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14. ABSTRACT Atomistic molecular dynamics simulations were undertaken to investigate the molecular structure of polymerized ionic liquids (polyILs), a class of promising electrolyte materials with enhanced mechanical characteristics of a polymer nature and unique physico-chemical properties inherent from ionic liquid components. We first developed a direct method to calculate the structure factors from simulation trajectories, complementary to the popular Fourier transform (FT) method. The validity and effectiveness of the direct method were corroborated by favorable comparison with experimental results and results from the FT method. We then performed detailed structural					
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Report Title

Final Report: Quantitative Determination of Partial Structure Factors for Polymerized Ionic Liquids with Molecular Dynamics Simulations

ABSTRACT

Atomistic molecular dynamics simulations were undertaken to investigate the molecular structure of polymerized ionic liquids (polyILs), a class of promising electrolyte materials with enhanced mechanical characteristics of a polymer nature and unique physico-chemical properties inherent from ionic liquid components. We first developed a direct method to calculate the structure factors from simulation trajectories, complementary to the popular Fourier transform (FT) method. The validity and effectiveness of the direct method were corroborated by favorable comparison with experimental results and results from the FT method. We then performed detailed structural analysis on extensive atomistic molecular dynamics simulations of polyILs and found excellent agreement between atomistic simulations and experimental X-ray scattering profiles in terms of peak shapes and positions. This quantitative comparison study of X-ray scattering and atomistic simulations will lead to a fundamental understanding of the structure and morphology of polyILs and pave a path forward toward the rational design of polyILs for electrochemical applications.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/29/2016	1 Hongjun Liu, Stephen J. Paddison. Direct Comparison of Atomistic Molecular Dynamics Simulations and X-ray Scattering of Polymerized Ionic Liquids, ACS Macro Letters, (): 537. doi:
08/29/2016	2 Hongjun Liu, Stephen J. Paddison. Direct calculation of the X-ray structure factor of ionic liquids, Phys. Chem. Chem. Phys., (): 11000. doi:
TOTAL:	2

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

“Quantitative Comparison of Atomistic Molecular Dynamics Simulations and X-Ray Scattering of Polymerized Ionic Liquids”, Symposium L06: Ionic Liquids as Electrolytes, 229th Meeting of the ECS, San Diego, CA May 29th – June 3rd, 2016.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Fellow of the Royal Society of Chemistry, UK, May 2016

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
Hongjun Liu	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Stephen J. Paddison	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

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FTE Equivalent:	
Total Number:	

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Names of personnel receiving PHDs

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Names of other research staff

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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

FINAL PROGRESS REPORT
For STIR project Grant W911NF-15-1-0501

Title Quantitative Determination of Partial Structure Factors for Polymerized Ionic Liquids with Molecular Dynamics Simulations

(1) Foreword

Atomistic molecular dynamics simulations were undertaken to investigate the molecular structure of polymerized ionic liquids (polyILs), a class of promising electrolyte materials with enhanced mechanical characteristics of a polymer nature and unique physico-chemical properties inherent from ionic liquid components. We first developed a direct method to calculate the structure factors from simulation trajectories, complementary to the popular Fourier transform (FT) method. The validity and effectiveness of the direct method were corroborated by favorable comparison with experimental results and results from the FT method. We then performed detailed structural analysis on extensive atomistic molecular dynamics simulations of polyILs and found excellent agreement between atomistic simulations and experimental X-ray scattering profiles in terms of peak shapes and positions. This quantitative comparison study of X-ray scattering and atomistic simulations will lead to a fundamental understanding of the structure and morphology of polyILs and pave a path forward toward the rational design of polyILs for electrochemical applications.

(2) Table of Contents

Report is less than 10 pages so omitted.

(3) List of Appendixes, Illustrations and Tables

Nothing to append. See attached papers.

(4) Statement of the Problem Studied

Polymerized ionic liquids (polyILs) are touted as the ideal solid-state electrolyte materials for electrochemical devices due to their enhanced mechanical characteristics of a polymeric nature and their unique physico-chemical properties inherent from ionic liquids. Previous studies have suggested that morphology and structure of polyILs have an significant effect on their ionic conductivities. Despite significant research effort, the key structural and dynamical relationships of polyILs remain poorly understood. In particular, the quantitative structure analysis of polyILs is relatively scarce, which is crucial to understanding the ion transport mechanism from a molecular point of view. The specific objective of this work were to obtain the quantitative structure information of polyILs via atomistic molecular dynamics simulations to directly compare with X-ray scattering experiments. The synergetic effort of molecular simulations and scattering experiments is expected to lead to a step forward for the rational design of polyILs in electrochemical application.

(5) Summary of the Most Important Results

A conceptually simple and computationally efficient direct method to calculate the total X-ray structure factor of ionic liquids from molecular simulations were advocated to be complementary to the popular Fourier transform method. Using tetradecyltriethylphosphonium bis(trifluoromethylsulfonyl)amide P14,666 Tf2N as a model system, the validity of the direct method was well formulated and established by comparison with FT results (see Figure 1). The three principal q sampling of the direct method has done a satisfactory job with most partial structure factors, but shows an overestimated trend with $S_{HH}(q)$, $S_{CC}(q)$, and $S_{HC}(q)$. The all- q sampling of the direct method remedies the aforementioned

overestimates with only a slightly higher computing overhead. Such a comparison unambiguously verifies that both methods are equally effective to investigate the liquid structure. Note that the noisier behavior of the direct structure factors at lower q might better reflect the low- q error explosion observed in scattering experiments.

