Macromolecules

Article

Cite This: Macromolecules 2019, 52, 5223−5230

pubs.acs.org/Macromolecules

Designing Solutions for Electrospinning of Poly(ionic liquid)s

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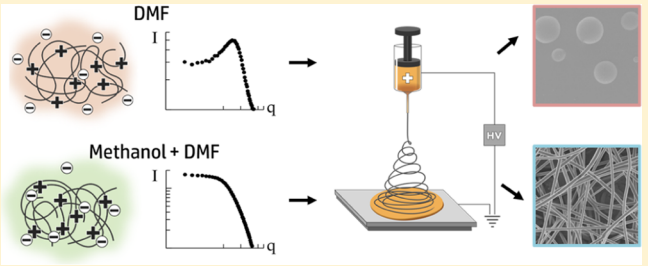
Supporting Information

ABSTRACT: Production of polyelectrolyte fibers via electrospinning is more challenging compared to neutral polymers because of their ionic nature. In this paper, a comprehensive approach to achieve poly(ionic liquid) fibers is presented. We show that small-angle X-ray scattering is a valuable tool to provide a deeper understanding of the structure of the polymer in solution and its relation to spinnability. We found that in dimethylformamide, the poly(ionic liquid) acted like a conventional polyelectrolyte with disassociated ions, and attempts to electrospin it resulted in bead formation. When methanol was added, the polymer structure was more neutral-like and fibers were successfully formed. Thus, tuning the solvent of the electrospinning solution could induce a change in the structure of the polyelectrolytes in the solution to a more neutral structure that favors fiber production. This approach could facilitate the development of future electrospun polyelectrolyte fibers.



INTRODUCTION

One-dimensional nanofibers have a high surface-to-volume ratio and controllable porosity, making them promising candidates in tissue engineering, catalysis, energy storage, water treatment, fiber reinforcement in composites, and more.[1−5] Nanofibers can be produced using different methods, including self-assembly, drawing, solution blow spinning, template-based synthesis, and electrospinning.[6] From these methods, electrospinning is the most established and widely used because of its simplicity, scalability, and top-down approach.[6,7] This technique allows for the production of continuous fibers with interconnected porosity to form a free-standing mat. The first large-scale commercial application of electrospun fibers dates back to the early 1980s when they were used in air filters.[8,9] Starting in the mid-1990s, the potential of electrospinning for the production of nanofibers was noticed by the academic community, which spawned new research directions to take advantage of this material architecture. To date, more than 100 polymers have been processed into fibers by means of electrospinning.[10] The polymers could be the final fiber material or a carrier for other materials such as metals and ceramics.[11] Of these polymers, polyelectrolytes are among the most difficult to electrospin because of their different properties in solution compared to neutral polymers. Yet, they have promising applications as scaffolds for tissue engineering and drug carriers, where many of the biocompatible polymers used are polyelectrolytes (e.g., alginate, polylactic acid, collagen, chitosan, and hyaluronic acid),[2,12] making their electrospinning to a scaffold that mimics the natural extracellular matrix a vibrant area of research. Polyelectrolytes are also favorable in applications that require ion conductivity, for example, in solid-state electrochromic devices as the electrolytes[13] and as proton conductors in membranes.[14] Finding an approach to shorten the development process for material fabrication would accelerate their implementation in these fields.

In an electrospinning process, a polymer solution is pumped through a spinneret, which is subjected to high voltage. If the electrical forces formed by the high voltage are high enough to overcome the surface tension of the polymer solution, a jet erupts from the spinneret. As the jet stretches and undergoes a whipping motion, the solvent evaporates, the jet solidifies, and fibers are deposited on the collector. Many parameters influence the electrospinning process, including ambient parameters (temperature and humidity), process parameters (e.g., flow rate, voltage, distance from tip to collector, and collector type), and solution parameters (e.g., polymer concentration, solvent or solvents, viscosity, conductivity, and surface tension).[15,16] The extent to which each parameter determines the spinning ability is still debated, as studies sometimes show contradicting results.[17,18] Although there is much research effort focused on understanding the mechanism of electrospinning and the influence of the different parameters,[19−22] theoretical models that encompass all variables are still not developed.[2,4] There are general guidelines pertaining the solution properties to its spinnability;[23] but there is still a need to expand existing principles to better predict spinning conditions for new polymers.

