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Ion channels in sulfonated copolymer-grafted nanoparticles in ionic liquids†

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The use of ionic liquids as solvents for polymers or polymer-grafted nanoparticles provides an exciting feature to explore electrolyte–polymer interactions. 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (HMIm–TFSI) can have specific interactions with the polymer through ion-dipole forces or hydrogen bonding. In this work, poly(methyl methacrylate)-*b*-poly(styrene sulfonate) (PMMA-*b*-PSS) copolymer-grafted Fe_3O_4 nanoparticles with different sulfonation levels (~4.9 to 10.9 mol% SS) were synthesized, and their concentration dependent ionic conductivities were reported in acetonitrile and HMIm–TFSI/acetonitrile mixtures. We found that conductivity enhancement with the particle concentration in acetonitrile was due to the aggregation of grafted particles, resulting in sulfonic domain connectivity. The ionic conductivity was found to be related to the effective hopping transfer within ionic channels. On the contrary, the conductivity decreased or remained constant with increasing particle concentration in HMIm–TFSI/acetonitrile. This result was attributed to the ion coupling between ionic liquids and copolymer domains.

Introduction

Room temperature ionic liquids (RTILs) have a low melting point, yet maintain extremely low vapor pressure and non-volatility. RTILs have high ion density and conductivity and are used as electrolytes for energy storage devices,[1–3] actuators[4–8] and nanoparticle stabilizers.[9–11] By mixing ILs with non-ionic diblock copolymers, solvation and specific interactions between polymers and ILs can be utilized to enhance the ionic conductivity.[12–14] Furthermore, copolymer morphologies and the ionic mobility of ILs within hydrophilic phases of copolymers have been investigated to understand these hybrid materials.[15,16] Interface and domain orientation were found to influence the ion transport in the imidazolium-based IL incorporated poly(methyl methacrylate) (PMMA)-*b*-polystyrene (PS) diblock copolymer system.[16]

We have studied 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIm–TFSI) incorporated PMMA-grafted nanoparticles in our previous studies.[12–14,17] Different particle aggregation states were found to influence the dynamics of imidazolium cations,[14] which was measured by quasi-elastic neutron scattering experiments. This was possible as the incoherent scattering signal was coming mostly from the $HMIm^+$ and the PMMA chains were deuterated and $TFSI^-$ anions contain no hydrogen. The ion-pair disassociation effect due to ion–dipole interactions between methyl groups of PMMA and $TFSI^-$ anions of HMIm–TFSI resulted in increasing the number of free $HMIm^+$ cations and the ionic conductivity.[13] It was also observed that the long-range unrestricted diffusion of $HMIm^+$ cations was enhanced in the well-dispersed grafted nanoparticles compared to the neat ILs.[14,18] The preferential interaction between PMMA and $TFSI^-$ anions also contributed to the solvation of ILs with the addition of solvents. Solvents with high dipole moments such as acetonitrile, acetone and methanol exhibited high ionic conductivity when mixed with ILs. Acetonitrile, with the highest polarity among several solvents tested, showed the highest conductivity when mixed with equal mass of ILs.[17] Thus, the complex solvation induced by ion–dipole interactions between PMMA and ILs influences the overall ion mobility and ionic conductivity of IL/solvent mixtures containing PMMA-grafted nanoparticles.[12,14,17]

In block copolymers of PMMA-*b*-poly(styrene sulfonate) (PSS) mixed with HMIm–TFSI, additional interactions between PSS and $HMIm^+$ by Coulombic forces co-exist with the solvated IL through interactions between PMMA and $TFSI^-$.[14,19] We have found that PMMA-*b*-PSS-grafted nanoparticles with the lower sulfonation amount (0.1 mol% SS) and the longer PMMA chains (398 kDa) exhibited the highest conductivity in acetonitrile and HMIm–TFSI mixtures compared to the particles with the higher sulfonation amount (3 mol%) and the shorter PMMA chains (123 kDa).[13] The high conductivity of the low sulfonated sample was explained by the asymmetric counterion distributions of ILs, where a higher portion of $TFSI^-$ anions interacted with the longer PMMA chains. The ion–polymer coupling in both copolymer domains facilitates the disassociation of ILs. TOA-protected SS groups and possible coupling of SS groups with

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$HMIm^+$ cations enhance the solubility of particles in HMIm–TFSI.

