ChemPhysChem

Confinement Effects in Dynamics of Ionic Liquids with Polymer-Grafted Nanoparticles --Manuscript Draft--

Manuscript Number:	cphc.202200219R2
Article Type:	Research Article
Corresponding Author:	Pinar Akcora, Prof. Stevens Institute of Technology Hoboken, NJ UNITED STATES
Corresponding Author E-Mail:	pakcora@stevens.edu
Order of Authors (with Contributor Roles):	Siqi Liu
	Ruhao Li
	Madhusudan Tyagi
	Pinar Akcora, Prof.
Keywords:	PMMA-grafted nanoparticles; ionic liquid; quasi-elastic neutron scattering; nanoconfinement; local cation diffusivity
Manuscript Classifications:	Materials Science: General; Physical Chemistry and Chemical Physics
Abstract:	Ionic liquid mixed with poly(methyl methacrylate)-grafted nanoparticle aggregates at low particle concentrations was shown to exhibit different dynamics and ionic conductivity than that of pure ionic liquid in our previous studies. In this work, we report on the quasi-elastic neutron scattering results on ionic liquid containing polymer- grafted nanoparticles at the higher particle concentration. The diffusivity of imidazolium (HMIM +) cations of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI) in the presence of poly(methyl methacrylate)-grafted iron oxide nanoparticles and the ionic conductivity of solutions were discussed through the confinement. Analysis of the elastic incoherent structure factor suggested the confinement radius decreased with the addition of grafted particles in HMIM- TFSI/solvent mixture, indicating the confinement that is induced by the high concentration of grafted particles, shrinks the HMIM-TFSI restricted volume. We further conjecture that this enhanced diffusivity occurs as a result of the local ordering of cations within aggregates of poly(methyl methacrylate)-grafted particles.
Response to Reviewers:	We did not include the solvent incoherent and coherent scattering contributions to the table in the response letter because we are subtracting the scattering contribution of the solvent from the sample signal. Thanks for correcting the sentence. We rephrased the line as noted by the reviewer.
Section/Category:	
Additional Information:	
Question	Response
Do you agree to comply with the legal and ethical responsibilities outlined in the journal's Notice to Authors?	Yes
Has a previous version of this manuscript been submitted to this journal?	No
Is this manuscript, or part of it, currently under consideration elsewhere?	No
Is this manuscript, or part of it, published, posted, or in press? This includes content posted on preprint servers (<u>preprint</u> <u>guidelines</u>) or published as part of a	No

thesis.	
Please provide us with information about the history of your manuscript, including previous submissions, transfers, or prior versions:	N/A
Do you or any of your co-authors have a conflict of interest to declare?	No
Does the research described in this manuscript include animal experiments or human subjects or tissue samples from human subjects?	No

±

Polymer-Grafted Nanoparticles

Dr. Siqi Liu[†], Ruhao Li[†], Dr. Madhusudan Tyagi[§] and Prof. Dr. Pinar Akcora^{†,*}

[†]1 Castle Point on Hudson, Department of Chemical Engineering and Materials Science, McLean

Hall 415, Stevens Institute of Technology, Hoboken, NJ 07030 USA

[§]NIST Center for Neutron Research, 100 Bureau Dr, Gaithersburg, MD 20899 USA and Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742 USA

* Corresponding Author: pakcora@stevens.edu; www.stevens.edu/akcora-group

Abstract

Ionic liquid mixed with poly(methyl methacrylate)-grafted Fe₃O₄ nanoparticle aggregates at low particle concentrations was shown to exhibit different dynamics and ionic conductivity than that of pure ionic liquid in our previous studies. In this work, we report on the quasi-elastic neutron scattering results on ionic liquid containing polymer-grafted Fe₃O₄ nanoparticles at the higher particle concentration. The diffusivity of imidazolium (HMIM⁺) cations of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI) in the presence of poly(methyl methacrylate)-grafted Fe₃O₄ nanoparticles was discussed through the confinement. Analysis of the elastic incoherent structure factor suggested the confinement radius decreased with the addition of grafted particles in HMIM-TFSI/solvent mixture, indicating the confinement that is induced by the high concentration of grafted particles, shrinks the HMIM-TFSI restricted volume. We further conjecture that this enhanced diffusivity occurs as a result of the local ordering of cations within aggregates of poly(methyl methacrylate)-grafted Fe₃O₄ nanoparticles.

Introduction

Ionic liquids (ILs) are molten salts with melting points lower than 100 °C. They are composed of organic cations and inorganic/organic anions which can be independently selected to optimize their physicochemical properties^[1]. ILs possess unique inherent properties, like low vapor pressure, high electrochemical and thermal stabilities which enable their uses in numerous applications including safe and versatile electrolytes for lithium batteries^[2], supercapacitors^[1d], fuel cell electrolytes^[3], membranes for CO₂ capturing^[4] and microfluidics^[5].

Dynamic properties of ILs have been investigated by molecular dynamics (MD) simulations^[6], quasi-elastic neutron scattering (QENS)^[6c, 7] and dielectric spectroscopy experiments^[7d, 8]. In neat ILs, counterions arrange around an ion that form a solvation shell and the dynamics of ions is often described by the caging effect^[9]. Nuclear magnetic resonance experiments^[10] and MD simulations^[6a, 11] identified different dynamic modes of IL, a ballistic motion at short times and a sub-diffusive motion at intermediate times. The non-Gaussian dynamics in glass-forming liquids is explained by the molecular caging effects^[10]. At longer times, large spatial displacements can be triggered by occasional cage rearrangement, in which ions escape from the local neighbor cage and ionic motion becomes diffusive. A similar cage model is also applied to IL in solid polymer electrolytes^[11c].