Polyelectrolytes are often more challenging to spin in comparison to neutral polymers for a number of reasons. First,

Received: April 5, 2019
Revised: June 9, 2019
Published: July 8, 2019

DOI: 10.1021/acs.macromol.9b00691
Macromolecules 2019, 52, 5223−5230

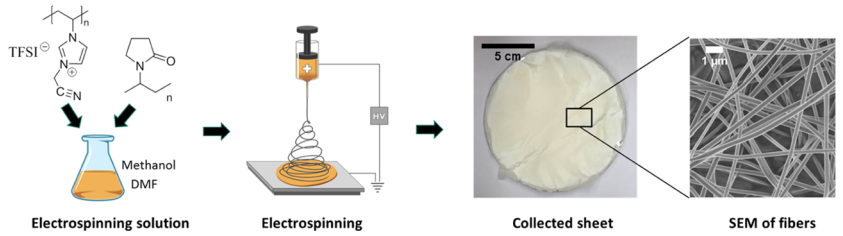


Figure 1. Scheme of the electrospinning process. A solution of PIL and PVP was prepared in DMF and methanol and electrospun to form fibers.

the relatively low mobility of the polyelectrolyte may cause instabilities in the electrospinning jet.[24] Second, many polyelectrolytes are only soluble in water, which is not ideal because of the high surface tension of water. Third, ion disassociation in some solvents leads to high electrical conductivity of the spinning solution,[25] which beyond a critical value (depending on the system used) hinders electrospinning.[4,26,27] Furthermore, the repulsion between the charged groups leads to different scaling and rheological behaviors. For example, a prerequisite to achieve bead-free fibers is that the polymer concentration in the spinning solution be above the entanglement concentration (C_e), more than 2.5 entanglements per chain in a good solvent.[28] For polyelectrolytes, the required concentration is estimated to be more than $8C_e$,[24] at which point the viscosity could be too high to flow through the spinneret. A possible way to overcome the obstacle of electrospinning polyelectrolytes is to make them more neutral de-facto by screening some of the charges; a few studies have investigated this route.[27,29] Long et al.[24] showed that by adding salt to the spinning solution, both the viscosity of the solution and the concentration required to achieve fibers decreased. Similarly, Green and co-workers studied the electrospinning of segmented imidazolium ionenes in acetonitrile (ACN) and observed that when the charge density is low, a lower value of C/C_e is required for the onset of fiber formation.[30]

Substantial research is dedicated to the structure of polyelectrolytes in solution; however, our understanding of their behavior in solution is not as developed as for neutral polymers. Historically, considerable attention was given to characterize polyelectrolytes in aqueous solutions compared to nonaqueous solutions because of their relevance in biology (proteins, DNA, and polysaccharides) and functions in polymer chemistry.[31−33] Not all charged polymers exhibit polyelectrolyte behavior in organic solvents;[34] however, the polyelectrolyte behavior in nonaqueous media has been observed in both polar[35−39] and nonpolar[32] solvents. Understanding the behavior of polymers in the spinning solution could lead to a more targeted design of materials for spinning. However, most research for developing electrospinning solutions focuses on measuring the viscosity, conductivity, and surface tension of the polymer solution, although they are not enough to give a complete picture.[40] Small-angle scattering of neutrons or X-rays is used to investigate the conformation of neutral and charged polymers in solution[41−43] but is infrequently applied to study the relationship between electrospinnability of solutions and the local and global conformation of the polymer.[40,44,45]

Poly(ionic liquid)s (PILs) are a class of polyelectrolytes that feature an ionic liquid (IL) species in each repeating unit, which may or may not be synthesized directly from IL monomers.[46] PILs extend the useful properties of ILs, such as chemical versatility, ion conductivity, high thermal stability, and high carbonization yields, to a polymer form, which expands the utility of ILs beyond their conventional applications.[47−52] Knowing how to process PILs to create new materials is essential to their broader application; electrospinning provides a unique architecture that is not possible with other processing methods. The one-dimensional fibers together with the flexible chemistry of PILs could enable production of ion conductive membranes, functionalization of membranes, modification of surface wetting properties for oil/water separations, and heteroatom doping for future carbon fibers. However, there are only a few examples of PIL fibers produced using electrospinning,[48,53−56] possibly because of their typical low molecular weight and highly charged nature. Unlike many polyelectrolytes, PILs are soluble in many conventional organic solvents and are thus good candidates to obtain electrospun polyelectrolyte fibers.