In this work, we prepared copolymers with various sulfonate amounts to further understand the solvation and interactions of the HMIm–TFSI with the PMMA-*b*-PSS copolymer. These interactions can result in aggregated strings or networks of strings as the copolymer composition and the particle concentration are varied. Furthermore, the aggregation of ionic clusters can be constrained *via* the disassociation of ILs with the preferential interactions of each counterion with the copolymer domains. Herein, we report the aggregation of copolymer-grafted nanoparticles at a moderately wide range of sulfonation levels (4.86–10.82 mol% SS). The ILs which are associated with the chains differently in various copolymer compositions are examined using impedance spectroscopy, and the measured ionic conductivities are analyzed by the percolation theory. Our results show that the percolation of sulfonated domains in particle-based ion conductors is essential to foster conductivity in particle-based ion conductors.

Experimental section

Preparation of particles

Fe_3O_4 nanoparticles (NPs) were prepared *via* solvothermal reduction of iron(III) acetylacetonate [$Fe(acac)_3$] with 1,2-tetradecanodiol as the reducing agent.[20] Oleic acid and oleylamine were used as surfactants that cease the growth and ripening of Fe_3O_4 grains during the reaction and render the product compatibility with benzyl ether. Grafted NPs were drop-cast on Formvar grids for imaging. Fe_3O_4 NPs of 7 nm in diameter were imaged using a transmission electron microscope (JEOL 2100 Plus S TEM) at 200 kV. Later, oleic acid and oleylamine on NPs were replaced by the chain transfer agent, 4-cyano-4-(phenylcarbonothioylthio)-pentanoic acid (CPDB). The anchoring of CPDB on Fe_3O_4 NPs is based on the reported procedure,[21] which was slightly modified with reduced CPDB amount and a longer reaction time. Equal volumes of 10 mg mL^{-1} Fe_3O_4/tetrahydrofuran (THF) and 20 mg mL^{-1} CPDB/THF were mixed to react for 72 h by magnetic stirring. Particles were precipitated in cyclohexane and ethyl ether mixture by centrifuging at 4000 rpm for 15 min and redissolved in THF. CPDB anchoring on NPs is confirmed by Fourier transform infrared (FTIR, Bruker Optics Tensor 27) spectroscopy (Fig. S1, ESI†). The amount of CPDB is measured using a thermogravimetric analyzer (Q50 TGA, TA Instruments).

SI-RAFT Polymerization of PMMA-*gr*-Fe_3O_4

PMMA chains were grown from CPDB-functionalized NPs by surface-initiated reversible addition-fragmentation chain-transfer (SI-RAFT) polymerization,[22] by which the chain length and graft density can be controlled by monomer, initiator and CTA amounts (Fig. S2, ESI†). The grafting of PMMA is confirmed by FTIR (Fig. S3, ESI†) and the amount of surface ligands (CPDB and PMMA) and graft density were measured by TGA. Concentrated HCl was added to the PMMA-grafted nanoparticle solution (10 mg mL^{-1} in 5 mL THF) to etch the Fe_3O_4 NPs, and the mixture solution was sonicated till the solution became clear. Methanol was later added, and the mixture was centrifuged at 6000 rpm for 10 min. The precipitated PMMA chains were dried in vacuum at room temperature to remove methanol, THF, HCl, and water. Finally, the product was redissolved 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 μm 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 of synthesized PMMA were measured as 67 kDa (*Đ*: 1.45) and 122 kDa (*Đ*: 1.53). Grafting density (GD) was determined through TGA using the following equation:

$$\mathrm{GD} = \frac{m_{\mathrm{polymer}}}{m_{\mathrm{NP}}} \frac{N_{\mathrm{A}} \rho R}{3 \bar{M}_{\mathrm{w}}} \quad (1)$$

m_{polymer} and m_{NP} are the mass of grafted chains and particle cores, respectively. N_{A} is the Avogadro constant; ρ is the particle density; R is the radius of iron oxide nanoparticles; and $\bar{M}_{\mathrm{w}}$ is the weight-averaged molecular weight of grafted chains.

Preparation of trioctylammonium *p*-styrenesulfonate (SS–TOA)

Trioctylammonium (TOA) capping was necessary to produce the hydrophobic SS-TOA monomer. TOA capped *p*-styrenesulfonate (SS-TOA) was prepared following the published procedure.[23,24] TOA protection solubilized the copolymer-grafted particles in toluene.

