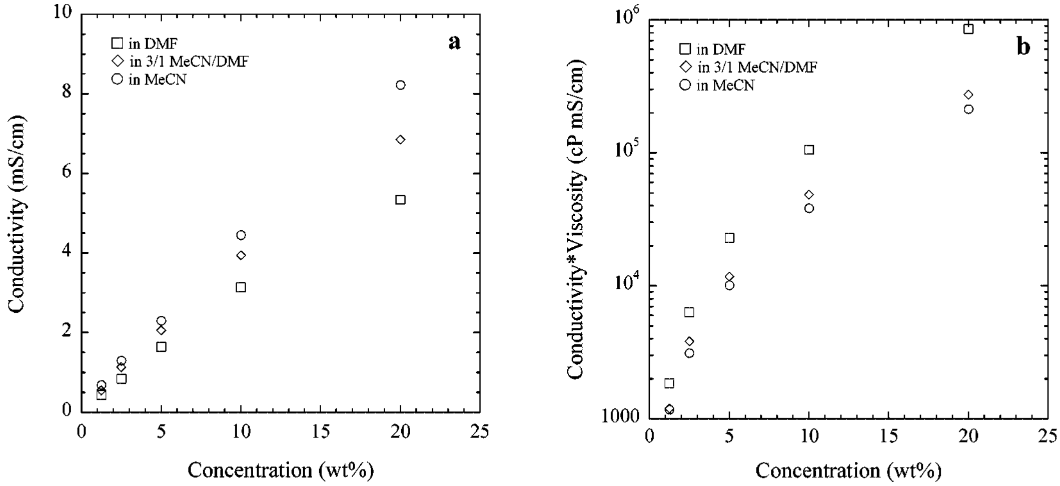


Figure 5. Concentration dependence of (a) conductivity and (b) product of conductivity and viscosity of poly(MEBIm-BF_4) in organic solvents.

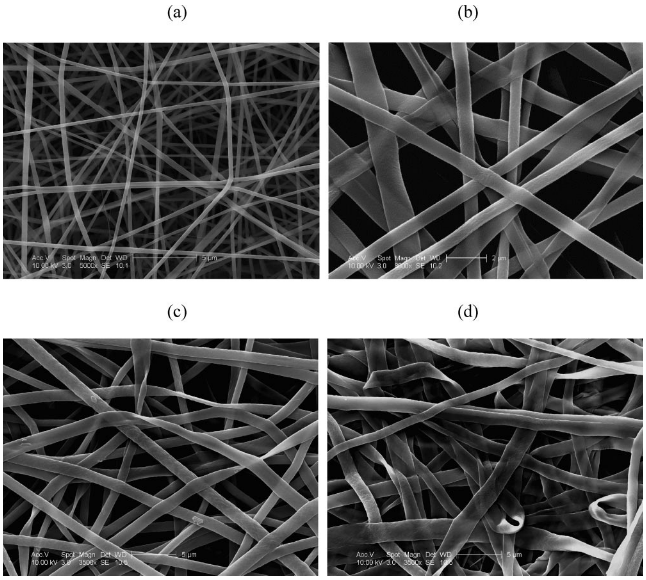

(a) (b) (c) (d)

Figure 6. Field emission scanning electron microscope images of electrospun Nafion−PAA−BMIm-BF_4 blend at ionic liquid weight fraction of (a) 0%, (b) 10%, (c) 20%, (d) 30%. The weight ratio of Nafion:PAA is 3:2 at a 10 wt % total polymer concentration.

Table 2. Ionic Conductivity[a] of the Ionic Liquid-Containing Electrospun Fiber Mat

		Nafion−PAA−BMIm-BF_4		
	poly(MEBIm-BF_4)[b]	BMIm-BF_4, 10 wt %	20 wt %	30 wt %
conductivity (mS/cm)	0.000712	3.15	5.19	17.4

[a] In-plane conductivity, measured by impedance spectroscopy at 30 °C and 10% relative humidity. [b] Electrospun fiber mat from 10 wt % poly(MEBIm-BF_4) in 3/1 MeCN/DMF.

Figure 6 shows the morphology of the fibers at various ionic liquid contents. Instead of reduced fiber sizes, the existence of ionic liquid results in larger fibers with a ribbon structure. This can be attributed to the nonvolatility of ionic liquid that hinders the solidification of fibers to smaller sizes. Moreover, the liquid component in the fiber collapses the fiber into a ribbon structure. With the increase of ionic liquid content, more ribbons were observed in the fiber mat (Figure 6).

Table 2 compares the conductivity of the solid-state electrospun fiber mat of poly(MEBIm-BF_4) and the Nafion−PAA−BMIm-BF_4 blends at various ionic liquid contents. The conductivity was measured by impedance spectroscopy at a low relatively humidity 10% at 30 °C. In the near absence of water, the Nafion−PAA−BMIm-BF_4 blend fiber mats still exhibit conductivity as high as 3.15 mS/cm at 10 wt % ionic liquid. The value increased by 5 fold as the ionic liquid content increased by 3-fold. The polymerized ionic liquid fiber mat shows a lower conductivity due to the constrained ionic structure, in which only the anion significantly contributes to ion conduction and the cation, which is covalently attached to the polymer chain has restricted mobility. More details on the ion conduction mechanism of poly(MEBIm-BF_4) can be found in previous work.[13] The promising ionic conductivity of the ionic liquid-containing fiber mat suggests the potential for use in solid-state electrochemical applications.[18]

Conclusions

The solution properties and electrospinning of a polymerized ionic liquid, poly(MEBIm-BF_4), was investigated. The specific viscosity-concentration scaling behavior was similar compared to typical polyelectrolytes in semidilute unentangled and semidilute entangled regime. Optimal electrospinning was observed for poly(MEBIm-BF_4) dissolved in a 3/1 (wt/wt) MeCN/DMF solution, where beaded fibers were observed at $\sim 1.25C_e$ and defect-free fibers at $\sim 2C_e$. This electrospinning-electrospraying transition occurs higher compared to neutral polymers (C_e), but lower compared to some polyelectrolytes ($8C_e$). The polymerized ionic liquid dissolved in organic solvents possessed solution conductivities comparable to typical polyelectrolytes dissolved in aqueous solutions. As a result, the average electrospun fiber diameters for the polymerized ionic liquid were approximately an order of magnitude lower than a neutral polymer at an equivalent concentration (C/C_e). This produced electrospun fiber mats with high solid-state ionic conductivities at dry conditions and even higher conductivities were observed for fiber mats produced from electrospinning polyelectrolyte-ionic liquid solutions. Interestingly, a different effect on electrospinning was observed for polyelectrolyte-ionic liquid solutions compared to polymerized ionic liquid solutions and typical polyelectrolyte solutions. In particular, larger fibers were produced in the presence of the small molecule ionic liquid due to the nonvolatility of the ionic liquid, which hinders fiber size reduction during solidification.

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