In this context, we developed an approach for electrospinning polyelectrolytes using the solvent composition as a way to affect the polyelectrolyte behavior in the solution. A scheme of the electrospinning process is shown in Figure 1. The polyelectrolyte used was poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoro methanesulfonyl)imide) (PIL) (Figure S1), a lipophilic PIL which allows electrospinning using organic solvents rather than water. Neutral polymers such as polyvinylpyrrolidone (PVP), poly(ethylene oxide), or poly(vinyl alcohol) (PVA)[48,57] are often added to polyelectrolyte solutions in order to increase chain entanglements without substantially increasing the viscosity;[58] we used PVP as the supporting polymer. We studied the effect of using a mixture of solvents, dimethylformamide (DMF) and methanol, on the electrospinning performance and recognized that this mixture was key to achieve fibers. Using small-angle X-ray scattering (SAXS), we observed that the structure of PIL was different in each solvent. In DMF, the PIL showed the characteristic polyelectrolyte scattering peak, whereas in methanol, the peak disappeared, indicating a more neutral behavior. This more neutral structure was met with improved spinnability. Thus, we show for the first time that altering the solvent composition could be an approach to achieve better spinnability, by driving the behavior of the polyelectrolyte to a more neutral-like polymer. This observation could allow for smarter design of electrospinning solutions and be implemented in future development of polyelectrolyte fibers.

RESULTS AND DISCUSSION

The molecular weight of a polymer is an important parameter for electrospinning. Sufficiently high molecular weight is required to allow for the entanglements of the polymer chains; however, a molecular weight that is too high could inhibit fiber formation.[59] Poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoro methanesulfonyl)imide) was synthesized according

DOI: 10.1021/acs.macromol.9b00691
Macromolecules 2019, 52, 5223−5230

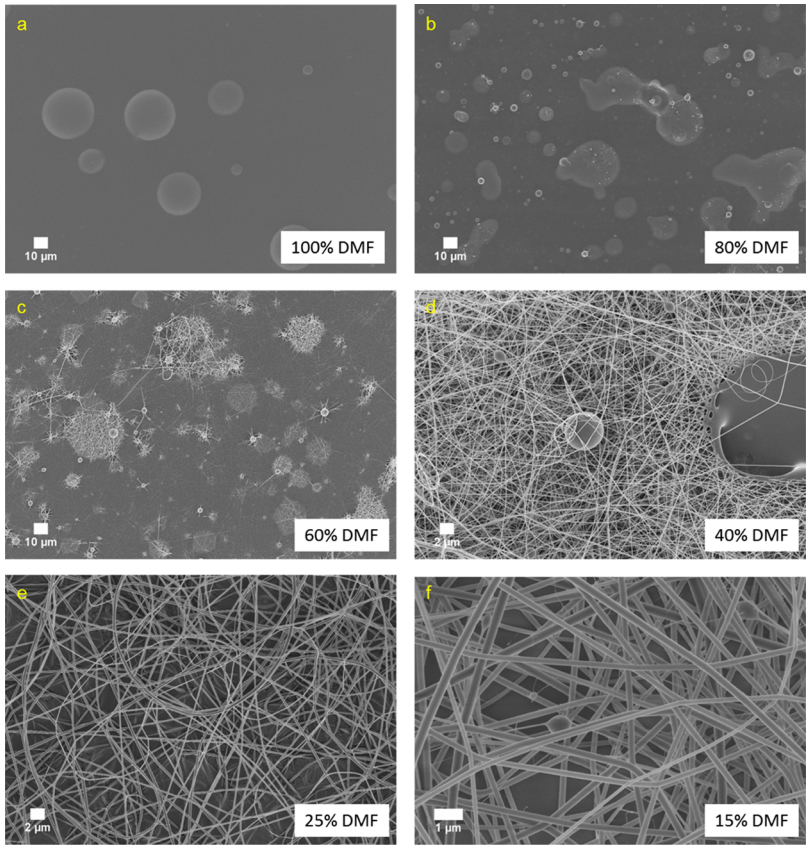


Figure 2. Scanning electron microscopy (SEM) micrographs of electrospinning MIX-*X* solutions. (a) **MIX-100**, (b) **MIX-80**, (c) **MIX-60**, (d) **MIX-40**, (e) **MIX-25**, and (f) **MIX-15**.

