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Ion-Containing Polymer-Grafted Nanoparticles in Ionic Liquids: Implications for Polymer Electrolyte Membranes

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ABSTRACT: Polymer-grafted nanoparticles offer several advantages in designing electrolyte systems for their uses in fuel cells, supercapacitors, or actuators. In this work, stabilization of poly(methyl methacrylate) (PMMA)-grafted magnetic nanoparticles with polystyrene sulfonate (PSS) end domains in ionic liquid/cosolvent mixtures is presented. We propose that anions and cations pertaining to ionic liquid preferentially interact with the methyl groups of PMMA and the sulfonated groups of PSS, respectively. These interactions can be used to mitigate the whole ionic conductivity and the free mobile counterion distribution in the copolymer-grafted nanoparticle-based electrolyte membranes. PMMA-*b*-PSS-grafted nanoparticles with low sulfonation amount and long PMMA chains are found to exhibit the highest conductivity in acetonitrile and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI) mixtures compared to the particles with the higher sulfonation amount and shorter PMMA chains.

KEYWORDS: polymer-grafted nanoparticles, ionic liquid, HMIM-TFSI, conductivity, solvation, electrolyte membrane

1. INTRODUCTION

Ionic liquids (ILs) are extensively investigated for their potential uses in electrochemical devices as they have a wide electrochemical stability window and exhibit high ionic conductivity.¹⁻³ Their nonflammability and nonvolatility make the ILs excellent electrolytes for lithium batteries⁴ and fuel cell membranes.⁵ Ionic polymer gels containing ILs and silica nanoparticles,⁶ or carbon nanotubes,⁷ or block copolymers⁸ are good candidates for solid electrolyte membranes. In this work, poly(methyl methacrylate) (PMMA)-grafted chains with poly(styrene sulfonate) (PSS) end groups are prepared to examine their dispersion and conductivity in 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide (HMIM-TFSI). The nonconductive PMMA domains of the polymer grafts repel the nanoparticles, hindering particle agglomeration. The repulsion forces as well as the interactions between PMMA and TFSI⁻ anions enable the solubilization of ion-containing chain ends by ILs. The PMMA and PSS groups of the copolymer preferentially interact with TFSI⁻ anions and HMIM⁺ cations, respectively. The grafted particle-based hybrid electrolyte offers enhanced mechanical stability and ionic conductivity,

which are both essential features for energy storage devices. In the following section, we present some prominent works on polymers with ILs, ionic gels, and also polystyrene (PS)-grafted nanoparticles in IL.

Selective incorporation of IL into one of the block copolymer domains yields fast transport of charge carriers and improves the ionic conductivity and mechanical durability of polyelectrolyte membranes.^{9–11} ILs also act as plasticizers affecting the phase behavior and morphology of block copolymers.^{12,13} Several diblock copolymers of polybutadiene-*b*-poly(ethylene oxide) (PB-*b*-PEO),¹⁴ polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO),¹⁵ polystyrene-*b*-poly-(methyl methacrylate) (PS-*b*-PMMA),^{16–18} and polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP)^{19–21} have been inves-

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	CPDB-anchored Fe ₃ O ₄ particles (mg)	MMA (mL, mmol)	AIBN (mmol)	THF (mL)	[SH]:[SS-TOA]
398 kDa PMMA 0.12 $chains/nm^2$	50	10, 0.09	0.003	10	1:5
123 kDa PMMA 0.7 chains/nm ²	50	2, 0.02	0.001	2	1:38

tigated in the presence of IL. It has also been shown that addition of TFSI⁻-containing ILs with varying alkyl chain lengths and cation types to block copolymers influenced their phase behavior.²² The asymmetry in the molecular volumes and interactions between anion and cation in IL affected phase transitions between the ordered microstructures of copolymers.²³