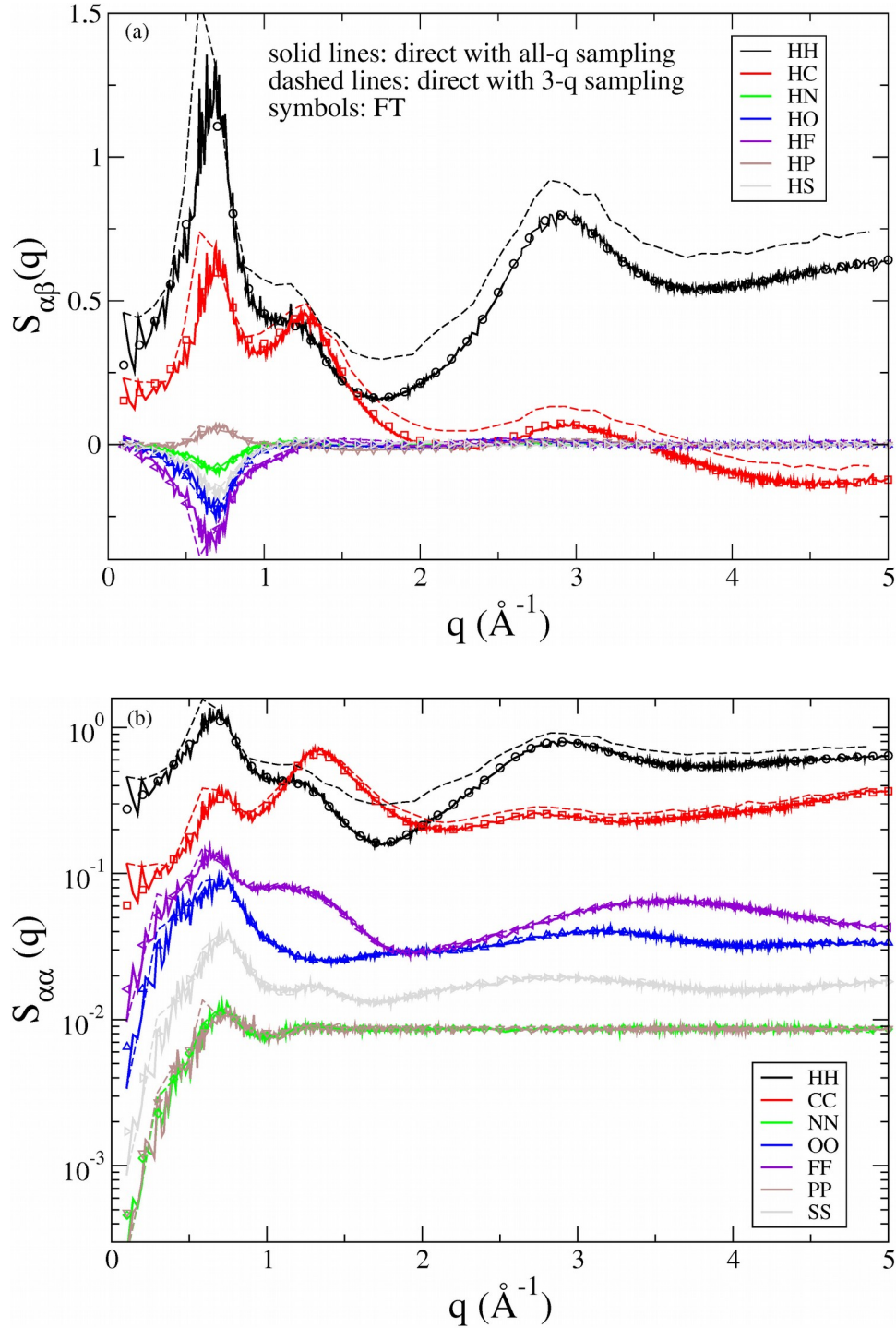


Figure 1: Comparison of representative partial structure factors between the FT results (symbols) and direct results (lines). Normally, three principal q vectors will be sufficient for the direct method. Improved all- q sampling leads to an excellent agreement between the FT and direct methods.