Synthesis of PMMA-*b*-PSSTOA-grafted nanoparticles

SS monomer was sequentially added to the living PMMA chains (Fig. 1). The CTA, initiator, and monomer amounts used to synthesize the sulfonated copolymer particles are given in Table S2 (ESI†).

Hydrodynamic sizes of grafted particles before and after sulfonation were measured in dynamic light scattering (DLS, Zetasizer NanoS, Malvern). PSS amounts were determined by the end-group analysis using ^{1}H NMR (Varian-400 spectrometer). The chemical shift was recorded in the unit of parts per million (ppm) and was calibrated by $CDCl_3$ at 7.26 ppm.

Electrochemical impedance spectroscopy (EIS)

The SP-300 electrochemical impedance spectrometer, Bio-Logic Science Instruments, was used for EIS measurements. The samples were tested in a home-made liquid cell with stainless steel electrodes. The Nyquist plots, frequency-dependent conductivity and ionic conductivity were acquired by AC with 10 mV amplitude at the 7 MHz–1 Hz frequency range. The Nyquist plot was fitted by an equivalent circuit (EC) with the ZView software. The frequency dependence of bulk conductivity is plotted in Fig. S4 (ESI†). Ionic conductivities (σ') were obtained from the high-frequency plateau, where ionic mobility dominates the impedance spectra.[25] The bulk conductivity

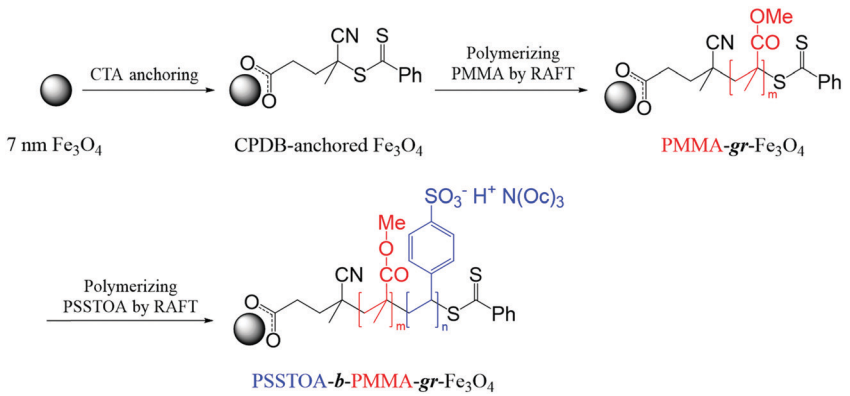

Fig. 1 Synthesis of PSSTOA-*b*-PMMA-grafted Fe_3O_4 nanoparticles by RAFT polymerization.

$\sigma'(\omega)$ was calculated as per the following eqn (2).[12]

$$\sigma'(\omega) = \frac{Z'}{k[(Z')^2 + (Z'')^2]} \quad (2)$$

where ω is the angular frequency, Z' and Z'' are the real and imaginary parts of impedance, respectively, k is the cell constant which was determined using a 0.01 M KCl standard solution (Ricca Chemical, 1412 μS cm^{-1} at 25 °C).

Results and discussion

We have synthesized PMMA-grafted chains of 67 kDa (in Samples 1–3) and used them to polymerize PSS chains at varying lengths and at sulfonation levels between 6.05 and 10.82 mol% SS, and we prepared another grafted Sample 4 with 122 kDa PMMA chains at 4.86 mol% SS (Fig. 2). The stoichiometric percentage of SS was calculated by

$$[SS]\% = \frac{n_{SS}}{n_{MMA} + n_{SS}} \times 100\% \quad (3)$$

where n_{SS} and n_{MMA} are the molar amounts of SS and MMA monomers in the copolymer chain, respectively.

The sample characteristics of $\bar{M}_w$ and $\overline{DP}_{w,\,PMMA}/\overline{DP}_{w,\,PSSTOA}$ (m/n) are given in Table 1. The molar ratio of blocks (m/n) varies between 8.3 and 19.7. Samples 1–3 are at lower graft density (GD: 0.15 chains nm^{-2}), and Sample 4 has GD: 0.69 chains nm^{-2}. The GD values are much larger than the $1/R_g^2$ of 67 kDa and 122 kDa PMMA chains, indicating the high graft density of chains around particles.