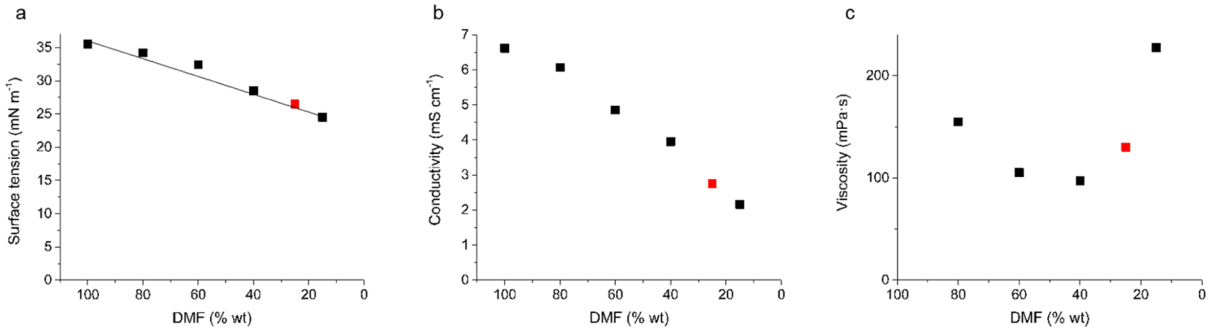


Figure 3. Surface tension (a), conductivity (b), and viscosity (c) of MIX-*X*. *X*-axis is the weight fraction of DMF in the DMF and methanol mixture. The red points are **MIX-25**, the best solution for electrospinning. The line in (a) represents the calculated surface tension of the mixture of solvents without any solute. In (c), the viscosity of **MIX-100** was visibly higher than **MIX-15**, and it was not possible to measure it in the same instrumental setup.

to a previous procedure[60] which resulted in highly viscous solutions that were not suitable for electrospinning. Performing the polymerization in more dilute solutions lowered the molecular weight to 110 kg mol^{-1} from the original 315 kg mol^{-1} and resulted in solutions with lower viscosities. The reaction conditions are detailed in the Materials and Methods. The lower molecular weight poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoro methanesulfonyl)imide) (PIL) was then electrospun from a solution containing 20 wt % PIL and 4 wt % PVP, with DMF or a mixture of DMF and methanol as solvents (Figure 1). A minimal amount of PVP was used to achieve spinnable solutions. The effect of the solvent ratio on the spinning outcome was investigated, while keeping other process parameters constant (high voltage 20 kV, flow rate 1.2 mL h^{-1}, and distance from tip to collector of 10 cm). Spinning solutions are labeled MIX-*X*, where *X* represents the weight percentage of DMF with respect to the weight of the mixture of solvents. In a similar manner, solutions with only 20 wt % PIL or 4 wt % PVP are written as PIL-*X* and PVP-*X*, respectively. Electrospinning **MIX-100** resulted in the formation of only particles (Figure 2a). Upon addition of methanol, a mixture of fibers and particles was observed (**MIX-80** and **MIX-60**, Figure 2b,c). For **MIX-40**, mostly fibers were produced; however, small beads and large droplets containing trapped solvent destroyed the fibers instantly, prohibiting the collection of a robust material (Figure 2d). The electrospinning of **MIX-25** was stable, and only fibers were formed (Figure 2e). Increasing the methanol content further (**MIX-**

DOI: 10.1021/acs.macromol.9b00691
Macromolecules 2019, 52, 5223−5230

15) produced spinning instabilities and some beaded fibers because of rapid solidification at the tip of the cone (Figure 2f). For this reason, 25 wt % DMF was found to be the appropriate concentration for producing PIL fibers. Fibers from **MIX-25** were collected for 1 h, during which the process was stable, without any dripping or build-up of fibers toward the spinneret as is sometimes observed for PILs,[53] and a 14 cm diameter mat was obtained (Figure S2).

The ideal polymer solution for electrospinning is dependent, among other things, on the combined contributions of viscosity, conductivity, and surface tension.[61−63] We first examined the surface tension of solutions **MIX-100** to **MIX-15** and found that the surface tension of the different spinning solutions is governed by the surface tension of the mixture of solvents only and did not change significantly when PIL and PVP were added (Figure 3a). A previous study on PILs and PVP in either DMF or methanol showed that some PILs change the surface tension of solution, whereas other types of PILs do not.[48] In addition, the value of surface tension, between that of DMF and that of methanol, did not seem to have an effect on the spinning outcome.

Although the PIL did not affect the surface tension, it increased the electrical conductivity of the solution significantly. **MIX-100** to **MIX-15** and **PIL-100** to **PIL-15** solutions had an electrical conductivity in the range of 2−7 mS cm^{-1}, 100 times higher than **PVP-100** to **PVP-15**, whose conductivities were 10−13 μS cm^{-1} (Table 1). The conductivity of the pure solvents was below the sensitivity of the probe (<10 μS cm^{-1}). Addition of PVP to PIL solutions decreased the electrical conductivity by 10−25% (Table 1), which we attribute to the significant increase in viscosity, leading to reduced charge mobility. Increasing the conductivity of neutral polymer solutions generally leads to the formation of fibers over beads because sufficient free charges can move to the surface of the jet, thus increasing the net charge density and initiating the Taylor cone.[64] For polyelectrolytes such as PILs, the solution already possesses a high conductivity,[65] which may hinder Taylor cone formation.[66] Although it is simple to increase the conductivity of neutral polymer solutions by adding an electrolyte, decreasing the conductivity is more challenging. We found that altering the solvent composition decreases the conductivity of the solutions with PIL by up to three times. PIL solutions possessing lower conductivity favored spinning; MIX-solutions with decreasing amounts of DMF were less conductive (Figure 3b) and produced more fibers.