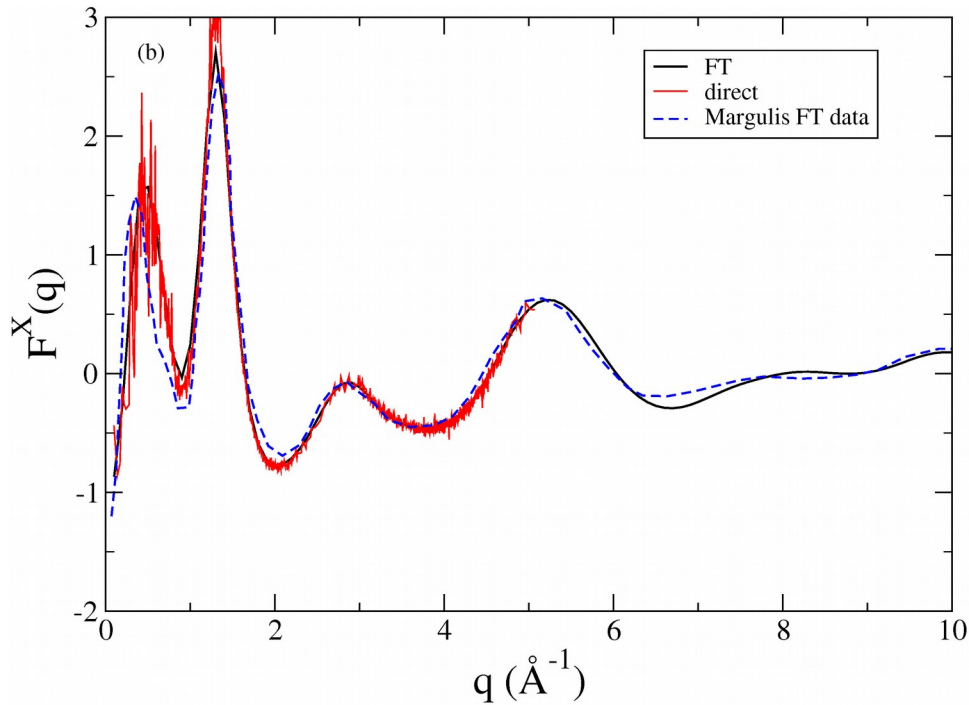


Figure 2: Total X-ray structure factors from both the direct method and FT method for P14,666 Tf2N compared with the previous FT data of Margulis.

Figure 2 presents the total X-ray structure factors compared with previous data. Evidently, this ionic liquid shows three characteristic intermolecular features below 2 \AA^{-1} : a prepeak at 0.45 \AA^{-1} , a shoulder at 0.77 \AA^{-1} , and an intense peak at 1.33 \AA^{-1} . The peaks above 2 \AA^{-1} are intramolecular in nature. All characteristic features are realistically reproduced by comparison of the simulated and previously published data through the Fourier transform method² at 400 K. Such a satisfactory agreement gives us confidence in utilizing simulations to analyze the ionic liquid structure in detail. Through the accumulated simulation and experimental X-ray scattering study of ionic liquids, it is well established that the prepeak below 0.5 \AA^{-1} originates from polar alternation, the peak or shoulder around 0.8 \AA^{-1} is associated with charge alternation, and the peak at 1.5 \AA^{-1} is ascribed to the adjacency of species of different charge and cationic tails.

The effectiveness of direct method was demonstrated through versatile partition schemes. We first partitioned $S^X(q)$ into ionic group contributions. The total structure factor is decomposed into the cation-cation, anion-anion, and cross subcomponents in Figure 3(a). It is clear that the anion-anion contribution dominates the prepeak. Likewise, we can identify the polar contribution is the major contributor to the prepeak (see Figure 3(b)). The out of phase behavior of peaks at 0.77 \AA^{-1} between self terms (S^{CC} and S^{AA}) and cross term (S^{CA+AC}), the signature of charge alternation in ionic liquids, leads to the intermediate shoulder in $S^X(q)$. Occasionally, the absence of this intermediate structure is solely because of the total cancellation of competing contributions and certainly not any indicator of missing charge ordering. Such a perfect cancellation of charge alternation peaks is not uncommon in ionic liquids.¹

The most intense peak at 1.33 \AA^{-1} is due to ions in close contact, a combined effect of ions of both same charges and opposite charges, with the cation-cation correlation as a dominant factor and anion-anion correlation and cation-anion cross correlation as the equal minor contributors. The close contact of oppositely charged ions is ubiquitous in ionic liquids, while hydrophobic interactions of tail parts exist

due to the long alkyl chains on the cations. To pinpoint the specific part of the cation-cation contribution responsible for the intense peak at 1.33 \AA^{-1} , the cation-cation partial structure factor is partitioned into head-head, tail-tail and head-tail subcomponents shown in Figure 3(c). There is no prepeak observed in S^{CC} since the fortuitous cancellation between positive contributions from the same groups (S^{HH} and S^{TT}) and a negative contribution from the cross group (S^{HT+TH}). The cationic tail group is the major contributor to the cation-cation intermolecular adjacency correlation, therefore the apolar cationic tail contributes significantly to the intense peak observed at 1.33 \AA^{-1} in $S^X(q)$.