^{1}H NMR is used to calculate the sulfonation level of copolymers after etching the NPs (Fig. 2c). Peaks at 7.2 ppm and 3.6 ppm are originated from the aromatic *ortho*-hydrogen on the PSSTOA block and methyl hydrogen on the PMMA block,

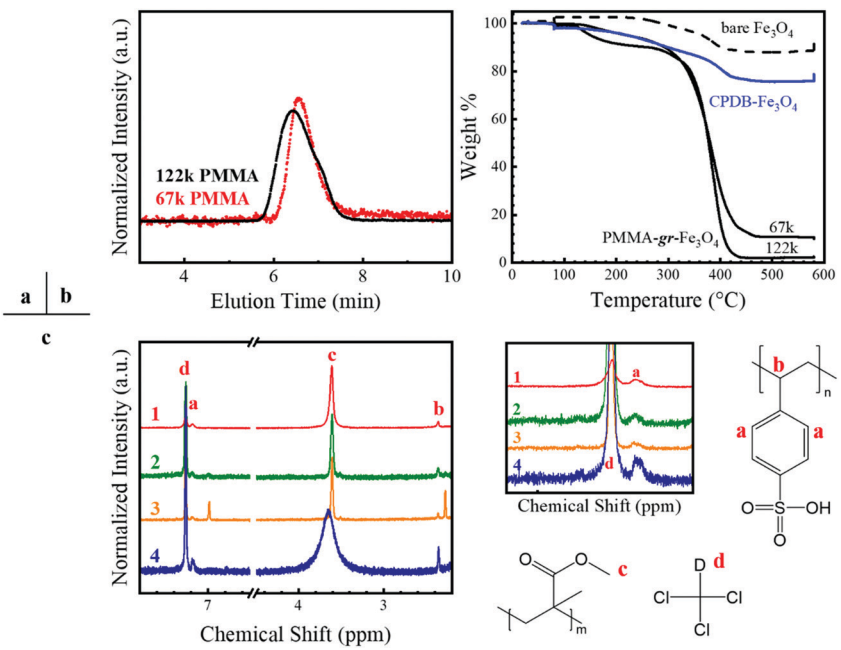

Fig. 2 (a) GPC-LS traces of 67 kDa and 122 kDa PMMA. (b) TGA data of the PMMA-grafted, the bare and CPDB-anchored Fe_3O_4 NPs. (c) ^{1}H NMR spectra of PMMA-*b*-PSSTOA copolymers (Samples 1–4).

Table 1 Characteristics of PMMA$_m$-*b*-PSSTOA$_n$ grafted Fe_3O_4 nanoparticles

Sample	$\bar{M}_{w,PMMA}$ (kDa)	$\overline{DP}_{w,\,PMMA}(m)$	$Đ$	GD (chains nm^{-2})	SS% (mol%)	$\overline{DP}_{w,\,PSSTOA}(n)$	m/n
1	67.0	669	1.45	0.15	6.05	43	15.6
2	67.0	669	1.45	0.15	9.42	70	9.6
3	67.0	669	1.45	0.15	10.82	81	8.3
4	122	1219	1.53	0.69	4.86	62	19.7

respectively. The ratio of integrated areas (A_{PSSTOA}/A_{PMMA}) for the PSSTOA and PMMA is directly proportional to the number of hydrogens ($N_{H,SSTOA}$, $N_{H,MMA}$) per monomer, as shown in the following equation:

$$\frac{A_{PSSTOA}}{A_{PMMA}} = \frac{n_{SS}N_{H,\,SSTOA}}{n_{MMA}N_{H,\,MMA}} \quad (4)$$

The integrated areas of all samples calculated prior to the intensity normalization are listed in Table S1 (ESI†).

All sulfonated samples have larger hydrodynamic sizes than their homopolymer precursors as shown in Fig. 3a. Within Samples 1–3, the hydrodynamic size increased from 100 nm to 225 nm as SS% is changed from 6.05 to 10.82 (Fig. 3b). In Sample 4, the high GD provides a stronger steric repulsion and particles have lower hydrodynamic sizes than Samples 1–3. TEM data show aggregated structures at all sulfonation levels. Samples were solution cast from toluene on grids. Sample 3 with the highest sulfonation amount showed the highly aggregated structures (Fig. 3c). Good dispersion in Sample 4 is not surprising due to its strong steric repulsion of high GD chains.

