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RPPR Final Report

as of 19-Apr-2018

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INVESTIGATOR(S):

Name: Venkat Ganesan
Email: venkat@che.utexas.edu
Phone Number: 5124714856
Principal: Y

Organization: **University of Texas at Austin**

Address: 101 East 27th Street, Austin, TX 787121532

Country: USA

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Title: Multiresolution Simulation Approaches For Elucidating the Morphology-Property Correlations in Block Copolymer Membranes

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Email: venkat@che.utexas.edu

Phone: (512) 471-4856

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Major Goals: Electrochemical devices such as batteries and fuel cells have recently become popular in the quest for clean and sustainable energy sources. Electrolytes that facilitate ion transport between electrodes are key components in such devices, and polymeric membrane materials have emerged as attractive candidates for such functions. However, high ionic conductivities in polymeric materials are often obtained in rubbery polymers which lack the requisite mechanical strength for solid state batteries. In an effort to enhance the mechanical properties of such polymer membranes, a variety of strategies have been explored, such as cross-linking of the conductive homopolymers, use of inorganic fillers (to create polymer nanocomposite membranes) and using diblock copolymers in which a mechanically strong block complements the conducting phase. While experiments have successfully demonstrated that the enhancement in the mechanical properties can be achieved without a concomitant deterioration of the conductivity and/or other transport properties, a number of intriguing observations have also been noted in the dependencies of transport properties upon the physicochemical parameters characterizing the polymer membranes:

(i) In the context of nanocomposite membranes, the addition of nanoscale particles have in some instances been shown to enhance the conductivity of the matrix above that of the pristine polymer matrix. Moreover, such enhancements were shown to be highly sensitive to the size, the loading, and the type of the nanofillers. Such observations contradict the conventional wisdom which would suggest that addition of (non-conducting) particles would block the diffusion pathways (by a factor which depends only the loading of the fillers) and lead to reduction in the conductivity of the ions. While a number of reasons have been proposed to explain these observations, a clear understanding of the influence of nanoparticles on the conformations and dynamics of the polymers and in turn on the coordination behavior and motion of ions has not yet emerged.

Goal 1: To use multiscale computer simulations to elucidate the mechanisms underlying conductivities and mechanical properties of polymer-nanoparticle mixtures. In this context, we propose to clarify the influences of polymer-nanoparticle, polymer-ion and ion-nanoparticle interactions and identify the conditions which promote enhancements in conductivity and/or mechanical properties.

(ii) In the context of block copolymer based membranes, a number of intriguing observations have been noted in the context of the block copolymer architecture and conductivity changes across order-disorder and order-order transitions. For instance, the conductivity of self-assembled lamellar block copolymer membranes was shown to increase with an increase in the molecular weight of the block copolymer at a fixed composition of the block copolymer, whereas the conductivity of the corresponding homopolymer decreases with increase in the molecular

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weight. A microscopic understanding of the mechanistic origins of such behaviors is still lacking.

Goal 2: To develop a new multiscale simulation approach to study the properties of self-assembled morphologies of block copolymer membranes and use such to elucidate the mechanisms underlying transport properties of such systems.

(iii) Ionic liquids (ILs) exhibit excellent properties including low vapor pressure, high thermal stability, nonflammability and large ionic conductivities at ambient temperatures. Due to these unique properties at ambient temperatures, ILs find numerous industrial applications such as gas storage, photovoltaics, heat transfer fluids, solvents, energy and batteries. Owing to their excellent conducting behavior, ILs are being used as electrolytes as well as solvents in polymer electrolytes to increase the conductivity of polymer electrolytes for battery applications. Transport properties of ions in polymer electrolytes containing ionic liquids as solvents has emerged as an important research area. The addition of ILs into the polymer electrolyte possess the advantage of high conductivities offered by ILs and mechanical stability offered by polymer electrolyte simultaneously where ILs are solidified by polymers. The observed ionic conductivities in such materials are found to be decoupled from the polymer segmental motion indicating a high mechanical stability of the resulting polymer/IL electrolyte.

Goal 3: Develop a multiresolution/multiscale computer simulation approach to study the electrochemical properties of polymerized ionic liquids and their block copolymer versions.

Accomplishments: Please attached document with figures.

Training Opportunities: This project involved the combined efforts of a graduate student and a postdoctoral scholar. The graduate student is continuing his doctoral research and plans to embark on an industrial position upon successful defense of his thesis. The postdoctoral scholar has completed his study and has gone onto accept a position as a research scholar in a different university.

Both the graduate student and the postdoctoral scholar were involved in analysis of the results and writing of the multiple articles describing the studies. Significant input and mentoring was provided in all stages of this process to render the content upto the standard of publication quality articles. In addition, relevant opportunities for professional development and networking were ensured by enabling their participation in annual meetings of American Physical Society and American Chemical Society.

Results Dissemination: The results have been communicated by three means:

(i) Peer-reviewed publications in major journals.

(ii) Presentations (both invited and contributed) in major societal meetings (American Physical Society, American Institute of Chemical Engineers, American Chemical Society).

(iii) Invited seminars in departments and symposia.

(iv) Invited seminars at Army Research Labs.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: This project involved collaborations with h Dr. Craig Knox and his team at the Edgewood ARL. The team at ARL study the diffusion of penetrants and nerve agents in polymer matrices. We adapted our programs for this purpose, and provided preliminary results indicating agreement with simulations (from their side) which were much more computationally intensive. Our first results on calibrating the diffusivities (and the transfer of programs, results and expertise) proved attractive enough for the collaborators to pursue an extension to multiple component systems.