Molecular level dynamical heterogeneity is usually associated with the caging phenomenon. The dynamical heterogeneity can be linked to the heterogeneous structures^[11b]. Polar domains rotate less than apolar domains due to the strong cation-anion association^[12]. Among all techniques used to investigate the dynamics of ILs, QENS is particularly suitable as it can probe specifically the cation dynamics at pico- to nanoseconds and access momentum transfer range (Q: $0.1 - 2 \text{ Å}^{-1}$) depending on instrumental energy resolution. Both imidazolium-based^[13] and pyridinium-based^[14] ILs have been investigated by the QENS technique.

Two diffusive processes are revealed by analyzing the QENS spectra of IL, the slow diffusion for ion association and the fast process for single particle confined within transient cage-like structure that is formed by neighbor ions^[7d, 14c, 15]. The dynamics of 1-ethyl-3-

methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) with PMMA has been studied by QENS. Two relaxations for the EMIM⁺ were attributed to the diffusion of free ions and to the ions that were bound to PMMA^[16]. Similarly, in the case of PMMA/1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI), ion-dipole interactions between carbonyl group of PMMA and TFSI⁻ anion of HMIM-TFSI increase the number of free HMIM⁺ cations^[17]. The ion-pair disassociation effect was verified by measuring the HMIM⁺ cation diffusion in QENS^[17]. We reported that the long-range unrestricted diffusion of HMIM⁺ cations was enhanced in the well-dispersed grafted nanoparticles compared to the neat IL^[17a]. This preferential interaction between PMMA and TFSI⁻ anions can also contribute to the solvation of IL with the addition of solvents^[18]. The competing interactions between PMMA/IL and solvent/IL, thus, determine the ion mobility and diffusion. Mixing ILs with solvents of different polarities alters viscosity and enhances the ion mobility and ionic conductivity in IL-based complex electrolytes as the polar solvent disassociates the ion pairs^[18-19].

Both PMMA and IL dynamics have been of interest to researchers as their glassy properties change when they are mixed^[16, 20]. Measuring IL dynamics within PMMA-grafted Fe₃O₄ particles is essential to interpret the structure, dynamic and conductivity results of polymer-grafted particle-based electrolytes. In grafted nanoparticles, the ionic aggregation and confinement can be achieved by nanoparticle structures. Particles that form string-like structures can form percolated structures at high particle concentrations and the diffusion of free ions can be confined within the formed physical pathways. Subsequently, the ion diffusivity can be enhanced as the formation of ion clusters is prohibited within the percolated structures of PMMA-grafted Fe₃O₄ particles in IL. In a dispersed particle system, the percolation of ionic pathways is also possible at high loadings,

however, the free ion diffusion is expected to be slower in the dispersed system due to dynamic heterogeneities and resistances of randomly dispersed particles. In this study, we present the dynamic results of IL in the presence of high polymer-grafted particle concentrations. We discuss the role of confinement on local cation diffusion at high particle concentration where particle aggregation becomes more apparent.

Results and Discussion

Ionic liquids possess inherent heterogeneous dynamics. Distinctive diffusion processes at fast and slow modes have been observed in pyridinium-based^[14a, 14c] and imidazolium-based^[7e, 13, 21] ionic liquids. The fast process results from spatially restricted translation diffusion, whereas the slow motion was described as unrestricted, long-range translational diffusion. In our previous work, non-homogeneous dynamics of HMIM⁺ cation was dependent on the dispersion states of polymergrafted nanoparticles in HMIM-TFSI^[17a]. It is also known that adding non-conducting materials into the bulk IL hinders the ion mobility and conductivity. Contrary to this known fact, adding PMMA-grafted particles enhanced the ionic conductivity of IL mixtures with the higher grafting density of particles^[22]. The unusual fast mobility of cations is observed for HMIM-TFSI containing high grafting density particles. Particles with higher density graft chains offer more PMMA chains that can interact with TFSI⁻ anions, and thus the increased number of free HMIM⁺ cations can lead to faster ion mobility in HMIM-TFSI/acetonitrile mixtures^[22]. This is the case of grafted chains swollen in good solvent (acetonitrile) where solvation of IL is better in acetonitrile compared to the less polar solvent (methanol). We found that HMIM-TFSI-acetonitrile containing high grafting density particles has a higher conductivity than that of the HMIM-TFSI-methanol mixture with grafted particles^[18]. In this study, we report transport properties of same ionic liquid with high polymer-grafted particle loadings in both acetonitrile and methanol. Local cation dynamics is found to be influenced by the confinement of ILs. Our results indicate that the local ordering of free HMIM⁺ cations in grafted particle networks enhances the diffusivity and lowers the ionic conductivity at higher particle concentrations.