The distribution of TFSI$^-$ anions around grafted particle aggregates is visualized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (Fig. 4). The Fe mapping easily locates the Fe_3O_4 NP cores. The dense fluoride (F) signal on the Fe_3O_4 shows the TFSI$^-$ anion distribution because TFSI$^-$ is the only molecule containing F. The S signals on the other hand are denser in the outer regions of Fe_3O_4, and they are attributed to PSS. The N signal matches the S mapping, revealing that it is from the HMIm$^+$. This matching between N and S signifies the affinity between HMIm$^+$ cations and the PSS block. While these results are qualitative, they help us to demonstrate the preferential interactions between cations and PSS as well as between anions and PMMA.

Copolymer samples 1–4 in acetonitrile at different concentrations were tested by EIS for conductive properties. The Nyquist plot shows the impedance in a complex plane. The shape of a typical Nyquist plot of an electrolyte solution contains Warburg impedance at lower frequency regions and single or multiple arcs at higher frequencies. The Warburg impedance is originated from the diffusion of ions and appears linear.[26] The arcs are attributed to both resistive and capacitive behaviors, which can be further explained by ion transfer, dielectric constant at the electrode–electrolyte interface.[27] Ionic conductivity (σ') is averaged from the AC frequency-dependent bulk conductivity in the plateau region, and the latter is

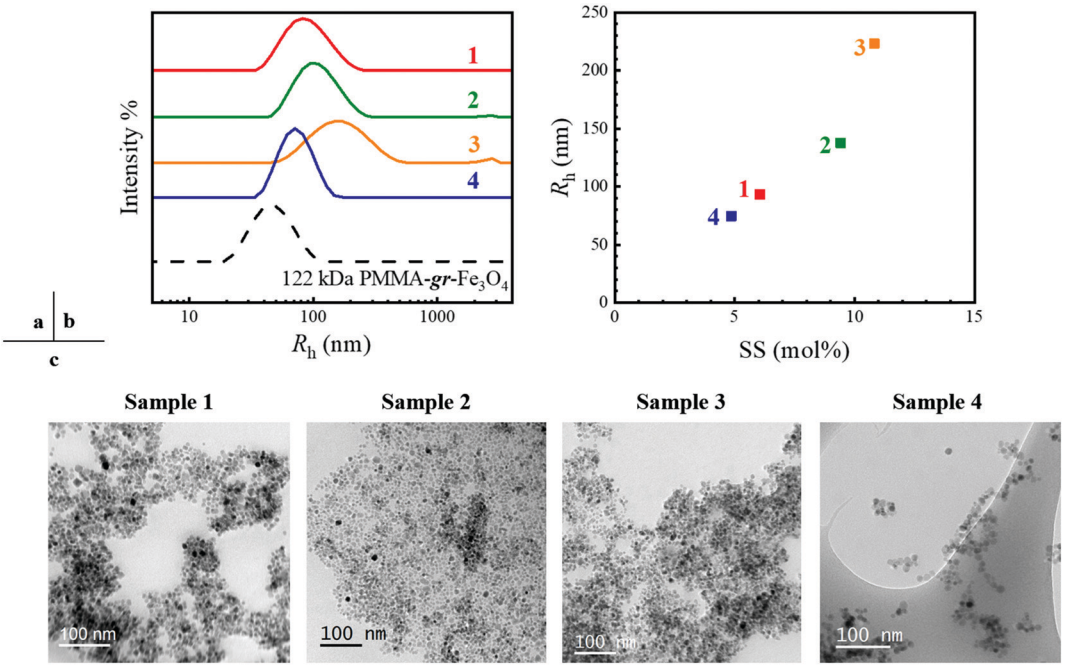

Fig. 3 (a) *Z*-averaged hydrodynamic size R_h distributions of all samples in toluene. (b) R_h of samples with varying SS mol% in toluene. (c) TEM data of PMMA-*b*-PSS grafted NPs.