Table 1. Viscosity and Conductivity of Solutions MIX-*X*, PIL-*X*, and PVP-*X* with Different Amounts of DMF

	viscosity (mPa·s)			conductivity (mS cm^{-1})		
% DMF[a]	MIX-*X*	PIL-*X*	PVP-*X*	MIX-*X*	PIL-*X*	PVP-*X*
100	>227	15.6	10.9	6.6	7.4	<0.01
25	130	4.7	8.3	2.7	3.4	0.013
15	227	4.4	8.7	2.2	2.8	0.013

[a]The weight percent of DMF from the mixture DMF + methanol.

Next, we examined the viscosity of **MIX-100** to **MIX-15** and whether it is a defining parameter for electrospinning of PIL. Solutions **MIX-80** and **MIX-60** possessed a viscosity similar to **MIX-25** (Figure 3c), yet fibers were only achieved for the latter case. This could suggest that the high conductivity of the solutions dominates the spinnability rather than the viscosity. The viscosities of **MIX-100** to **MIX-15** solutions are 2 orders of magnitude higher than the viscosities of the individual components solutions, **PIL-100** to **PIL-15** and **PVP-100** to **PVP-15**, which could indicate a transition to the semidilute entangled regime. The viscosity of PIL-*X* decreased as methanol content increased, whereas for PVP solutions, the viscosity of **PVP-100** and **PVP-15** is higher than that of **PVP-25** (the viscosity of **PVP-0** was 9.3 mPa·s, higher than that of **PVP-15**). The phenomenon of minimum viscosity at **MIX-40** could thus be related to the PVP itself; however, the effect is more pronounced when PIL is present. One possible explanation for the higher viscosity of PIL in DMF compared to methanol is the presence of more electrostatic charges. It is commonly observed for polyelectrolytes that upon salt addition, the charges are screened and the viscosity decreases.[67] Consistent with this observation, the viscosity of **MIX-100** was higher than that in **MIX-15**, which is less charged.

The local and global conformation of the polymer in different solvents may affect the spinning behavior. For example, electrospinning of bovine serum albumin (BSA) in water resulted in spray, but when a denaturing agent was added, the conformation of BSA changed and fibers were formed.[44] This conformational change was detected using SAXS, a direct method to study the structure of polymer in the solution. Upon addition of the denaturing agent, the electrostatic peak disappeared, suggesting that the conformation of BSA changed to a random coil. These results show that by forcing different structures of the macromolecule, it is

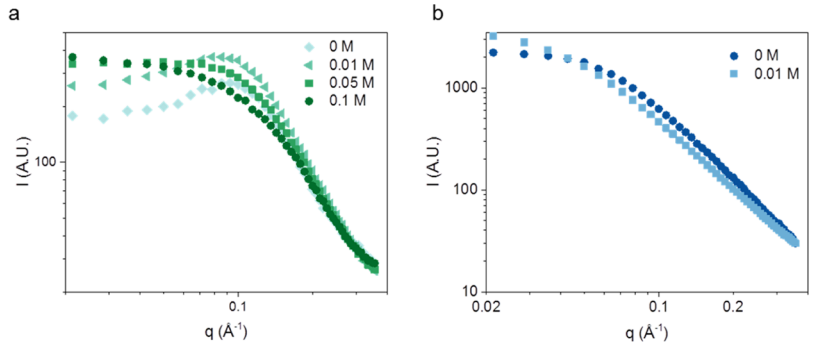


Figure 4. SAXS plots of 105 mg mL^{-1} PIL solutions with varying concentrations of salt, intensity (arbitrary units) vs scattering vector *q*. (a) PIL in DMF, with LiTFSI 0 M (blue diamond), 0.01 M (left-pointing green triangle), 0.05 M (green square), and 0.1 M (green circle). (b) PIL in methanol, with LiTFSI 0 M (blue circle) and 0.01 M (blue square).