High ionic conductivity can be attained by creating sharp interfaces between ionic and nonionic domains of block copolymers, where IL is confined within the ionic domain.^{24,25} Other parameters that can enhance ionic conductivity in ion gel systems are IL amount, molecular weight of the conducting block, IL polarity, and local IL concentration in the conductive phase.^{15,16,26} In the PS-*b*-PEO block copolymer with imidazolium-based IL and lithium salt, the high conductivity was attributed to the dissociation of lithium salt that migrates from the PS-PEO interface to the PEO domains.²⁷ The protons move by two well-known mechanisms in ion gels: a vehicle mechanism, where protons transport with the imidazole rings of protic ionic liquid,²⁸ and by a protonhopping mechanism, where the protons are transferred from one SO_3^- site to another along the styrene sulfonate domains.²⁴ The proton hopping occurs through the hydrogen-bonded imidazole molecules.^{29,30} In addition, the type of anion in IL can significantly impact the activation barrier for proton conduction.³

In prior work, we synthesized the PS-*b*-PSS copolymergrafted iron oxide nanoparticles³¹ using a similar synthesis approach utilized in this study. We showed that a sample with 3 mol % SS exhibited the highest ionic conductivity in HMIM-TFSI, which was attributed to the planar-like aggregation of particles, driven by the preferential interaction between sulfonated domains and HMIM-TFSI.^{31,32} Rearrangements of the SS groups at the interface of ionic liquid were also proposed, and the packing number of ionic aggregates was calculated from the fitting analysis to the small-angle X-ray scattering data.³¹

The solvation behavior of HMIM-TFSI with addition of solvents at different polarities was studied in our previous works.^{33,34} It was shown that solvents with high dipole moments screen the interactions between cations and anions and dissociate the counterions.^{33–35} The diffusivity of HMIM⁺ in acetonitrile was measured to be higher than in methanol. Next, we studied the effect of adding PMMA-grafted nanoparticles into HMIM-TFSI/solvent mixtures in quasielastic neutron scattering (QENS) spectroscopy.^{34,36} Dissociation of HMIM-TFSI by ion-dipole interactions between PMMA and the TFSI⁻ was found to improve the diffusion of HMIM⁺ cations with the addition of good solvent.³⁴ Further, the ion-dipole interactions became prominent when PMMA chains were swollen in good solvents. Consequently, with the high graft density of chains, the number of interacting chain segments with TFSI⁻ anions increased the number of free HMIM cations, leading to the faster ionic mobility and conductivity in HMIM-TFSI/acetonitrile mixtures.³⁴

In this study, colloidal stability and dispersion of two samples of PMMA-b-PSS copolymer-grafted Fe₃O₄ nano-

particles in HMIM-TFSI are presented. The dispersion states of copolymer-grafted nanoparticles in IL/solvent mixtures depend on the solvation of the copolymer by HMIM-TFSI. In addition to the interactions between PMMA and TFSI-, the coupling between HMIM⁺ cations and SO₃⁻ groups is also affected by the solvation upon solvent addition. PMMA chains are very long in the two synthesized copolymers compared to the PSS, and any changes in measured conductivities are attributed to the increased amount of free HMIM⁺ cations that do not associate with the sulfonated groups. It is, thus, easy to speculate that for the high-sulfonated sample in a fixed volume of ionic liquid, there is less amount of free HMIM⁺ cations; hence, ionic conductivity decreases compared to the low sulfonation sample. These findings have important implications for designing polymer electrolytes with asymmetric conduction and enhanced conductivity for electromagnetic actuators.

2. EXPERIMENTAL SECTION

2.1. Materials. HMIM-TFSI was purchased from IoLitec, Ionic Liquids Technologies. 4-Cyanopentanoic acid dithiobenzoate (CPDB), diethyl ether and oleic acid (90%), and butylamine (99.5%) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) and cyclohexane (both ACS grades) were purchased from Pharmco-AAPER. 2,2'-Azobis(isobutyronitrile) (AIBN; 98% technical grade) was recrystallized from methanol. All other chemicals were used as received.

2.2. Nanoparticle Synthesis. Fe_3O_4 nanoparticles were synthesized by the high-temperature thermal decomposition method. The synthetic procedure of nanoparticles capped with oleic acid has two steps:³⁷ synthesis of iron–oleate complex by ion exchange of iron chloride and sodium oleate salts; and thermal decomposition of the iron–oleate precursor. Particle diameters are 20 ± 2 nm and 22 ± 1.5 nm, obtained by analyzing the transmission electron microscopy (TEM) data in ImageJ by sampling over hundreds of particles.