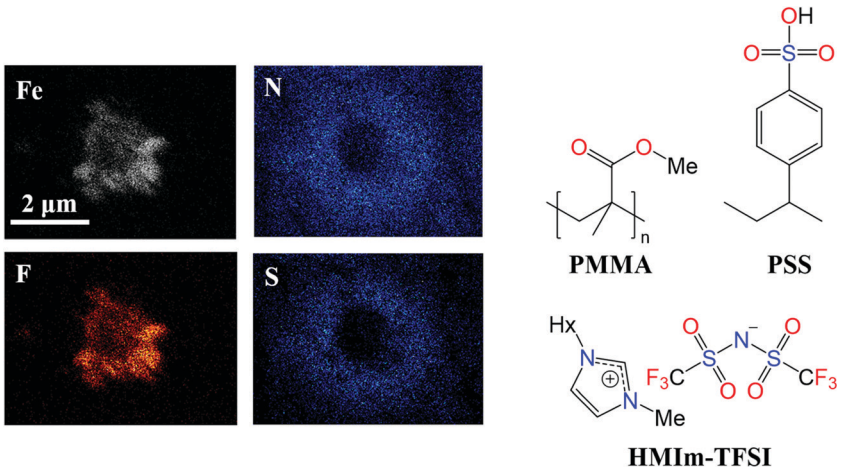

Fig. 4 SEM-EDS data of PMMA-*b*-PSS copolymer-grafted Fe_3O_4 NPs for Fe, F, N and S element mappings, and the chemical structures of species.

calculated from the Nyquist plot *via* eqn (2). Fig. 5 shows the ionic conductivity dependence on the volume fraction of PSS. Sample 4 with high GD (0.69 chains nm^{-2}) has lower conductivity than the other samples in acetonitrile. The conductivity increased sharply at low concentrations and then reached to more-like plateau values. We thus estimated the percolation threshold (Φ_c) to be 0.001%, suggesting the percolating structure occurs at a slightly lower concentration than our experiment range. The apparent enhancement in conductivity values with the increasing sulfonation amount was seen at high concentrations. Polymer ($f_{polymer}$) and PSSTOA (f_{SSTOA}) volume fractions are calculated using the equations:

$$f_{polymer} = \frac{Cw}{\rho_{PMMA}},\ f_{NP} = \frac{C(1-w)}{\rho_{NP}} \quad (5)$$

$$f_{SSTOA} = f_{NP}x \quad (6)$$

C is the mass concentration of polymer-grafted nanoparticles and w is the weight loss fraction of polymer-grafted NPs; ρ_{PMMA} and ρ_{NP} are densities of PMMA and Fe_3O_4, respectively; and x is the sulfonation molar fraction. Φ_{SSTOA}, Φ_{PGNP}, $\Phi_{polymer}$ are volume percentages of PSSTOA, PMMA-*b*-PSSTOA-grafted NPs and PMMA-*b*-PSSTOA, respectively.

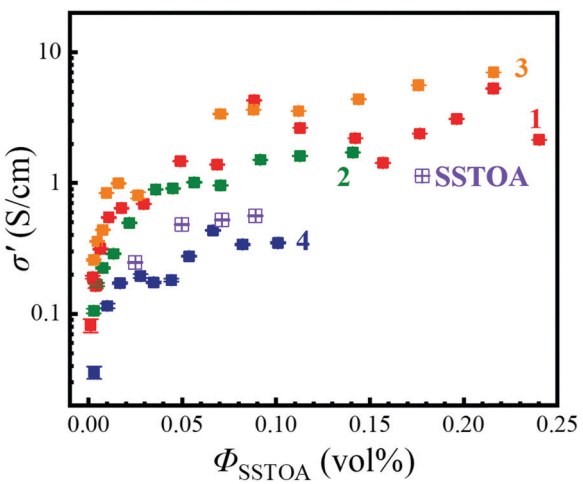

Fig. 5 Ionic conductivities (σ') of PMMA-*b*-PSS-grafted Fe_3O_4 NPs (Samples 1–4) and SSTOA monomer in acetonitrile with varying PSS volume percentages (Φ_{SSTOA}).