The influence of spatial nanoconfinement on IL structures and diffusion properties have been reported in previous works^[23]. Some studies found increased mobility within nanopores^[6c, 21b, 24]. Other works reported the suppressed diffusion in systems of bimodal porosity^[25] and in biopolymer-silica matrix^[26] and when confined between graphene electrodes^[23a]. We hypothesize that ionic liquids that interact with polymer chains can also create confinement for the ions at high concentration of grafted nanoparticles. For this study, PMMA-grafted Fe₃O₄ nanoparticles with two different graft molecular weights 15.8 kDa at 0.05 chains/nm² and 61.8 kDa at 0.01 chains/nm² were prepared (**Figure 1a**). The hydrodynamic size (R_h) distribution verifies the stability of grafted nanoparticles in ionic liquids^[27]. **Figure 1b** shows the hydrodynamic size distributions for 61.8 kDa and 15.8 kDa PMMA-grafted particles in acetonitrile. Z-average sizes of 241.5 nm and 505.7 nm were measured, respectively.



Figure 1. (a) Thermogravimetric analysis and **(b)** hydrodynamic size distributions in acetonitrile of PMMA (61.8 kDa and 15.8 kDa)-grafted Fe₃O₄ nanoparticles.

Transmission electron microscopy (TEM) imaging of particles in IL is possible due to the low vapor pressure of IL. TEM data is collected in HMIM-TFSI after acetonitrile or methanol is evaporated. TEM images of PMMA-grafted particles with 61.8 kDa and 15.8 kDa graft lengths in HMIM-TFSI/CD₃CN show good particle dispersion in **Figures 2a-b**. Acetonitrile screens the cation-anion interactions of IL. The additional solvation effect of IL through anion interactions with PMMA further facilitates the colloidal stability and ionic conductivity of solutions. Methanol significantly changes the grafted particle dispersion states in IL (**Figure 2c-d**). Non-homogeneous aggregations were observed in both 61.8 kDa and 15.8 kDa of PMMA-grafted particles in HMIM-TFSI/methanol mixture.



Figure 2. TEM micrographs of (**a**) 61.8 kDa PMMA-grafted particles, (**b**) 15.8 kDa PMMAgrafted particles dispersed in HMIM-TFSI/CD₃CN, (**c**) 61.8 kDa PMMA-grafted Fe₃O₄ particles and (**d**) 15.8 kDa PMMA-grafted Fe₃O₄ particles dispersed in HMIM-TFSI/CD₃OD.

Ionic conductivity of PMMA-grafted Fe₃O₄ nanoparticles in HMIM-TFSI/acetonitrile and HMIM-TFSI/methanol mixtures (both at 6.3 wt%) were measured using AC impedance spectroscopy over 1 Hz - 1 MHz frequency range (**Figure 3**). In polymer-grafted particle systems, solvent-induced ion dissociation and anion interactions with the grafted PMMA chains affect the number of free ion carriers and the ionic confinement within high particle concentration^[22]. As graft length increased from 27.4 kDa to 38.2 kDa, the conductivity values of mixtures increased, surpassing

the value of pure IL/solvent (sample labeled no gr-NP)^[22]. These two samples with 27.4 kDa PMMA-grafted particles of 0.01 chains/nm² and 38.2 kDa PMMA-grafted particles of 0.04 chains/nm² were at 2 wt% solution. The new samples prepared for this work are 61.8 kDa and 15.8 kDa PMMA-grafted Fe₃O₄ particles and they are at high particle concentrations (6.3 wt%). 15.8 kDa PMMA-grafted nanoparticles of 0.05 chains/nm² possess higher MMA monomer concentration in solution compared to the 61.8 kDa PMMA-grafts with 0.01 chains/nm² graft density, which explains their higher ionic conductivity in both HMIM-TFSI/CD₃CN and HMIM-TFSI/CD₃OD solutions. The mass ratio of HMIM-TFSI and solvent for all samples is 50/50.



Figure 3. Ionic conductivity of 6.3 wt% PMMA (61.8 kDa, 15.8kDa)-grafted Fe₃O₄ nanoparticles in HMIM-TFSI/solvent; and 2 wt% PMMA (27.4 kDa, 38.2 kDa)-grafted Fe₃O₄ nanoparticle in HMIM-TFSI/solvent. Data with (*) were adapted from Reference 22. The mass ratio of HMIM-TFSI and solvent is 50/50.

The high diffusivity measured with the PMMA-grafted magnetic nanoparticles at low concentration was associated to the polymer-coupled ionic liquid dynamics, which was effective in increasing the free cation amount and, therefore, ionic conductivity in particle-based electrolytes^[22]. With the heterogeneous structures of high concentration of particles in ionic liquids, it is not possible to postulate a plausible conductivity mechanism from the bulk impedance measurements. QENS has been used successfully to differentiate different dynamic modes in ionic liquids, particularly for the spatially confined IL structures and diffusion^[23]. QENS is a powerful technique to reveal dynamic properties in picosecond time scale and nanometer length scale. A large difference in the incoherent scattering cross sections of deuterium and proton enables measuring the signal of the moiety of interest via selective deuteration. The incoherent signals from Fe₃O₄ nanoparticles and deuterated solvents (CD₃CN or CD₃OD) are relatively low compared to the protons. All PMMA chains are deuterated, therefore, diffusivity of molecules probed in QENS is ionic diffusivity of the imidazolium cations. The pure deuterated solvent signal collected from QENS is subtracted from the sample spectra to eliminate its scattering contribution, as represented by Equation 1:

$$I_{IL}(Q, E) = I_{solution}(Q, E) - \phi I_{d-solvent}(Q, E)$$
(1)