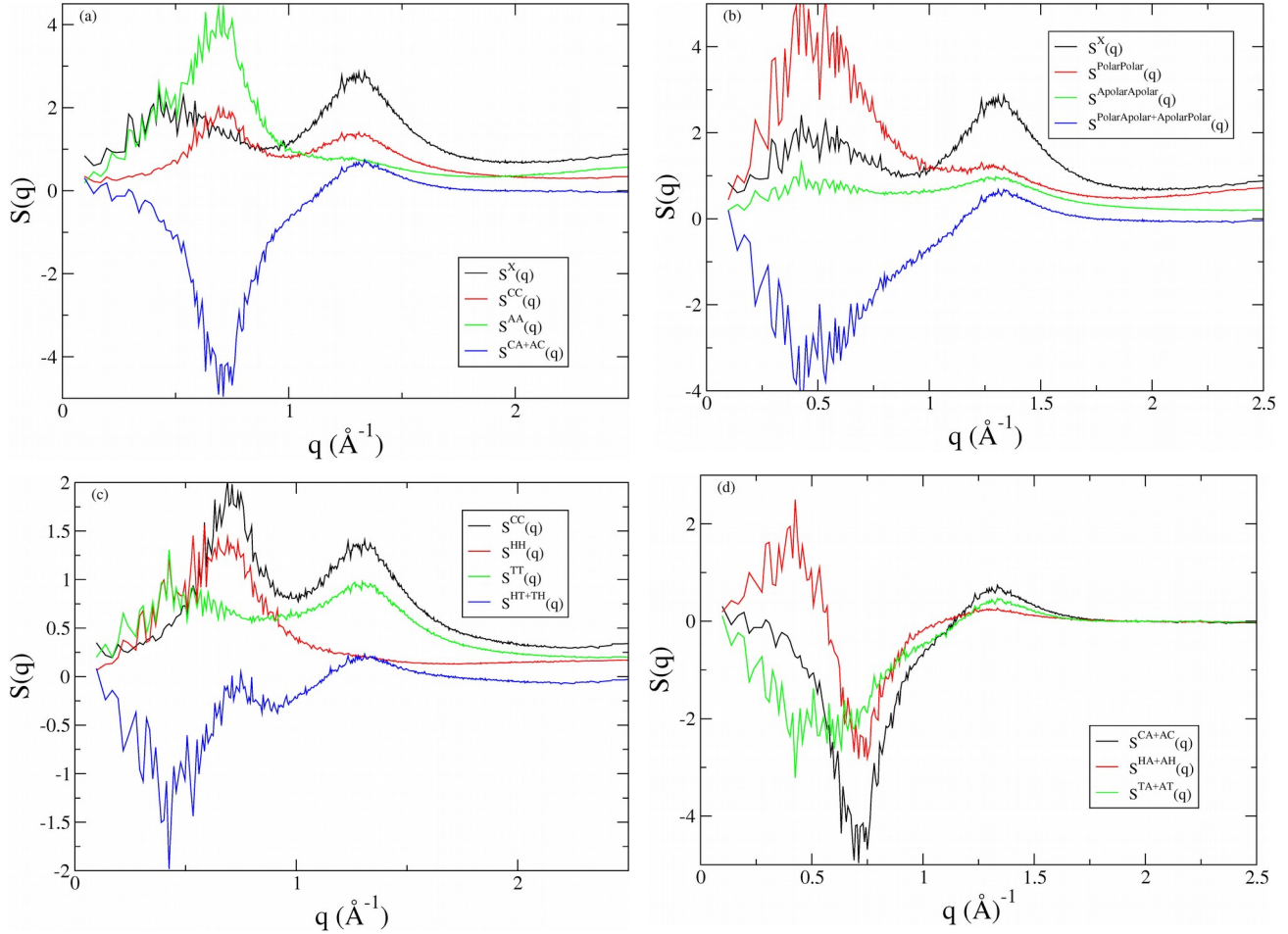


Figure 3: Decomposed structure factors. (a) Total structure factor S^X decomposed into the cation-cation (S^{CC}), anion-anion (S^{AA}) and cross (S^{CA+AC}) partial components; (b) total structure factor decomposed into the polar-polar ($S^{PolarPolar}$), apolar ($S^{ApolarApolar}$) and cross ($S^{PolarApolar+ApolarPolar}$) subcomponents; (c) cation-cation partial structure factor (S^{CC}) separated into the head-head (S^{HH}), tail-tail (S^{TT}) and head-tail (S^{HT+TH}) subcomponents; (d) cation-anion partial structure factor (S^{CA+AC}) split into the cation head-anion (S^{HA+AH}), and cation tail-anion (S^{TA+AT}) subcomponents.

Additional insight can be gained by further partitioning the cation-anion cross contribution into cationic head-anion, and cationic tail-anion subcomponents (see Figure 3(d)). Atoms in anions having higher electronic density usually display larger X-ray form factors and therefore play a significant role as structure reporter in X-ray scattering experiments.¹ Through examining the cationic head-anion curve (S^{HA+AH}) in red we can clearly appreciate the significance of three length scales observed in ionic liquid of interest. The first peak at the prepeak region corresponds to the polarity alternation, and the intermediate antipeak is due to the charge alternation. The peak around 1.33 \AA^{-1} is ascribed to the

adjacent correlation or close contact of cation and anion. The very cationic tail-anion correlation $S^{\text{HA+AH}}$ is uniquely posed to identify all three important length scales (polar alternation, charge alternation, and adjacency) even if there are complete cancellations in the prepeak or intermediate peak of the total structure factor $S^{\text{X}}(q)$.

In summary, we have presented an extensive structural study of P14,666 Tf2N ionic liquid with an emphasis on the calculation of the X-ray structure factor using the direct method. The proposed direct method for structure factor calculation is conceptually simpler and computationally more efficient compared with the widely used Fourier transform method. With atomistic simulations, one can readily derive information on specific atom/ion/group correlations to disentangle the mysterious scattering peaks thereby leading to an unambiguous explanation on the ionic liquid structure. Through various partition schemes, three characteristic intermolecular peaks observed below 2 \AA^{-1} are found to be the signatures of ionic liquid structure. The prepeak corresponds to the polarity alternation, and the intermediate shoulder or peak is due to the charge alternation. The intense peak is mainly ascribed to the adjacent contact of apolar cationic tails. The cationic head-anion correlation function is found to be a unique reporter for all three characteristic length scales even if certain peaks are concealed by fortuitous cancellation in $S^{\text{X}}(q)$.