We plotted the conductivity *versus* $\Phi_{PGNP} - \Phi_c$ and fitted to a $\sigma' = \sigma_0 (\Phi_{PGNP} - \Phi_c)^t$ equation that describes the percolation model of the infinite-size network connectivity.[28] The linear fittings of the conductivity are ascribed to particle connectivity (Fig. 6a). Φ_c is the percolation threshold, and t is the critical exponent that depends on the connectivity of nanoparticles and it is the slope of the linear fitting line. The geometric percolation threshold of hard spheres is reported to be 0.297.[21] The threshold Φ_c depends on aspect ratio and can be low (0.001 vol%) for anisotropic nanofillers such as carbon nanotubes and carbon black.[29–31] The percolation threshold of our grafted particles is much lower than that of hard spheres as grafted particles have large hydrodynamic sizes (Fig. 3). The interfacial stretching in PMMA-*b*-PSS[32] and the anisotropic self-assembly of particles[33,34] are other ruling phenomena that govern the aggregation of grafted particles. Another important factor is the electric percolation threshold occurring at a lower concentration than the mechanical percolation threshold as the ions hop between localized particle aggregates.[30] The exponent t is found to be around 0.6 in Samples 1–3 indicating a similarity to their network topologies (Table S3, ESI†).

It is important to note that the sharp increase of ionic conductivity was not seen for bare NPs and PMMA-grafted NPs (Fig. S5, ESI†). We compared the particle-grafted samples with the SSTOA monomer (Fig. 5, purple open dots). In SSTOA, ions freely diffuse as there is no structure effect or ion coupling to the polymer. The ionic conductivity of SSTOA is expected to be higher than that of polymer-grafted NPs, but was measured to be lower than all the 3 samples. Thus, the high conductivity in Samples 1–3 with low GD was attributed to the percolating structures as illustrated in Fig. 6b. The steric repulsion of Sample 4 with high GD hinders entanglements between ionic groups of PSS. The relatively lower value of t (0.542) signifies the lowest connectivity, and the lowest value of R^2 represents a low explanatory power of percolation theory for this

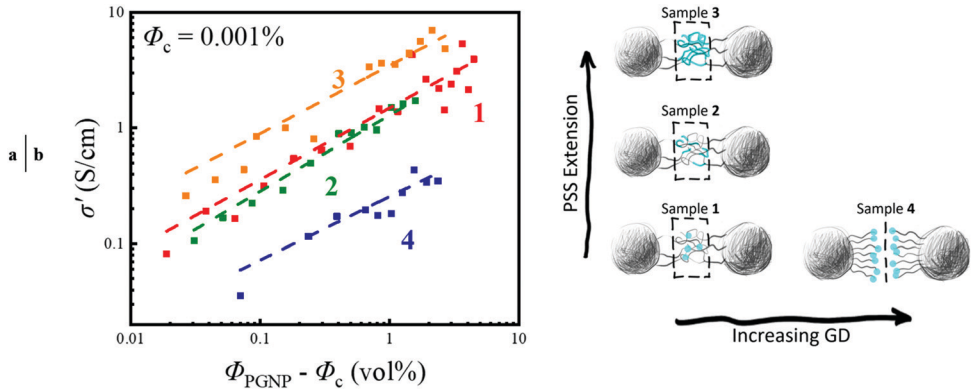

Fig. 6 (a) Ionic conductivity (σ') of PMMA-*b*-PSS copolymer-grafted NPs in acetonitrile as a function of the volume percentage, $\Phi_{PGNP} - \Phi_c$. (b) Schematic illustration of ionic connectivity between PMMA-*b*-PSS-grafted NPs for varying sulfonation amount in SS% (Samples 1–3) and graft density (Samples 1 and 4). The cyan parts refer to PSS blocks.

sample (Table S3, ESI†). Interestingly, Sample 4 has lower ionic conductivity than the SSTOA monomer.

Furthermore, we used equivalent circuit (EC) models to analyze the impedance data of copolymer-grafted NPs in acetonitrile. Two EC models (Fig. S6, ESI†) numerically reproduce the Nyquist plots for the low and high conductivity ranges (Fig. S7, ESI†). The values of circuit elements (R_1, C_1 and CPE_1) are related to the polymer-grafted nanoparticle concentration. The R_1 element refers to the resistance of ions moving through the bulk electrolyte[35] and decreases with the particle concentration (Fig. S8a, ESI†). Sample 3 has the strongest concentration dependence of R_1 value, and Sample 4 has the weakest. The other elements (C_1 and CPE_1) refer to the capacitance and increase with concentration in Samples 1–3 unlike Sample 4 (Fig. S8b and c, ESI†). The ion transport in Samples 1–3 enhances by the percolated sulfonated domains within the aggregated particles. Sample 4 does not exhibit this behavior because it does not form such effective networks. We note that the vehicular diffusion of free TOA^+ ions in acetonitrile has a minor effect on the conductivity.