 ϕ is the volume fraction of deuterated solvent in HMIM-TFSI/d-solvent mixtures or in HMIM-TFSI/d-solvent/d-PMMA grafted particles. Next, the intensity of the scattering data, I_{IL}(Q, E) was fitted using Equation 2:

$$I_{IL}(Q, E) = [X(Q)\delta(E) + (1 - X(Q))S(Q, E)] \otimes R(Q, E) + B(Q, E)$$
(2)

X(Q) represents the fraction of elastic scattering, $\delta(E)$ is the delta function for the elastic contribution to measured spectra, (1 - X(Q)) is the quasi-elastic component of QENS contributing to the overall scattering intensity. S(Q, E) is the dynamic structure factor, R(Q, E) is

the instrument resolution function and B(Q, E) is the linear background term. The symbol \otimes represents the convolution operator. S(Q, E) is fitted to a single Lorentzian function as shown in the following:

$$S(Q, E) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma(Q)^2 + E^2}$$
 (3)

where $\Gamma(Q)$ represents the broadening of the S(Q, E) functions in terms of half widths at half maxima (HWHM) of the Lorentzian function. The overlaid QENS spectra of HMIM-TFSI/CD₃CN solution with two different PMMA (61.8 kDa and 15.8 kDa)-grafted nanoparticles in the solution are seen in **Figure 4a** with total fitting of delta, single Lorentzian function and linear background. The strong Q-dependence of spectral broadening is a feature of diffusive motion. When it is purely Fickian diffusion, $\Gamma(Q)$ changes linearly as a function of Q² according to :

$$\Gamma = \hbar D Q^2 \qquad (4)$$

where \hbar is the reduced Planck's constant, D is the diffusion coefficient and Q is the scattering vector. The deviation from the linear relationship between $\Gamma(Q)$ and Q^2 at high Q values (seen in **Figure S1**) suggested the existence of strong intermolecular interactions in the case of ionic liquid. Jump diffusion model is widely used to describe translational diffusion with concrete events with the given equation^[28]:

$$\Gamma(\mathbf{Q}) = \frac{\hbar D \mathbf{Q}^2}{1 + D \mathbf{Q}^2 \tau} \qquad (5)$$

 τ is the characteristic residence time describing the average time a particle spends at a site before moving rapidly or jumping to another site.

The broadening of quasi-elastic spectrum is indicative of the enhanced diffusive motion. The broadening, HWHM of the single Lorentzian function at various Q values of HMIM-TFSI/CD₃CN is shown in **Figure 4c** and of HMIM-TFSI/CD₃OD group in **Figure 4d**. The slight leveling-off of HWHM at low Q suggests the local diffusion is spatially confined. The broadening of QENS spectra showed clear differences, albeit small, between pure HMIM-TFSI/d-solvent mixture and HMIM-TFSI/d-solvent/PMMA-grafted particles; the translational diffusivity obtained from jump diffusion model is higher in CD₃CN solution compared to CD₃OD solution (**Figures 4c-d**). The inclusion of particles with longer graft molecular weight (61.8 kDa) into HMIM-TFSI/d-solvent accelerates the translational diffusion of HMIM⁺ cation by 4% in CD₃CN and 6% in CD₃OD solution. At high concentration of PMMA-grafted particle mixtures, high number of TFSI⁻ anions are coupled with PMMA, thus leaving out free HMIM⁺ cations.



0.4

1.8

Figure 4. Experimental QENS spectra of (a) HMIM-TFSI/CD₃CN mixtures and (b) HMIM-TFSI/CD₃OD at 1:1 mass ratio containing PMMA-grafted nanoparticles with two graft molecular weights of 61.8 kDa and 15.8 kDa at Q = 0.7 Å⁻¹. The grafted particle concentration is 6.3 wt% in both solutions. The solid lines are the total fitting to the scattering data. Quadratic dependence of

HWHM from Lorentzian broadening of (c) HMIM-TFSI/CD₃CN/PMMA-grafted nanoparticles and (d) in HMIM-TFSI/CD₃OD/PMMA-grafted nanoparticles. Solid lines are jump diffusion model fits to the HWHM extracted from QENS data. Error bars represent the standard deviation of the Lorentzian fits. (e) Diffusivities deduced from the jump diffusion model fits for all samples. The grafted particle concentration is 70 mg/mL and the mass ratio of HMIM-TFSI/solvent is 50/50 in all solutions.

Further, the confined nature and amount of immobile cation can be obtained by analyzing the elastic incoherent structure factor (EISF), which is the ratio of the elastic intensity to the total scattering intensities (elastic plus quasi-elastic) and defined as:

$$EISF = \frac{A_D}{A_D + A_L} \tag{6}$$

 A_D is the area of delta function and A_L is the area of Lorentzian function. The geometry of intramolecular, intermolecular or diffusive motions can be mirrored through the calculation of Q-dependent EISF factor. Several EISF models were developed for different types of motions in IL^[7c]. A three-fold jump model is usually applied for the rotation of methyl groups in the cation^[13, 29]. The random jump model describes the intramolecular rotation of alkyl side chain of imidazolium cation^[13] or pyrrolidinium cation^[30]. Another model describes diffusive motion within a restricted space, like the vibrational motion of cation rings^[13, 30] or the localized confinement^[7d]. We will use this last model which captures the cation diffusion inside a confined sphere with radius a using the Equation^[21a, 29a, 31]:

EISF =
$$c_1 + (1 - c_1)(\frac{3j_1(Qa)}{Qa})^2$$
 (7)

where j_1 is the first order of spherical Bessel function, c_1 is the immobile fraction of cations, and a is the confinement radius.