2.3. Preparation of CPDB-Anchored Fe_3O_4 Nanoparticles. To prepare grafted particles with long PMMA chains and low grafting density, CPDB solution (10 mg in 5 mL of THF) was added dropwise into the nanoparticle solution (100 mg in 5 mL of THF) and sonicated in a bath sonicator. The mixture was stirred at room temperature for 24 h. Particles were washed to remove excess CPDB. Every 3 mL of the anchored mixture was precipitated by adding 25 mL of cyclohexane and ethyl ether (4:1 volume ratio), centrifuged at 3000 rpm for 15 min, and redissolved in 3 mL of THF. The washing procedure was repeated three times. Particles with short and dense PMMA brushes (123 kDa PMMA grafts at 0.7 chains/nm² graft density) were prepared in a similar way by adding CPDB solution (50 mg in 10 mL THF) into the nanoparticle solution (100 mg in 10 mL THF).

2.4. Surface-Initiated Reversible Addition–Fragmentation Chain Transfer (SI-RAFT) Polymerization of MMA from Fe₃O₄ Nanoparticles. CPDB-anchored Fe₃O₄ particles, MMA and AIBN in THF solution, were degassed in freeze–pump–thaw for three cycles. The stoichiometric ratio of each component is listed in Table 1. The flask was placed in an oil bath and stirred at 60 °C for 6 h. The flask was immersed in liquid nitrogen to terminate the polymerization via quenching. To purify the grafted particles from the free chains, ethanol was added to the solution of tethered and free PMMA chains in THF drop by drop until the homogeneous solution turns cloudy. The solution was then centrifuged at 6000 rpm for 10 minutes. The supernatant was removed, and particles were redissolved in THF.This

Scheme 1. Reaction Scheme of PMMA_m-b-PSS_n Copolymer-Grafted Fe₃O₄ Nanoparticles



washing step was repeated several times till the supernatant solution was cleared after ethanol addition. $^{\rm 38}$

2.5. Aminolysis of Grafted PMMA Chains. The synthesized PMMA-grafted particles were dissolved in toluene at 1 mg/mL and degassed from three cycles of freeze–pump–thaw. N-Butylamine (50-fold in excess) was added to the solution under a flow of nitrogen with a syringe and mixed for 24 h at room temperature.³⁹ Particles were precipitated from ethanol three times and redissolved in toluene.

2.6. Preparation of Trioctylammonium *p*-Styrene Sulfonate (SS-TOA). Trioctylammonium (TOA) capping was necessary to produce the hydrophobic SS-TOA monomer. TOA-capped *p*-styrene sulfonate (SS-TOA) was prepared following the published procedure.^{40,41} TOA-protected PSS groups solubilized the grafted particles in toluene.

2.7. Synthesis of PMMA-*b*-PSSTOA-Grafted Nanoparticles. Thiol groups at the end of PMMA chains react with the AIBN radicals to form thiyl radicals at 80 °C, which can initiate propagation of the styrene sulfonate (SS-TOA) monomers. This thiol-based chain transfer polymerization yields the final product, PMMA-*b*-PSSTOA-grafted Fe₃O₄ nanoparticles. Initiation of radical thiol–ene reactions between thiolated polystyrene and a series of ene monomers, such as methyl methacrylate (MMA), has been studied using different initiators in previous studies.⁴² The molar ratio of [SH]/[AIBN] was kept as 1:0.5, and [SH]/[SS-TOA] was varied to control the amount of SS-TOA per PMMA ([SH]/[SS-TOA] = 1:5 and 1:38 to yield target 0.1 mol % SS and 3 mol % SS amounts, respectively). The polymerization was carried out at 80 °C in an oil bath for 4 h under nitrogen. Particles were precipitated from ethanol three times and redissolved in toluene.

2.8. Structural Characterization. We collected the TEM data using two instruments, FEI CM20 FE S/TEM at 200 keV in the Laboratory for Multiscale Imaging at Stevens, and FEI TITAN THEMIS 200 TEM located at the CUNY-ASRC Imaging Facility operated at 200 keV. PMMA-grafted particles in ionic liquid solution

were drop-cast on lacey carbon grids. Fourier transform infrared spectroscopy (Bruker Optics Tensor 27 Fourier transform infrared (FTIR) spectrometer) was utilized to determine the presence of the sulfonated group. Copolymer-grafted nanoparticles were mixed with KBr powder and then pressed into pellets for testing. The spectra were recorded for wavenumbers between 4000 and 400 cm⁻¹.