DOI: 10.1021/acs.macromol.9b00691
Macromolecules 2019, 52, 5223−5230

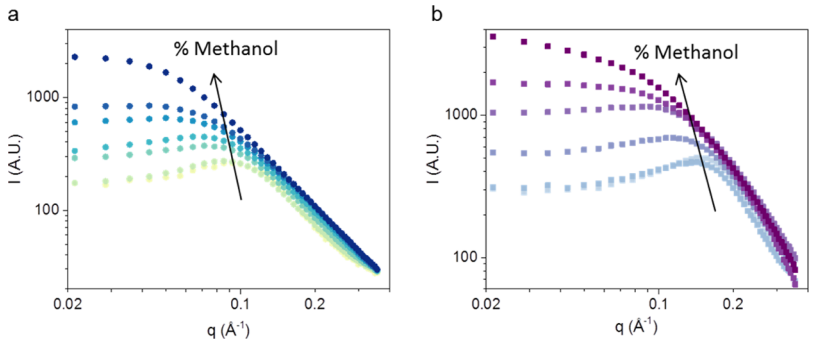


Figure 5. SAXS patterns of (a) 105 mg mL^{-1} PIL in mixtures of DMF and methanol, with weight ratios of DMF/methanol from bottom to top 100:0, 80:20, 60:40, 40:60, 25:75, and 15:85 (b) from bottom to top **MIX-100**, **MIX-80**, **MIX-60**, **MIX-40**, **MIX-25**, and **MIX-15**.

possible to obtain spinnable solutions. To determine if this is the case for PIL, we used SAXS to probe the nanostructure of the different solutions. First, we looked into the pristine system, where PIL is dissolved at a fixed molarity and only the composition of the solvent changes. Next, we measured the more complex spinning solutions, containing both PIL and PVP, where both the molarity of the polymers and the solvent composition changed. The conventional nomenclature for polymer concentration is different in electrospinning research and in fundamental polymer structure research, which also demonstrates a basic obstacle to the comparison of studies of the two fields. In electrospinning, the concentration of polymers and other components in the spinning solutions is routinely expressed as weight percent. In studies looking into the structure of polymers in solutions on the other hand, the typical units used are mass or molar concentration (e.g., milligram per millilitre). Therefore, in the following section, we will describe the polymer solutions in terms of mass concentration. A solution of 105 mg mL^{-1} PIL (which corresponds to 10 wt % in DMF) was examined first because this concentration is attainable in both DMF and methanol, allowing the structure in each solvent to be examined. The scattering of 105 mg mL^{-1} PIL in DMF revealed a structure peak, likely originating from electrostatic interactions between polymer chains (Figure 4a). When the structure peak is a result of electrostatic interactions, screening these interactions causes the peak to decrease in intensity and with enough screening to disappear. A simple way to screen the electrostatic interactions is by the addition of salt. The PIL itself was found to contain very low amounts of salt impurities, measured using inductively coupled plasma optical emission spectrometry (ICP-OES) (details in the Materials and Methods). Following this, we added different concentrations of the salt bis-(trifluoromethane)sulfonimide lithium salt (LiTFSI) to 105 mg mL^{-1} PIL in DMF and observed the scattering patterns (Figure 4a). Indeed, with greater amounts of added salt, the peak diminished in intensity and disappeared, indicating screening of electrostatic interactions. Thus, the interaction peak is the characteristic polyelectrolyte peak, representing disassociation of the counterions in DMF. An electrostatic peak was observed before for polystyrene sulfonic acid in dimethyl sulfoxide (DMSO) and ethanol.[35] At the same PIL concentration in methanol, a peak was not observed (Figure 4b), suggesting that in methanol, PIL is more neutral-like. However, the existence of electrostatic interactions between PIL chains in methanol cannot be ruled out, even without the appearance of a peak. LiTFSI (0.01 M) caused a change in the scattering pattern (Figure 4b), illustrating that the salt does induce a change in the conformation of the polymer. At 0.05 M LiTFSI, the PIL precipitated, demonstrating the importance of the charge on the solubility of PIL in methanol. Furthermore, this suggests that methanol is a poor solvent for the PIL backbone because electrostatic interactions are important for the solubility of the PIL.

To investigate whether the behavior observed in PIL solutions is similar to the behavior in solutions containing both PVP and PIL, we measured the scattering of **MIX-25**. We found that the scattering of the polymer blend is controlled by the scattering of PIL itself because the scattering from PVP itself is negligible in comparison (Figure S3). It is well understood that when two non-interacting components are mixed, the scattering from the mixture equals the sum of scattering of each component.[68] This sum for PVP and PIL (black line in Figure S3) is similar to the scattering of **MIX-25**, indicating that PVP does not have a significant effect on the structure of the PIL at length scales of the chain radius, persistence length, or correlation length. We note that thermal gravimetric analysis (TGA) of the spun fibers indicates that there is an interaction between PVP and PIL in the fiber form (Figure S4).