Figure 5 shows that EISF increases systematically with the incorporation of PMMA grafted particles and it accelerates the mobility of the IL. The confinement radius (a) in HMIM-TFSI/solvent and HMIM-TFSI/solvent/PMMA-grafted particles are plotted in **Figure 6** and the immobile fractions of HMIM⁺ cations (c₁) are listed in **Table S4**. The confinement radius in CD₃CN solution (a= 7.32 ± 0.38 Å) is found to be higher than in CD₃OD solution (a= 5.86 ± 0.28), which is reasonable because CD₃CN can better screen the interactions between cations and anions, and therefore impair the inherent ionic clustering. The confinement radius decreases with the addition of grafted particles in HMIM-TFSI/solvent mixture, indicating the confinement effect that is induced by the high concentration of grafted particles that shrinks the HMIM-TFSI restricted volume. The mobile fraction (1- c₁) of HMIM⁺ cation ranges between 0.91 - 0.98 and decreases with the addition of grafted particles.



Figure 5. Elastic incoherent structure factor of HMIM-TFSI/PMMA (61.8 kDa and 15.8 kDa)grafted nanoparticles in (a) CD₃CN and (b) CD₃OD at 1:1 mass ratio.



Figure 6. Confinement radius of HMIM-TFSI in CD₃CN and CD₃OD mixtures with PMMA-grafted nanoparticles.

Conclusions

PMMA chains grafted on magnetic nanoparticles preferentially interact with IL, which subsequently influence particle dispersion and solvation of IL. Samples of deuterated PMMA-grafted nanoparticles in solvated IL/solvent mixtures were run in DCS. The results show that the local diffusion of HMIM⁺ cations enhanced with the addition of PMMA-grafted particles. By increasing the particle concentration, chains swollen with IL formed a confined geometry. The elastic incoherent structure factor (EISF) analysis indicated that the confinement radius decreased with the addition of grafted particles in HMIM-TFSI/solvent mixtures. It is surmised that the local ordering of free HMIM⁺ cations increased the cation diffusivity, however not the ionic conductivity. We further conjecture that enhancement of both cationic diffusivity and conductivity may be achieved by ordering cations within aligned grafted nanoparticle structures.

Experimental Section

Materials. Deuterated methyl methacrylate (d8-MMA 98%) was purchased from Polymer Source. 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI) was purchased from IoLitec, Ionic Liquids Technologies. Acetonitrile-D3 (99.8 mol% D, CD₃CN) and methanol-D4 (99.8 mol% D, CD₃OD) were purchased from Cambridge Isotope Laboratories, Inc. 4cyanopentanoic acid dithiobenzoate (CPDB), diethyl ether, oleic acid (90%) and oleylamine (70% technical grade, 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.

Nanoparticle Synthesis. Fe₃O₄ nanoparticles were synthesized by high-temperature thermal decomposition method^[32]. The one-step reaction of nanoparticles utilizes iron(III)acetylacetonate, Fe(acac)₃ as a precursor and uses both oleic acid and oleylamine as surface ligands which results in nanoparticles at high yields with no by-products^[32]. Particle size and distributions were 6.40 ± 0.81 nm in diameter, obtained by analyzing the transmission electron microscopy (TEM) data in ImageJ by sampling over hundreds of particles (**Figure S2**).

Preparation of CPDB-Anchored Fe₃O₄ Nanoparticles. CPDB solution (1.2 g in 15 mL THF) was added dropwise into nanoparticle solution (300 mg in 15 mL THF) and sonicated in a bath sonicator. The mixture was stirred at room temperature for 24 h. Particles were washed to remove excess CPDB, following the previously reported protocol^[33]. Every 3 mL of anchored mixture was precipitated by adding 25 mL of cyclohexane and ethyl ether (4:1 volume ratio), centrifuged at 3,000 rpm for 15 min and re-dissolved in 3 mL of THF. The washing procedure was repeated three times.

Surface-Initiated Reversible Addition-Fragmentation Chain-Transfer (SI-RAFT) Polymerization of d-MMA. CPDB-anchored Fe₃O₄ particles, d-MMA and AIBN in THF solution were degassed in freeze-pump-thaw for three cycles. 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, ethanol was added to the solution and centrifuged at 6,000 rpm. The washing step was repeated several times till the supernatant solution was cleared after ethanol addition. The supernatant was removed, and particles were re-dissolved in THF. This procedure was repeated several times to remove the free d-PMMA chains.

Structural Characterization. TEM data were collected using JEOL 2100Plus S/TEM equipped with cold-field emission gun in the Laboratory for Multiscale Imaging operated at 200 kV. PMMA-grafted particles in ionic liquid solution were drop cast on lacey carbon grids.