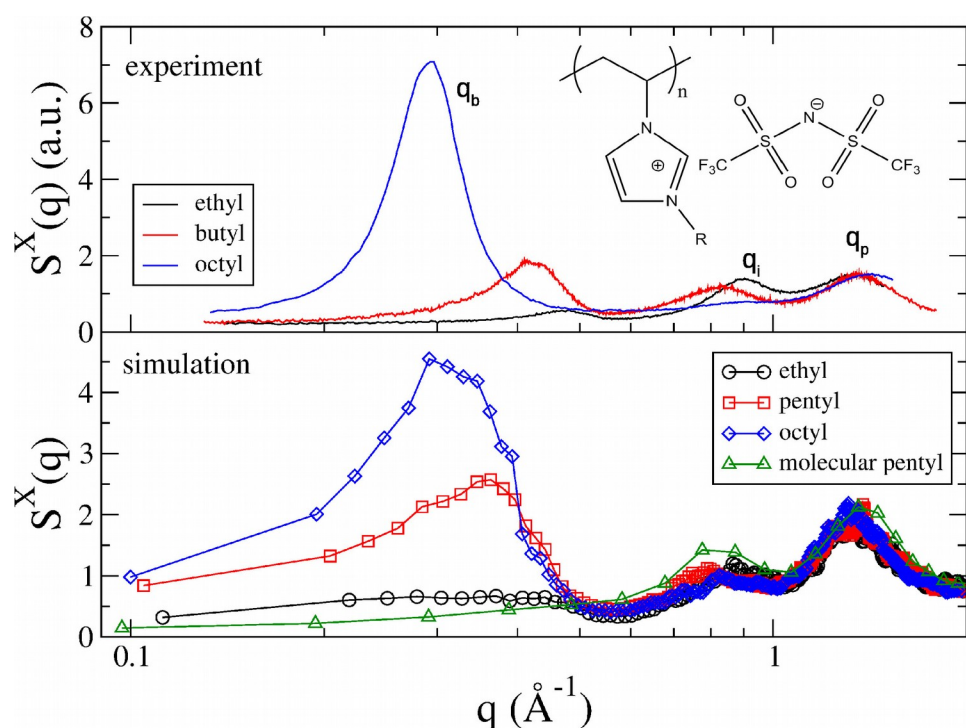


Figure 4: Simulated X-ray scattering profiles of poly(*n*Vim Tf2N) (chemical structure sketched in inset) as a function of alkyl side chain length in comparison with experiment.³ Experimental intensities in arbitrary units were scaled to obtain the same height of the q_p peaks around 1.4 \AA^{-1} . Simulated scattering $S^{\text{X}}(q)$ of the molecular IL pVim Tf2N is also included for comparison.

Extensive atomistic MD simulations for a homologous set of poly(*n*-alkyl-vinylimidazolium bistrifluoromethylsulfonylimide) poly(C*n*Vim Tf2N) ($n = 2, 5, 8$) were carried out to directly compare with X-ray scattering experiment. The total X-ray structure factor was calculated using the newly minted direct method. We observed excellent agreement between atomistic simulations and experimental X-ray scattering profiles in terms of peak shapes and positions. Simulated X-ray structure factors of poly(*n*Vim Tf2N) as a function of alkyl side chain length are compared with experiment in

Figure 4. Evidently, this homologous series of poly(nVim Tf2N) shows three characteristic intermolecular features below 2 \AA^{-1} : The low-q peaks at $0.2\text{-}0.6 \text{ \AA}^{-1}$ are taken to be the backbone-to-backbone peak (q_b), the intermediate-q peaks at $0.8\text{-}1.0 \text{ \AA}^{-1}$ are denoted as the ionic peak (q_i , correlation between anions), and the high-q peaks at $1.0\text{-}2.0 \text{ \AA}^{-1}$ as the pendant-to-pendant peak (q_p , correlation between pendant groups of the polycation).³ Three characteristic peaks are well reproduced by the atomistic simulations and the trends seen in the simulations and experiments are strikingly similar. Such a satisfactory agreement gives us confidence in utilizing simulations to analyze the structure of poly(nVim Tf2N) in detail. The most noticeable feature of Figure 4 is that q_b shifts to lower q with stronger intensity as the alkyl chain length is increased. The peak q_b is insignificant compared with the other two scattering peaks for poly(eVim Tf2N), and becomes much more dominant for the polyILs with longer alkyl chains. As demonstrated later, the introduction of longer side chains indeed expands the backbone-to-backbone correlation length ($2\pi/q_b$) thereby leading to a lower q_b position. The increase in q_b intensity arises from the elevated electron density contrast due to the increasing local compositional heterogeneity between polar and nonpolar domains. In contrast, a molecular IL with the same alkyl chain length does not have this conspicuous low-q peak (see poly(pVim Tf2N) vs. molecular IL pVim Tf2N in Figure 4). The absence of a prepeak in pVim Tf2N is ascribed to the fact that the disperse aggregates formed by the nonpolar alkyl chains are not large enough to form a percolating mesoscopic phase. The similar threshold (around C5) was also observed in the homologous series of n-alkyl-methylimidazolium Tf2N ILs.⁴ Before the threshold is reached, nonpolar domains are dispersed in the continuous polar network and no prepeak is observed. In contrast to q_b , there is no substantial q shift observed on q_i and q_p : q_i slightly moves to lower q with decreasing intensity as the alkyl chain becomes longer, while there is very little shift in q_p . The weaker correlation and slightly larger separation between anions with increasing alkyl chain length can be explained by the fact that the ionic separation must increase to accommodate progressively larger nonpolar domains. q_p peaks were originally assigned as the pendant-to-pendant peak by Winey et al.³ Alternatively, we also attribute it to the correlation between close contact of the cations and anions as indicated by the agreement between the correlation length $l_p=2\pi/q_p$ and the first $g(r)$ peak of the cations and anions. The direct contact pair distance is unaffected by the presence of the nonpolar domains so that there is no q shift in the q_p position. The scattering similarity between molecular ILs and polyILs at the intermediate and high peaks corroborates the existence of a polar network suggesting both classes of material exhibit the medium-range structural features of ionic systems.