On the contrary, we observed that the conductivity of particles dispersed in HMIm–TFSI/acetonitrile decreased with concentration (Fig. 7a). The coupling of PMMA with $TFSI^-$ and PSS with $HMIm^+$ reduces the free ion concentration, hence diffusion. Such interactions solvate the IL and aid in better dispersion in HMIm–TFSI (Fig. S9, ESI†) compared to that in acetonitrile as shown in Fig. 3. Since both blocks of copolymer impair ion motion, increasing the polymer concentration ($\Phi_{polymer}$) lowers the free ion conductivity in Samples 1 and 4. In Samples 2 and 3 that can form a network by their longer chain and lower graft density, ionic conductivities decrease only slightly. At very low concentrations, Samples 1 and 3 have higher conductivity than the neat IL/acetonitrile. The decline of conductivity with particle concentration increase suggests that ion coupling of polymers becomes effective in Samples 1 and 3. The conductivity of ions that are coupled with PMMA and PSS balances out the high conductivity that is for the low particle concentration. Percolation is stronger in Sample 1 compared to Sample 4 and the large decrease in conductivity of Sample 4 is attributed to the weaker connectivity of PSS domains.

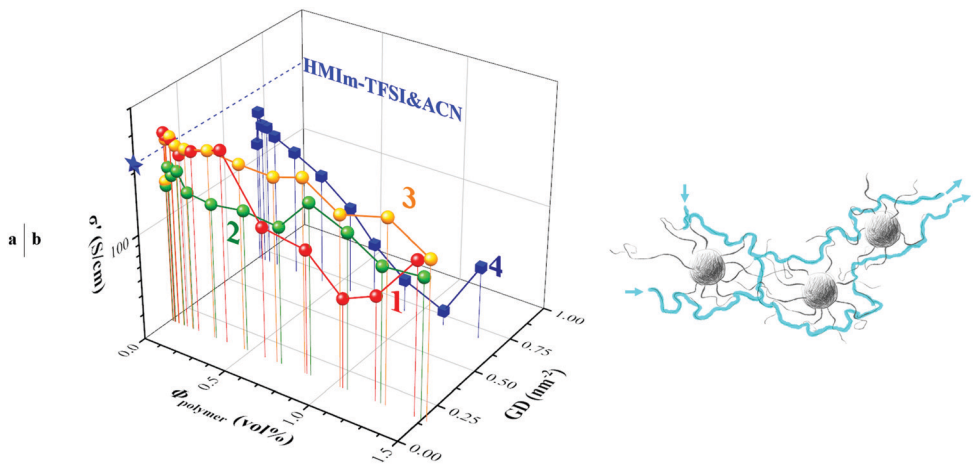

Fig. 7 (a) Ion conductivities of copolymer-grafted NPs in HMIm–TFSI/acetonitrile (ACN) for varying polymer concentration, $\Phi_{polymer}$. The data point shown with a star is for the neat HMIm–TFSI/ACN. (b) Sulfonated chain percolation is represented with an illustrative work of aggregated grafted nanoparticles.

Conclusions

A series of PMMA-*b*-PSS copolymer-grafted Fe_3O_4 nanoparticles at varying sulfonation levels were prepared to study the macroscopic ionic conductivities of particles solvated in HMIm–TFSI. It is known that pure HMIm–TFSI conducts ions in a vehicular mode. This work aims to understand how copolymer grafted NPs interfere with the conductivity of HMIm–TFSI. SEM-EDS elemental mapping demonstrates the PMMA–$TFSI^-$ and PSS-$HMIm^+$ affinities. Herein, we show that the network of polymer-grafted particles establishes *ion channels* where ions hop through the percolating sulfonated polymer in acetonitrile, which significantly enhances the ionic conductivity with concentration. The equivalent circuit analysis of EIS data also supports that the percolating structures guide ion transport *via* hopping rather than free diffusion. Particles in HMIM–TFSI exhibited an opposite trend where conductivity decreased with grafted polymer concentration. The coupling of each polymer domain with the IL counterparts through ion–dipole interactions led to lower conductivity than that of neat ILs. The low graft density and polymer interactions with ILs can enhance the dispersion state of polymer-grafted nanoparticles, but lower the transport of IL species. In conclusion, polymer–ion coupling and organization of sulfonated domains (in an IL or a solvent) both contribute to the ion transport in grafted-particle based electrolytes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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