Molecular Weight and Grafting Density Determination. HCl (2 wt%) solution was added to the PMMA-grafted nanoparticle solution (10 mg/mL in 5 mL THF) to etch the nanoparticles and the mixture solution was sonicated till the top organic layer became clear. Methanol was later 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 5.0µm 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 61.8 kDa (Đ: 1.05) and 15.8 kDa (Đ:

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

$$\sigma = \frac{m_{polymer}}{m_{NP}} \frac{N_A \rho R}{3M_w}$$

 $m_{polymer}$ 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, M_w is the weight averaged molecular weight of grafted chains.

Electrochemical Impedance Spectroscopy (EIS). Bulk ionic conductivity was measured using the SP-300 EIS from the Bio-Logic Science Instruments. 0.3 mL of grafted particles 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 10 mV amplitude was applied in the frequency range of 1 kHz to 1 MHz. The real component of the complex conductivity, σ' , was calculated using the equation^[34] $\sigma'(\omega) =$ $\frac{Z'(\omega)}{k[(Z'(\omega))^2+(Z''(\omega))^2]}$. The real and imaginary impedance, Z' and Z'', were obtained from the highfrequency plateau, where ionic mobility dominates the impedance spectra^[35]. The conductivity cell constant, k, was determined using 0.01 M KCl standard (Ricca Chemical, 1412 µS/cm at 25 °C). Quasi-Elastic Neutron Scattering: The QENS measurements were performed at the Disk Chopper Spectrometer (DCS) at National Institute of Standards and Technology Center for Neutron Research (NCNR). An incident neutron wavelength of 9 Å and an energy resolution of μ eV were used to provide Q range at 0.13 – 1.56 Å⁻¹. The spectra were collected at 298 K for at least 8 h. Grafted particles at ~6.3 wt% concentration was mixed with pure HMIM-TFSI, mixtures of HMIM-TFSI/CD₃CN and of HMIM-TFSI/CD₃OD at 50/50 mass ratio. Annular aluminum holders with 0.15 mm gaps were used to minimize multiple scattering. Indium wire was

used to seal the sample holder effectively. The instrument resolution was measured using a vanadium standard. The DAVE software package^[36] was used to execute the data reduction, background subtraction and analysis. Scattering of pure deuterated solvent (CD₃CN and CD₃OD) was also collected under same condition and subtracted from both HMIM-TFSI/solvent mixtures based on deuterated solvent volume fraction during data reduction.

Acknowledgements

This work was supported by the National Science Foundation DMR Polymers program under award #1807802. Access to the HFBS was provided by the Center for High-Resolution Neutron Scattering, a partnership between the NIST and the NSF under agreement no. DMR-1508249.

Certain commercial material suppliers are identified in this article to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Keywords: PMMA-grafted nanoparticles, ionic liquid, quasi-elastic neutron scattering, nanoconfinement, local cation diffusivity, elastic incoherent structure factor

References

[1] a) D. M. Correia, J. C. Barbosa, C. M. Costa, P. M. Reis, J. M. S. S. Esperança, V. de Zea Bermudez, S. Lanceros-Méndez, *The Journal of Physical Chemistry C* 2019, *123*, 12744-12752; b) N. C. Osti, B. Dyatkin, A. Gallegos, D. Voneshen, J. K. Keum, K. Littrell, P. Zhang, S. Dai, J. Wu, Y. Gogotsi, E. Mamontov, *Journal of The Electrochemical Society* 2019, *166*, A507-A514; c) H. Wang, S. Gu, Y. Bai, S. Chen, N. Zhu, C. Wu, F. Wu, *Journal*

of Materials Chemistry A 2015, 3, 22677-22686; d) B. Dyatkin, N. C. Osti, A. Gallegos, Y. Zhang, E. Mamontov, P. T. Cummings, J. Wu, Y. Gogotsi, *Electrochimica Acta* 2018, 283, 882-893.

- [2] H. Shobukawa, H. Tokuda, M. A. B. H. Susan, M. Watanabe, *Electrochimica Acta* 2005, 50, 3872-3877.
- [3] A. K. Mishra, T. Kuila, D.-Y. Kim, N. H. Kim, J. H. Lee, *Journal of Materials Chemistry* 2012, *22*, 24366-24372.
- [4] a) S. Voskian, P. Brown, C. Halliday, K. Rajczykowski, T. A. Hatton, ACS Sustainable Chemistry & Engineering 2020, 8, 8356-8361; b) W. Ying, J. Cai, K. Zhou, D. Chen, Y. Ying, Y. Guo, X. Kong, Z. Xu, X. Peng, ACS Nano 2018, 12, 5385-5393.
- [5] C. A. Gunawan, M. Ge, C. Zhao, *Nature Communications* **2014**, *5*, 3744.
- [6] a) M. Sha, X. Ma, N. Li, F. Luo, G. Zhu, M. D. Fayer, *The Journal of Chemical Physics* 2019, *151*, 154502; b) H. Liu, E. Maginn, *The Journal of Chemical Physics* 2011, *135*, 124507; c) B. Dyatkin, N. C. Osti, Y. Zhang, H.-W. Wang, E. Mamontov, W. T. Heller, P. Zhang, G. Rother, P. T. Cummings, D. J. Wesolowski, Y. Gogotsi, *Carbon* 2018, *129*, 104-118.
- [7] a) M. Busch, T. Hofmann, B. Frick, J. P. Embs, B. Dyatkin, P. Huber, *Physical Review Materials* 2020, *4*, 055401; b) M. Kofu, M. Nagao, T. Ueki, Y. Kitazawa, Y. Nakamura, S. Sawamura, M. Watanabe, O. Yamamuro, *The Journal of Physical Chemistry B* 2013, *117*, 2773-2781; c) E. Mamontov, H. Luo, S. Dai, *The Journal of Physical Chemistry B* 2009, *113*, 159-169; d) C. J. Jafta, C. Bridges, L. Haupt, C. Do, P. Sippel, M. J. Cochran, S. Krohns, M. Ohl, A. Loidl, E. Mamontov, P. Lunkenheimer, S. Dai, X.-G. Sun, *ChemSusChem* 2018, *11*, 3512-3523; e) F. Nemoto, M. Kofu, M. Nagao, K. Ohishi, S.-i.