Figure 5 presents the correlation lengths calculated from peak positions in $S^X(q)$ of poly(nVim Tf2N) using $l=2\pi/q$ as a function of alkyl side chain length. The overall agreement between simulation and experiment is excellent. The correlation length, l_p , remains a constant 4.7 \AA regardless of n, while l_i around 7.6 \AA slightly increases with n. The correlation length, l_b , increases linearly with n at a rate of 1 \AA/CH_2 , a little lower than the experimental rate of 1.5 \AA/CH_2 (n = 2, 4 and 8)³ or 1.3 \AA/CH_2 (n = 2, 3, 6 and 8).⁵ The low-q scattering peaks have also been identified as a signature feature for nanoscale aggregation in both polymers and ionic liquids. Nanophase separation of incompatible parts is a general phenomenon in amorphous side-chain polymers and ILs with long alkyl groups. The accumulated studies on various flexible and rigid polymers suggest that the size of nonpolar nanodomains is mainly dictated by the number of alkyl carbon atoms per side chain, and depends slightly on the microstructure of the polymer backbone chain.⁶ Our simulated trend is consistent with the experimental observations for poly(n-alkyl acrylate) or poly(n-alkyl methacrylate) copolymers and homopolymers, where the slope of 1.05 \AA/CH_2 was found for n < 10.⁷ A similar slope of 1.1 \AA/CH_2 has been reported for n-alkyl methyl piperidinium based ILs,⁸ but the slope of 2.1 \AA/CH_2 was also reported for n-alkyl methyl imidazolium based ILs.⁹ The finding of sensibly different slopes for different systems implies a different organization of the alkyl chains into the nonpolar domains involving substantial interdigitation between multiple neighboring chains. It should be noted that our estimate is consistent with a structural

scenario involving the nonpolar domains built up by noninterdigitating stretched alkyl chains. If fully interdigitated, the slope of a plot of l_b versus n in an all-trans configuration is expected to be 1.25 \AA/CH_2 .

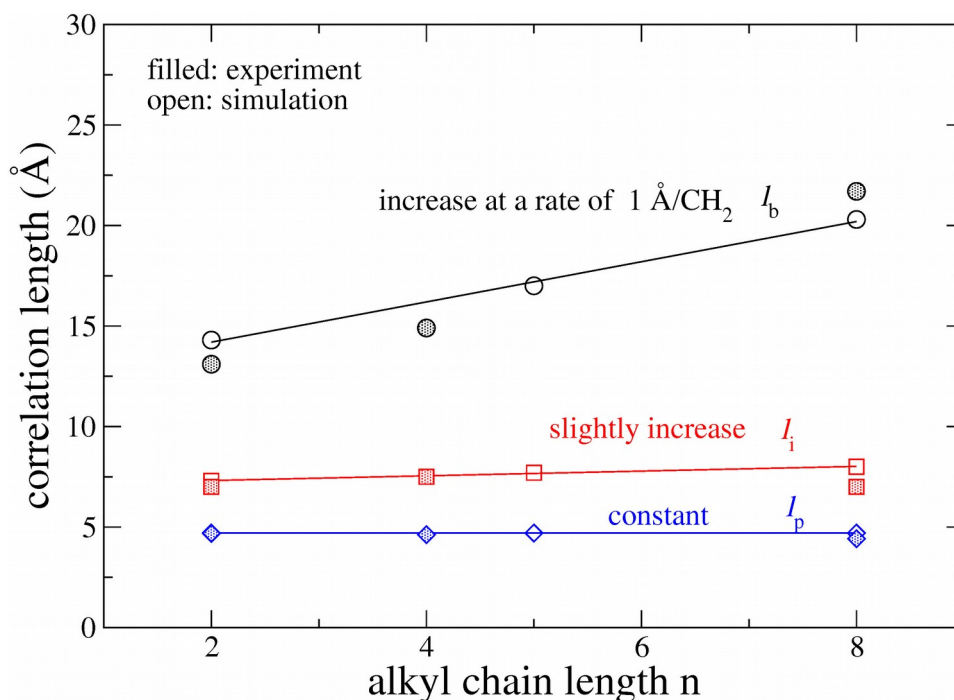


Figure 5: Comparison of correlation lengths of poly(nVim Tf2N) as a function of alkyl side chain length. The lines are the least-squares fitting of simulated data. l_b , l_i and l_p are the backbone-to-backbone correlation length, ionic correlation length and pendant-to-pendant correlation length, respectively.