2.9. Molecular Weight and Grafting Density Determination. Nanoparticles were etched with a 2 wt % HCl solution. HCl was simply added to the PMMA-grafted nanoparticle solution (10 mg/mL in 5 mL THF), and the mixture solution was sonicated till the top organic layer became clear. Then, methanol was added and the mixture was centrifuged at 6000 rpm for 10 min. The precipitated grafted PMMA chains were dissolved in toluene. The washing step was repeated three times to wash away HCl and THF. The cleaved PMMA chains were then dissolved in toluene. The weight-averaged molecular masses of grafted PMMA chains were measured using a gel permeation chromatography-light scattering (GPC/LS) device after etching the particles. The GPC/LS system in our laboratory is equipped with a VARIAN PL 5.0 μ m Mixed-C gel column (7.5 mm ID), a light scattering detector (miniDawn, Wyatt Technology), and a refractive index (RI) detector (Optilab rEX, Wyatt). Averaged molecular masses were measured as 398 kDa (D: 1.09) and 123 kDa (D: 1.05). The GPC curves of the two grafted PMMA chains are presented in Figure S2.

Grafting density was determined through thermogravimetric analyzer (TGA) using a Q50 TGA (TA instruments) with the given equation

$$\sigma = \frac{m_{\rm polymer}}{m_{\rm NP}} \frac{N_{\rm A} \rho R}{3M_{\rm w}}$$

 $m_{\rm polymer}$ and $m_{\rm NP}$ are the mass of grafted chains and particle cores, respectively, $N_{\rm A}$ is the Avogadro constant, ρ is the particle density, R

is the radius of iron oxide nanoparticles, and $M_{\rm w}$ is the weightaveraged molecular weight of grafted chains.

2.10. Dynamic Light Scattering (DLS). A Zetasizer NanoS instrument, Malvern Instruments, was equipped with a He–Ne laser (wavelength $\lambda = 633$ nm and a detector angle of 173°) to show the effect of medium viscosity on particle diffusion. PMMA-grafted nanoparticles in HMIM-TFSI/solvent mixtures (at 60/40 volume ratio) were bath-sonicated for about 2 min. The measurement time was set to 15 s, and data were averaged over 13 runs for three measurements at 25 °C. The refractive index of neat HMIM-TFSI is 1.4295 at 25 °C, and it is considered constant for solvent–IL mixtures. The viscosity (η) of neat HMIM-TFSI is 70.09 mPa·s at 25 °C, and viscosities of HMIM-TFSI/solvent mixtures were measured by an ARES-G2 rheometer (Figure S3).

2.11. Electrochemical Impedance Spectroscopy (EIS). Bulk ionic conductivity was measured using the SP-300 electrochemical impedance spectrometry from the Bio-Logic Science Instruments. Grafted particles (0.3 mL) in HMIM-TFSI/solvent mixtures (at 50/ 50 mass ratio) were placed into a tube with two stainless steel electrodes. AC impedance measurements were performed at room temperature. An alternating current signal with a 10 mV amplitude was applied in a frequency range of 1 kHz to 1 MHz. The real component of the complex conductivity, σ' , was calculated using the equation⁴³ $\sigma'(\omega) = \frac{Z'(\omega)}{k [(Z'(\omega))^2 + (Z^*(\omega))^2]}$. The real and imaginary impedances, Z' and Z'', were obtained from the high-frequency plateau, where ionic mobility dominates the impedance spectra.⁴⁴ The conductivity cell constant, k, was determined using 0.01 M KCl standard (Ricca Chemical, 1412 μ S/cm at 25 °C).