Next, different ratios of DMF and methanol were mixed with 105 mg mL^{-1} PIL. As the ratio of methanol to DMF increased, the scattering peak shifted to lower q values and diminished (Figure 5a). Scattering patterns of solutions **MIX-100** to **MIX-15** (Figure 5b) exhibited a similar trend of diminished peak as methanol content increased. Hence, the PIL undergoes a change in the different solvent ratios, switching from a polyelectrolyte behavior in DMF to a more neutral polymer behavior in methanol. This is in line with the observed decrease in electrical conductivity as methanol content increases, which indicates a smaller disassociation degree of the counterion. More neutral behavior could be favorable to produce fibers by electrospinning because the electrical conductivity is lower, as well as the concentration of polymer required for onset of fiber formation. Long et al. found that spinning was facilitated by adding salt to polyelectrolyte solutions, thereby screening the charges and shifting the viscoelastic behavior from polyelectrolyte toward a neutral polymer.[24] However, as much as 50 wt % NaCl was required to achieve neutral polymer behavior, which also increased the conductivity of the solution by an order of magnitude. In our case, we found that by changing the solvent composition, it was possible to access a more neutral behavior of the polymer, where there was improved spinnability of this PIL. Future work should be conducted to investigate whether this approach can be applied to other PILs and polyelectrolytes. Nonetheless,

DOI: 10.1021/acs.macromol.9b00691
Macromolecules 2019, 52, 5223−5230

small-angle scattering can be a tool to investigate the structure of polymers in different spinning solutions. We suggest that SAXS could serve as a guide for solvent choice and be the first step before screening different polymer concentrations, thus aiding in eliminating some of the many parameters investigated during the development process of fibers from new materials.

CONCLUSIONS

A comprehensive approach to achieve spinnable PIL solutions was demonstrated. It was found that low-molecular-weight PIL supported by a long neutral polymer circumvent the viscosity problems associated with the high-molecular-weight PIL. In addition, a solvent mixture of DMF and methanol was crucial to obtain a stable process and beaded-free fibers. Starting from DMF and increasing methanol content, the ratio of fibers to beads grew, until only fibers were produced at 25:75 DMF/methanol (w/w). Higher methanol fractions resulted in exceedingly high evaporation rates which resulted in solidification of the solution at the tip of the spinneret. Although there are many parameters that affect the spinnability, we showed that conductivity is an important parameter for PIL spinnability and that solvent composition is an approach to achieve appropriate conductivity. Increasing concentration of methanol in the mixture decreased the counterion disassociation degree, which in turn affected the structure of the chains in solution. SAXS was used to detect the changes in the structure, showing that PIL in DMF behaves like a polyelectrolyte, whereas in methanol, charges are screened and the polymer assumes a more neutral structure. Understanding the behavior of PIL in mixed solvents is not trivial, and further experiments should be carried out to investigate the extent of contribution of other parameters, such as the quality and volatility of the solvent, to the spinnability of these solutions. However, changing the solvent composition could be an approach to access a more neutral behavior of the polymer chains, achieve better spinnability, and contribute to the development of future polyelectrolyte fibers.

MATERIALS AND METHODS

PVP (1.3 MDa), 1-vinylimidazole, and bromoacetonitrile were supplied from Alfa Aesar. All solvents were of analytical grade and supplied from Merck: DMF, methanol, DMSO, acetone, ACN, and diethyl ether. LiTFSI was from IoLiTech. All materials were used as received except azobisisobutyronitrile (AIBN), which was recrystallized in methanol.

Synthesis. *IL-Monomer Synthesis.* Synthesis of PIL followed a previously described procedure.[60] 1-Vinylimidazole (20.0 g, 212 mmol) and butylated hydroxytoluene (0.1 g, 0.45 mmol) were dissolved in ACN (200 mL) in a round bottom flask. Bromoacetonitrile (16.2 mL, 27.9 gr, 232 mmol) was slowly added to the solution and stirred for further 2 h and then heated to 45 °C for 16 h. The solution was then cooled to room temperature, the ACN discarded, and the white precipitate washed with diethyl ether (3 × 100 mL). After drying in a vacuum oven, a white powder was isolated and identified as the IL monomer, 3-cyanomethyl-1-vinylimidazolium bromide (CMVImBr) (33.5 g, 70%).