Structural analysis using radial distribution functions of poly(nVim Tf2N) demonstrates the existence of a continuous polar network composed of cationic heads and anions of the polyILs. Figure 6 shows several representative snapshots of poly(nVim Tf2N) to highlight the percolating npolar network and progressive increase of the nonpolar domains as the alkyl chains become longer along the homologous series. Concomitant with increasing backbone-to-backbone correlation length, discrete nonpolar islands first form within the continuous polar network, then nonpolar domains grow beyond the percolation threshold, finally interconnect with the polar network into a bicontinuous 'sponge-like' nanostructure, as quantified by the cluster size distribution of nonpolar domain in Figure 7(b). This evolution progression appears similar to their molecular counterparts. It is noteworthy to stress the importance of proper identification of cutoff threshold for the definition of connectivity in the cluster analysis algorithm. The deconvolution of first coordination peak of radial distribution function⁴ poses a clear advantage as demonstrated in Figure 7(a).

In summary, we have carried out extensive atomistic MD simulations for a homologous set of poly(nVim Tf2N), in which we varied the alkyl side chain length in order to directly compare with experiment. The total X-ray structure factor was calculated using the direct method.

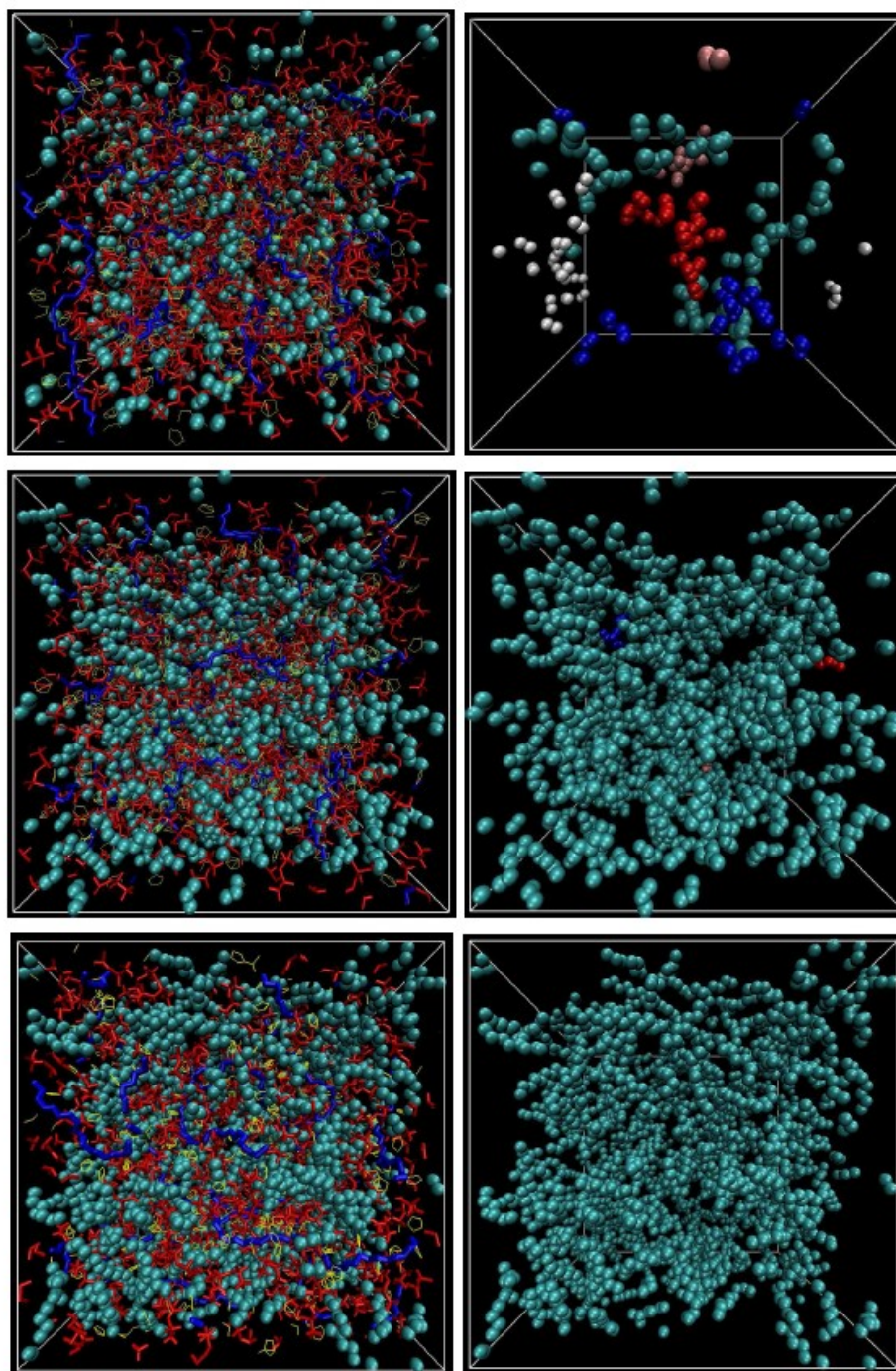


Figure 6: Representative snapshots of poly(*n*Vim Tf₂N) (*n* = ethyl, pentyl, and octyl from top to bottom) in perspective. Left panels are shown for all (anions are denoted as red bonds, cationic side chains as cyan spheres, cationic imidazolium rings as yellow lines, cationic backbones as blue bonds, and all H atoms are omitted for clarity.) Right panels depict the nonpolar domain where individual clusters are colored via the cluster analysis. The largest cluster is colored in cyan. Only the clusters with a size greater than 20 carbon are shown for poly(eVim Tf₂N). The simulation box sizes are 56.0, 60.0, 63.0 Å for *n* = ethyl, pentyl, and octyl, respectively.