Takata, J.-i. Suzuki, T. Yamada, K. Shibata, T. Ueki, Y. Kitazawa, M. Watanabe, O. Yamamuro, *The Journal of Chemical Physics* **2018**, *149*, 054502.

- [8] F. Pabst, J. Gabriel, P. Weigl, T. Blochowicz, *Chemical Physics* 2017, 494, 103-110.
- [9] Y. Zhang, E. J. Maginn, *The Journal of Physical Chemistry Letters* 2015, *6*, 700-705.
- [10] M. Casalegno, G. Raos, G. B. Appetecchi, S. Passerini, F. Castiglione, A. Mele, *The Journal of Physical Chemistry Letters* 2017, 8, 5196-5202.
- [11] a) M. G. Del Pópolo, G. A. Voth, *The Journal of Physical Chemistry B* 2004, *108*, 1744-1752; b) S. S. Sarangi, W. Zhao, F. Müller-Plathe, S. Balasubramanian, *ChemPhysChem* 2010, *11*, 2001-2010; c) M. Casalegno, F. Castiglione, G. Raos, G. B. Appetecchi, S. Passerini, A. Mele, E. Ragg, *ACS Applied Materials & Interfaces* 2020, *12*, 23800-23811; d) Z. Hu, C. J. Margulis, *Proceedings of the National Academy of Sciences of the United States of America* 2006, *103*, 831.
- [12] M. Sha, Y. Liu, H. Dong, F. Luo, F. Jiang, Z. Tang, G. Zhu, G. Wu, Soft Matter 2016, 12, 8942-8949.
- [13] M. Kofu, M. Tyagi, Y. Inamura, K. Miyazaki, O. Yamamuro, *The Journal of Chemical Physics* 2015, 143, 234502.
- [14] a) T. Burankova, E. Reichert, V. Fossog, R. Hempelmann, J. P. Embs, *Journal of Molecular Liquids* 2014, *192*, 199-207; b) T. Burankova, R. Hempelmann, A. Wildes, J. P. Embs, *The Journal of Physical Chemistry B* 2014, *118*, 14452-14460; c) J. P. Embs, T. Burankova, E. Reichert, R. Hempelmann, *The Journal of Physical Chemistry B* 2012, *116*, 13265-13271.
- [15] T. Burankova, J. F. Mora Cardozo, D. Rauber, A. Wildes, J. P. Embs, *Scientific Reports* 2018, *8*, 16400.

- [16] M. Kofu, T. Someya, S. Tatsumi, K. Ueno, T. Ueki, M. Watanabe, T. Matsunaga, M. Shibayama, V. G. Sakai, M. Tyagi, O. Yamamuro, *Soft Matter* 2012, *8*, 7888-7897.
- [17] a) S. Liu, C. Liedel, N. V. Tarakina, N. C. Osti, P. Akcora, *Nanoscale* 2019, *11*, 19832-19841; b) M. Cai, Q. Yu, W. Liu, F. Zhou, *Chemical Society Reviews* 2020, *49*, 7753-7818.
- [18] S. Liu, M. Walton, N. V. Tarakina, P. Akcora, *The Journal of Physical Chemistry. B* 2020, 124, 4843-4850.
- [19] a) N. C. Osti, K. L. Van Aken, M. W. Thompson, F. Tiet, D.-e. Jiang, P. T. Cummings, Y. Gogotsi, E. Mamontov, *The Journal of Physical Chemistry Letters* 2017, *8*, 167-171; b) H. Tokuda, S.-J. Baek, M. Watanabe, *Electrochemistry* 2005, *73*, 620-622; c) W. Li, Z. Zhang, B. Han, S. Hu, Y. Xie, G. Yang, *The Journal of Physical Chemistry B* 2007, *111*, 6452-6456; d) E. T. Fox, E. Paillard, O. Borodin, W. A. Henderson, *The Journal of Physical Chemistry C* 2013, *117*, 78-84; e) M. W. Thompson, R. Matsumoto, R. L. Sacci, N. C. Sanders, P. T. Cummings, *The Journal of Physical Chemistry B* 2019, *123*, 1340-1347.
- [20] a) S. Seki, M. A. B. H. Susan, T. Kaneko, H. Tokuda, A. Noda, M. Watanabe, *Journal of Physical Chemistry B* 2005, *109*, 3886-3892; b) M. A. B. H. Susan, T. Kaneko, A. Noda, M. Watanabe, *Journal of the American Chemical Society* 2005, *127*, 4976-4983; c) C. Chen, J. K. Maranas, V. García-Sakai, *Macromolecules* 2006, *39*, 9630-9640.
- [21] a) C. J. Jafta, C. Bridges, L. Haupt, C. Do, P. Sippel, M. J. Cochran, S. Krohns, M. Ohl, A. Loidl, E. Mamontov, P. Lunkenheimer, S. Dai, X.-G. Sun, *ChemSusChem* 2018, *11*, 3512-3523; b) S. M. Chathoth, E. Mamontov, S. Dai, X. Wang, P. F. Fulvio, D. J. Wesolowski, *EPL (Europhysics Letters)* 2012, *97*, 66004.
- [22] S. Liu, M. Tyagi, P. Akcora, *Macromolecules* **2020**, *53*, 6538-6546.