3. RESULTS AND DISCUSSION

It is known that the phenyl Z-group of the RAFT agent has a higher addition rate, and the R-group, $-(CH_3)(CH_3)CN$, has a higher fragmentation rate for the MMA monomer.^{45,46} The carboxylic acid functional of the end -R-group of chain transfer agent, 4-cyanopentanoic acid dithiobenzoate, was used for the ligand exchange with the oleic acid-coated iron oxide nanoparticles to produce the RAFT-anchored particles. The monomer adds in between R- and Z- groups of the RAFT agent, so there is the COO⁻ group on the particle surface and the dithiobenzoate group on the chain end. The dithiobenzoate termini of grafted PMMA chains can be easily converted to thiol groups by aminolysis with butylamine.^{31,39} Thiol groups act as chain transfer agents in the free-radical polymerization of vinyl monomers.^{47,48} Here, the thiol group is initiated to form a thiyl radical by reacting with the AIBN radical, which then initiates styrene sulfonate (SS) to polymerize, as shown in Scheme 1. We prepared two batches of $PMMA_m$ -*b*-PSS_n copolymer-grafted particles (Table 2). SS

Table 2. Characteristic Parameters of $PMMA_m$ -b-PSS_n Copolymer-Grafted Fe₃O₄ Nanoparticles Synthesized in This Work

particle core diameter (nm)	graft density, σ (chains/nm ²)	$\begin{array}{l} \text{PMMA } M_{\rm w} \\ \text{(kDa)} \ (\mathcal{D}) \end{array}$	SS amount (mol %)	number of ions/chain
20 ± 2.0	0.12	398 (1.09)	0.1	5
22 ± 1.5	0.70	123 (1.05)	3.0	38

molar percent is calculated by eq 1, and the number of ions per particle is calculated by eq 2. [MMA] and [SS-TOA] are the molar amounts of monomers, and N_A is the Avogadro constant

$$SS \text{ mol } \% = \frac{[SSTOA]}{[MMA] + [SSTOA]} \times 100\%$$
(1)

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number of ions/chain = ([SSTOA] /chain) $\cdot N_{A}$ (2)

Reaction details are presented in the Experimental Section. The grafted sample (398 kDa) may appear to be unusually high molecular weight. It is worth noting that it is possible to synthesize \sim 300 kDa molecular weight polymers by the RAFT method. In our previous work, we showed that SI-RAFT kinetics of styrene polymerization is different from the RAFT process in solution.⁴⁹ The chain transfer exchange rates are found to be influenced by the chain transfer agent (CTA) density on nanoparticles. With the highest CTA density, we found that grafted chains grow longer than the coexisting free chains in solution, indicating that the free CTA does not play a role in the chain transfer on the particles, and the grafted chains grow as in free-radical polymerization.⁴⁹

Figure 1a,b presents the FTIR spectra of PMMA₃₉₇₄-b-PSS₅and PMMA₁₂₂₅-b-PSS₃₈-grafted particles before and after sulfonation. Both spectra were normalized by the peak height of the acrylate carboxyl group at 1732 cm⁻¹. The appearance of two bands at 1098 and 1028 cm⁻¹ for the asymmetric stretch of the SO₃⁻ group indicates the existence of sulfonated groups on PMMA chains. The spectra of PMMA₃₉₇₄-b-PSS₅ and PMMA₁₂₂₅-b-PSS₃₈ copolymer-grafted particles are overlaid in Figure 1c. The ratio of the integrated peak area of the SO₃⁻ group of two particles is 1.98, indicating that the sulfonation amount for PMMA₁₂₂₅-b-PSS₃₈-grafted particles is almost twice as in PMMA₃₉₇₄-b-PSS₅-grafted particles. However, the C-S and C-S-H groups cannot be confirmed by FTIR since the stretching vibrations of C-S are known to result in very weak IR absorptions.⁵⁰ It is important to note that the sulfonation ratio from FTIR data is lower than the molar monomer concentration used. We cannot quantify the exact amount of sulfonation in PMMA chain ends, but we present the FTIR data as qualitative means of showing different sulfonation amounts. Free sulfonated polystyrene formation is not anticipated since there is no radical transfer to solvent or monomer. In addition, the existence of any free PSS chains would change the solubility of the PMMA-grafted nanoparticles in toluene and particles would precipitate in pure toluene. We did not observe any significant solubility problem of grafted particles in toluene.