We observed excellent agreement between atomistic simulations and experimental X-ray scattering results. Specifically, three characteristic peaks below 2 \AA^{-1} can be identified: low-q backbone-to-backbone peak, immediate ionic peak and high-q pendant-to-pendant peak. As the alkyl chain length increases, the backbone-to-backbone peak becomes stronger, moving to larger distance, the anion-to-anion separation slightly increases with weaker intensity, and the pendant-to-pendant or close contact peak remains essentially intact. This quantitative comparison of X-ray scattering and atomistic simulations is a step towards a molecular-level understanding of the structure and morphology of polyILs.

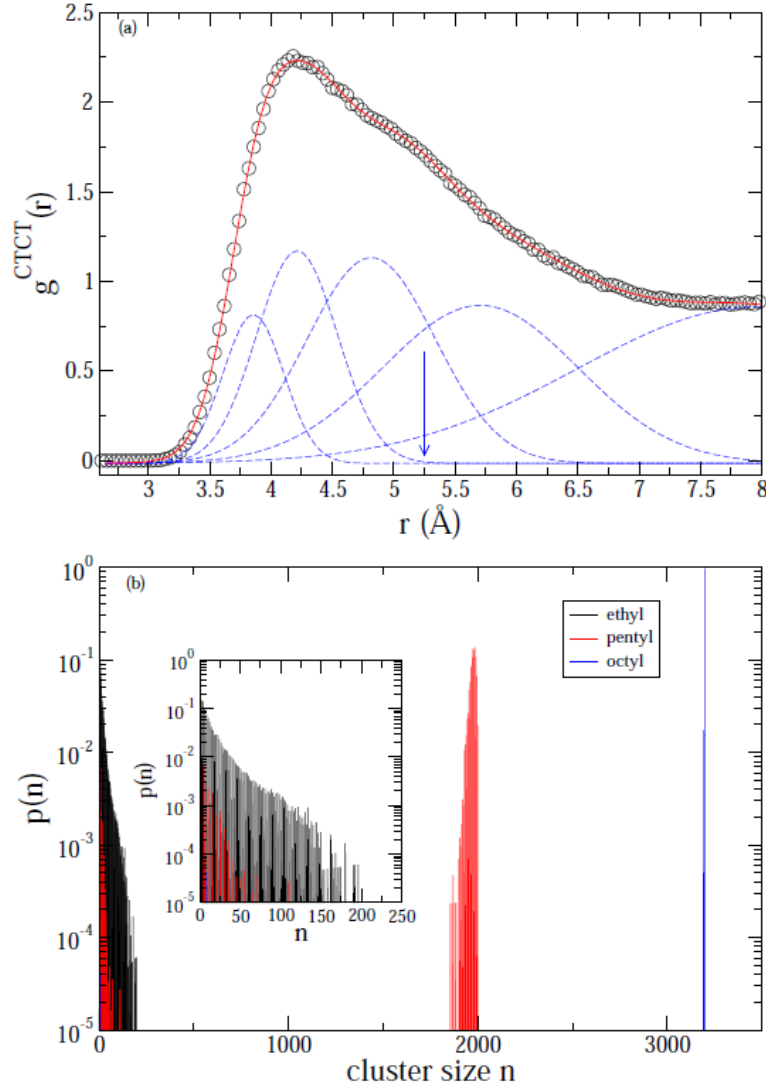


Figure 7: (a) Deconvolution of radial distribution function of terminal carbons of poly(pVim Tf2N). The open circles are the RDF data, the dashed lines are the deconvolution results of the first coordination peak using a series of Gaussian functions, and the solid lines are the fitted curves. The limit of the strongest Gaussian peak is denoted by arrows as the cutoff for the definition of connectivity. (b) Cluster size distribution of nonpolar domains of poly(nVim Tf2N) using the cutoffs obtained from the RDF deconvolution.

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Conferences

“Quantitative Comparison of Atomistic Molecular Dynamics Simulations and X-Ray Scattering of Polymerized Ionic Liquids”, **229th ECS Meeting**, San Diego, CA May 29 - June 3, 2016.

Journal Papers

Direct calculation of the X-ray structure factor of ionic liquids. Hongjun Liu and Stephen J. Paddison. **Phys. Chem. Chem. Phys.**, 2016, **18**, 11000-11007

Direct Comparison of Atomistic Molecular Dynamics Simulations and X-ray Scattering of Polymerized Ionic Liquids. Hongjun Liu and Stephen J. Paddison. **ACS Macro Lett.**, 2016, **5**, 537–543