- [23] a) S. Park, J. G. McDaniel, *The Journal of Chemical Physics* 2020, *152*, 074709; b) M. L.
 Hoarfrost, M. S. Tyagi, R. A. Segalman, J. A. Reimer, *Macromolecules* 2012, *45*, 3112-3120.
- [24] a) Q. Berrod, F. Ferdeghini, P. Judeinstein, N. Genevaz, R. Ramos, A. Fournier, J. Dijon, J. Ollivier, S. Rols, D. Yu, R. A. Mole, J. M. Zanotti, *Nanoscale* 2016, *8*, 7845-7848; b)
 W. Tu, K. Chat, G. Szklarz, L. Laskowski, K. Grzybowska, M. Paluch, R. Richert, K. Adrjanowicz, *The Journal of Physical Chemistry C* 2020, *124*, 5395-5408.
- [25] D. Noferini, O. Holderer, H. Frielinghaus, *Physical Chemistry Chemical Physics* 2020, 22, 9046-9052.
- [26] C. V. Cerclier, J.-M. Zanotti, J. L. Bideau, *Physical Chemistry Chemical Physics* 2015, *17*, 29707-29713.
- [27] a) S. Liu, M. Walton, N. V. Tarakina, P. Akcora, *The Journal of Physical Chemistry B* 2020, *124*, 4843-4850; b) K. Ueno, A. Inaba, M. Kondoh, M. Watanabe, *Langmuir* 2008, *24*, 5253-5259; c) K. Ueno, T. Fukai, T. Nagatsuka, T. Yasuda, M. Watanabe, *Langmuir* 2014, *30*, 3228-3235.
- [28] K. S. Singwi, A. Sjölander, *Physical Review* **1960**, *119*, 863-871.
- [29] a) E. Mamontov, H. Luo, S. Dai, J. Phys. Chem. B 2009, 113, 159-169; b) F. Ferdeghini,
 Q. Berrod, J.-M. Zanotti, P. Judeinstein, V. G. Sakai, O. Czakkel, P. Fouquet, D.
 Constantin, Nanoscale 2017, 9, 1901-1908.
- [30] F. Lundin, H. W. Hansen, K. Adrjanowicz, B. Frick, D. Rauber, R. Hempelmann, O. Shebanova, K. Niss, A. Matic, *The Journal of Physical Chemistry B* 2021, *125*, 2719-2728.
- [31] E. Mamontov, G. A. Baker, H. Luo, S. Dai, *ChemPhysChem* 2011, *12*, 944-950.

- [32] S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. Li, *Journal of the American Chemical Society* 2004, 126, 273-279.
- [33] C. Li, J. Han, C. Y. Ryu, B. C. Benicewicz, *Macromolecules* 2006, 39, 3175-3183.
- [34] V. Di Noto, M. Vittadello, S. Lavina, M. Fauri, S. Biscazzo, *The Journal of Physical Chemistry B* 2001, 105, 4584-4595.
- [35] M. Singh, O. Odusanya, G. M. Wilmes, H. B. Eitouni, E. D. Gomez, A. J. Patel, V. L. Chen, M. J. Park, P. Fragouli, H. Iatrou, N. Hadjichristidis, D. Cookson, N. P. Balsara, *Macromolecules* 2007, 40, 4578-4585.
- [36] R. T. Azuah, L. R. Kneller, Y. Qiu, P. L. W. Tregenna-Piggott, C. M. Brown, J. R. D. Copley, R. M. Dimeo, J. Res. Natl. Inst. Stand. Technol. 2009, 114, 341-358.

Entry for the Table of Contents



Additional Material - Author

Click here to access/download Additional Material - Author manuscript_DCS_no_highlights_Submitted2.docx Supporting Information

Click here to access/download Supporting Information DCS paper SI2.pdf The highlighted statement in page 10 is not completely accurate. The numbers in the table of the response to reviewer 2 fail to address the incoherent and coherent contributions from the quite large amount of solvent (50/50 as stated by the authors). From a quick back of the envelope calculation, the incoherent contribution from the IL to the total signal is around 85% for all samples (with noting an additional 10 to 20% coherent contribution from the IL that the authors do not mention at all). However, the main contribution to the total measured signal from the solvent comes from the coherent part which varies from around 2 to 10%. I would suggest that the sentence is rephrased to "The pure deuterated solvent signal collected from QENS is subtracted from the sample spectra to eliminate its scattering contribution as represented by equation 1:"

Response: We did not include the solvent incoherent and coherent scattering contributions to the table in the response letter because we are subtracting the scattering contribution of the solvent from the sample signal. Thanks for correcting the sentence. We rephrased the line as noted by the reviewer.