Polymer Synthesis. IL monomer (6.0 g, 28 mmol) was dissolved in DMSO (240 mL) in a 500 mL round bottom flask. After the monomer was dissolved, the AIBN initiator (120 mg, 0.731 mmol) was added. The mixture was purged with nitrogen for 30 min and then heated to 70 °C and stirred for 16 h. After cooling to room temperature, the solution was slowly added to stirring acetone (400 mL), resulting in the formation of a white oil. The solvent was then decanted and the oil dissolved in DMSO (60 mL) and precipitated in acetone (200 mL), followed by rinsing of the oil with acetone (4 × 100 mL) to remove residual DMSO. With each consecutive wash, the oil began to form a beige precipitate. After drying in a vacuum oven (75 °C, 16 h), a beige powder was isolated and identified as a CMVImBr polymer (4.7 g, 78%). The number averaged molecular weight (M_n) was measured by gel permeation chromatography and found to be 70 kDa with a polydispersity index of 2.4.

Ionic Exchange. The CMVImBr polymer (4.0 g, 19 mmol) was solubilized in deionized water (400 mL). LiTFSI (5.63 g, 20 mmol) was solubilized in deionized water (40 mL). The polymer solution was added slowly to the salt solution while mixing. The resultant mixture was stirred for 1 h before filtering the solution using Por. 4 Buchner filter. The polymer was washed five times with water and dried in a vacuum oven overnight at 70 °C (5.6 g, 72%). A ^{1}H NMR spectrum of the polymer can be found in the Supporting Information (Figure S5). The concentration of residual lithium in the polymer was measured using ICP-OES (Optima 8000, PerkinElmer with multi elemental standard). It was found to be less than the detection limit of 0.1 mg lithium per gram polymer, corresponding to less than 0.006 mol Li per mol monomer.

Preparation of PIL Fibers. To prepare spinning solutions, PIL and PVP were mixed with DMF and MeOH using a magnetic stirrer heated to 35 °C. Solutions were transferred to a 2 mL syringe and mounted on the syringe pump in a spinning machine (Professional Electrospinner, Yflow, Spain). A positive high voltage was connected via an alligator clip to a needle with an inner diameter of 0.5 mm and outer diameter of 1 mm. The collecting plate was covered with an aluminum foil and connected to a ground. Process parameters were fixed at a voltage of 20 kV, flow rate of 1.2 mL/h, and distance from tip to collector of 10 cm. The temperature was 23 °C and the humidity 40−50%.

Characterization. SEM was performed on a GEMINI LEO 1550 microscope at 3 kV; samples were coated with a thin layer of gold and palladium before examination. SAXS was carried using a Nanostar (Bruker AXS, Karlsruhe, Germany) device, equipped with a SIEMENS KFF CU 2K-90 X-ray tube, operating at 40 kV and 100 mA, and generating an X-ray beam with a wavelength of 1.5418 Å (Cu Kα radiation) and a focal spot size of 550 μm. A silver behenate standard was used to calculate beam center and the exact sample-to-detector distance. 2D scattering plots were corrected for background, transmission, and empty capillary.

Surface tension was measured using the drop profile analysis tensiometer (PAT-1, SINTERFACE Technologies). Conductivity of solutions was measured using an InLab 751-4mm sensor connected to a conductivity meter (Mettler Toledo). The density of the sample at 25 °C was determined in a density oscillation tube (DMA 5000M, Anton Paar, Graz). The viscosity at 25 °C was measured and evaluated with an Automated Microviscometer (AMVn, Anton Paar, Graz), a capillary with a diameter of 3 mm at 70° angle and 2 × 6 repeated measurements.

Molecular weight of the polymers was measured using analytical ultracentrifugation (AUC), performed on an Optima XLI centrifuge (Beckman Coulter, Palo Alto CA) and Rayleigh interference optics at 25 °C and a speed of 60 000 rpm. The sedimentation coefficient distributions were evaluated with the least squares $g^*(s)$ evaluation implemented in the software SEDFIT (version 15.01b[69]). For the equilibrium experiments, concentrations between 1 and 5 mg/mL were analyzed at different speeds starting from 5000 rpm up to 10 000 rpm for the 110 kDa PIL and at 3500 rpm for the 315 kDa PIL. Data were evaluated with the program MSTAR (Kristian Schilling, Nanolytics, Germany).[70]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00691.

DOI: 10.1021/acs.macromol.9b00691
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^{1}H NMR spectrum of the PIL and its structure, pictures of the spun sheet, SAXS of PVP and **MIX-25**, and TGA of the fibers, PVP and PIL (PDF)

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Aliyar Javadi (surface tension), Antje Völkel (AUC and viscosity), and Daniel Werner (SAXS measurements).

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