3.1. Stability and Structure of Copolymer-Grafted Nanoparticles in lonic Liquid. The copolymer-grafted particles' stability and aggregation in solution were characterized by dynamic light scattering (DLS). The hydrodynamic size distributions of PMMA₃₉₇₄-b-PSS₅ copolymer-grafted particles in different solvent/HMIM-TFSI mixtures are shown in Figure 2. The dissociation between ion pairs in IL is affected by solvent polarity in the IL-rich phase.³⁵ Toluene is less polar compared to methanol and acetone; thus, the electrostatic interactions between HMIM⁺ cations and TFSI⁻ anions can still hold the ion pairs together in toluene. Subsequently, PMMA-b-PSS copolymer-grafted particles have limited solubility in the IL/toluene mixture. On the contrary, HMIM-TFSI can be solvated in more polar solvents like methanol or acetone, which are also good solvents of the SS-TOA monomer.⁴⁰ Dissociation of HMIM-TFSI gives rise to the swelling of PMMA and PSS. The Z-average size of copolymer-grafted particles is measured to be 176 nm in acetone/HMIM-TFSI, 357 nm in methanol/HMIM-TFSI, and 530 nm in toluene/HMIM-TFSI (Figure 2). The copolymergrafted nanoparticles obviously do not disperse at the individual particle level and they form ionic clusters due to



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Figure 1. FTIR spectra of (a) PMMA-grafted particles with 398 kDa PMMA grafts with a 0.12 chains/nm² graft density and the corresponding copolymer of PMMA₃₉₇₄-*b*-PSS₅-grafted particles; (b) 123 kDa PMMA-grafted particles with a 0.7 chains/nm² graft density and its copolymer of PMMA₁₂₂₅-*b*-PSS₃₈-grafted particles; and (c) overlaid FTIR spectra of the two copolymer-grafted particles. All spectra were normalized to the peak height of the acrylate carboxyl group at 1732 cm⁻¹.



Figure 2. Hydrodynamic size distribution of $PMMA_{3974}$ -b- PSS_5 copolymer-grafted particles in toluene; and solvent/HMIM-TFSI mixtures with 60 vol % IL.

ionic interactions between sulfonated groups. TEM images confirm the well-dispersed state of particles prior to sulfonation in Figure 3a. The sample for TEM is prepared by drop-casting from the toluene solution on a formvar-coated copper grid. The sample with the longer PMMA graft length (PMMA₃₉₇₄-*b*-PSS₅) remains well dispersed at low sulfonation (0.1 mol %),

whereas the sample with the shorter PMMA graft (PMMA₁₂₂₅*b*-PSS₃₈) presented small clusters in toluene due to sulfonic group aggregation with the higher sulfonation amount (3 mol %) (Figure 3b). Adding IL to the PMMA₃₉₇₄-*b*-PSS₅ particles in toluene created aggregation of particles into close-packed monolayers (Figure 3c, image on the left). Clusters at larger sizes are observed for the PMMA₁₂₂₅-*b*-PSS₃₈ sample after adding IL to the particles in acetone (Figure 3c, image on the right). The structure sizes observed in TEM are not directly comparable to the size of the sample aggregates in solution because hydrodynamic interactions between the grafted chains and solvent are effective in solution. Thus, different aggregate sizes are observed in DLS results of our samples in cosolvent/ IL mixtures.

3.2. Ionic Conductivity Enhancement with the Addition of Copolymer-Grafted Nanoparticles. In our previous work, we showed that the ionic conductivity of HMIM-TFSI can be maximized at equal masses of IL/solvent mixtures.³³ Furthermore, with the addition of PMMA-grafted particles, the ionic conductivity in IL/acetonitrile can be increased by 5–20% because acetonitrile can effectively solvate both grafted PMMA and HMIM-TFSI,³³ as shown with orange data points in Figure 4. Ionic conductivity of HMIM-TFSI with copolymer-grafted particles decreases with the less polar cosolvents (i.e., toluene and methanol). In all other three

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Figure 3. (a) Transmission electron micrographs (TEM) of PMMAgrafted Fe_3O_4 nanoparticles before sulfonation. Samples were solution-cast from THF. TEM data of (b) PMMA₃₉₇₄-*b*-PSS₅ (0.1 mol % SS) and PMMA₁₂₂₅-*b*-PSS₃₈ (3 mol % SS) copolymer-grafted Fe_3O_4 nanoparticles solution-cast from toluene; and (c) PMMA₃₉₇₄-*b*-PSS₅ (0.1 mol % SS) in HMIM-TFSI/toluene (image on the left) and PMMA₁₂₂₅-*b*-PSS₃₈ (3 mol % SS) in HMIM-TFSI/acetone (image on the right).

solvent mixtures (acetonitrile (ACN)/IL, acetone/IL, and toluene/IL), PMMA₃₉₇₄-b-PSS₅ copolymer-grafted particles exhibit higher conductivity compared to PMMA1225-b-PSS38 (Figure 4). The conductivity data of PMMA₁₂₂₅-b-PSS₃₈ copolymer-grafted particle in methanol (MeOH)/IL were not measurable because PMMA is not soluble in methanol. While the actual sulfonation degree is not largely different in these two samples (only by a factor of 2), the higher number of MMA in the long (398 kDa) PMMA chains interacting with the TFSI⁻ anions may increase the number of dissociated free HMIM⁺ cations. The higher conductivity of a system with a low sulfonation amount is explained by the effective solvation phenomenon of HMIM-TFSI with the longer chains since PMMA interacts with TFSI⁻ anions. At low sulfonation levels, there are excess free (HMIM⁺) cations, and the asymmetry in anion and cation distributions from the associations to the PMMA and PSS, respectively, determines the high conductivity values. This asymmetric ion distribution influences the reorientation of the dipoles and the local dielectric response of the solvent. This effect was demonstrated by a recent theory, which studied the chain length and connectivity factors on the local dielectric function.⁵¹ Nakamura suggested

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Figure 4. Ionic conductivity of $PMMA_{3974}$ -*b*-PSS₅ (0.1 mol % SS, in blue) and $PMMA_{1225}$ -*b*-PSS₃₈ (3 mol % SS, in green) copolymergrafted Fe₃O₄ nanoparticles. Conductivity of PMMA-grafted Fe₃O₄ nanoparticles in various HMIM-TFSI/acetonitrile (ACN) and HMIM-TFSI/methanol (MeOH) mixtures is shown in orange. The purple diamond is the conductivity of pure HMIM-TFSI/toluene. HMIM-TFSI/solvent mixtures are prepared at a 1:1 mass ratio. Conductivity of PS-*b*-PSS copolymer-grafted Fe₃O₄ nanoparticles (with 3 mol % SS) in the HMIM-TFSI/toluene mixture with 30 wt % IL is shown with a red star. This data point is taken from ref 31.

that the correlation between the chain length and the dielectric response can have an important role for solvation of ion pairs in diblock copolymers.⁵¹

The pure toluene/IL has the lowest conductivity, as seen in Figure 4. When particles are aggregated into large clusters in toluene/IL, the conductivities of different particles are the same as of pure toluene/IL. The real part of the complex conductivity as a function of frequency for samples in ACN/IL, acetone/IL, methanol/IL, and toluene/IL mixtures is shown in Figure S1. Repulsion and interfacial stretching between PMMA and PSS domains will be investigated in future studies on samples with different copolymer compositions.

4. CONCLUSIONS

In this study, the stability of PMMA-b-PSS-grafted nanoparticles in IL/solvent mixtures is presented. Adding the styrene sulfonate (SS) groups greatly influences the solubility of PMMA-grafted particles in IL/solvent mixtures. TOAprotected SS groups and possible coupling of SS groups with HMIM⁺ cations enhance the solubility of particles in HMIM-TFSI. The high conductivity of the low sulfonated sample was explained by the asymmetric counterion distributions of IL, where the higher number of TFSI⁻ anions interact with the long PMMA chains. Moreover, solvation of HMIM-TFSI with the addition of a polar solvent (acetonitrile or acetone) ultimately disassociates the ion pairs of IL. The aggregation state of copolymer-grafted particles in IL/solvent mixtures is affected by the polar cosolvent addition. Our results show that the anionic and cationic groups of the IL interacting with the copolymer can be used to control the free counterion distribution in the copolymer-grafted nanoparticle-based electrolyte membranes. This design strategy can be used to enhance the conductivity of electromagnetic actuators with mechanical robustness.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.1c01369.

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Real part of conductivity versus frequency for PMMAgrafted and PMMA-*b*-PSS copolymer-grafted nanoparticles in HMIM-TFSI/solvent mixtures; GPC traces of PMMA; viscosity data for methanol/HMIM-TFSI and acetonitrile/HMIM-TFSI mixtures; additional TEM data at high magnification; and table of abbreviations (PDF)

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