PARTICIPANTS:

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Participant Type: PD/PI

Participant: Venkat Ganesan

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Santosh Mogurampelly

Person Months Worked: 8.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Vaidyanathan Sethuraman

Person Months Worked: 8.00

Funding Support:

Project Contribution:

International Collaboration:

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Other Collaborators:

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Date Submitted:

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Article Title: Improving Energy Relay Dyes for Dye Sensitized Solar Cells by Increasing Donor Homotransfer

Authors:

Keywords: solar cells

Abstract: The use of energy relay dyes in dye sensitized solar cells presents an opportunity to improve efficiency by increasing the range of absorption of the solar spectrum. In experiments, relay dyes have achieved high efficiency of energy transfer to the sensitizing dye, but the overall power conversion efficiencies of the solar cells is not yet competitive with single-dye dye sensitized solar cells. Using kinetic Monte Carlo simulations, we explored how energy transfer among relay dyes affects the energy transfer to sensitizing dyes and found that high concentrations of energy relay dyes with high rates of homotransfer (a large donor-to-donor Förster radius) can be used to improve the efficiency of excitation transfer to the sensitizing dyes. We examined the effect of Förster radii, quenching, pore size, and dye concentration on the excitation transfer efficiency. The improved understanding of the interplay between the donor–donor and donor–acceptor Förster transfer radii effectively relaxe

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Publication Identifier: 10.1021/ma501014u

Volume: 0

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Date Submitted:

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Article Title: Interplay between Depletion and Electrostatic Interactions in Polyelectrolyte–Nanoparticle Systems

Authors:

Keywords: depletion, electrostatic interactions

Abstract: We use a numerical implementation of polymer self-consistent field theory to study the effective interactions between two spherical particles in polyelectrolyte solutions. We consider a model in which the particles possess fixed charge density and the polymers contain a prespecified amount of dissociated charges. We quantify the polymer-mediated interactions between the particles as a function of the particle charge, polymer concentrations and particle sizes. We study the interplay between depletion interactions, which arise as a consequence of polymer exclusion from the particle interiors, and the electrostatic forces which result from the presence of charges on the polymers and particles. Our results indicate that for weakly charged and uncharged particles, the polymer-mediated interactions predominantly consist of a short-range attraction and a long-range repulsion. When the particle charge is increased, the interactions become purely repulsive. A longer range, albeit weaker, bridging

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Article Title: Efficacy of Different Block Copolymers in Facilitating Microemulsion Phases in Polymer Blend Systems

Authors:

Keywords: block copolymers

Abstract: Polymeric microemulsions are formed in a narrow range of phase diagram when a blend of immiscible homopolymers is compatibilized by copolymers. In this study, we consider the ternary blend system of A and B homopolymers mixed with block copolymers containing A and B segments and probe the efficacy of different copolymer configurations in promoting the formation of microemulsion phases. Specifically, we consider (a) monodisperse diblock copolymers (D), (b) diblock copolymers with bidisperse molecular weights (MW) (BDL), (c) block copolymers having MW polydispersity in one of the blocks (PD), (d) diblock copolymers having monodisperse MW but bidispersity in average composition (BDC), and (e) gradient copolymers exhibiting a linear variation in the average composition (G). Using single chain in mean field simulations effected in two dimensions, we probe the onset of formation and the width of the bicontinuous microemulsion channel in the ternary phase diagram of homopolymer blended with c

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Article Title: Ordering poly(trimethylsilyl styrene-

Authors:

Keywords: block copolymers, solvents

Abstract: Controlling the morphology, domain orientation, and domain size of block copolymer (BCP) thin films is desirable for many applications in nanotechnology. These properties can be tuned during solvent annealing by varying the solvent choice and degree of swelling which affect the effective miscibility and volume fraction of the BCP domains. In this work, we demonstrate with a bulk lamellae-forming BCP, poly(4-trimethylsilylstyrene-block-D,L-lactide) (PTMSS-b-PLA), that varying the composition of a mixture of solvent vapors containing cyclohexane (PTMSS-selective) and acetone (PLA-selective), enables formation of perpendicularly oriented lamellae with sub-20-nm pitch lines. The BCP domain periodicity was also observed to increase by 30%, compared to bulk, following solvent annealing. Furthermore, solvent annealing alone is shown to induce a transition from a disordered to an ordered BCP. We rationalize our observations by hypothesizing that the use of a combination of domain selective sol

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Article Title: Influence of Block Copolymer Compatibilizers on the Morphologies of Semiflexible Polymer/Solvent Blends

Authors:

Keywords: semiflexible polymers, compatibilizers

Abstract: We study the influence of block copolymer (BCP) compatibilizers on the domain and interfacial characteristics of the equilibrium morphological structures of semiflexible polymer/solvent blends. Our study is motivated by the question of whether block copolymer compatibilizers can be used to influence the phase separation morphologies resulting in conjugated polymer/fullerene blends. Toward this objective, we use a single chain in mean field Monte Carlo simulations for the phase behavior of semiflexible polymer/solvent blends and study the influence of BCP compatibilizers on the morphologies. Our results reveal a range of blend compositions and molecular chemistries that result in equilibrium structures with domain sizes on the order of 5–20 nm. To elucidate the morphological characteristics of these structures, we first present a series of ternary phase diagrams and then present results demonstrating that the blend composition, semiflexible chain rigidity, BCP composition, and component

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Article Title: Computer Simulations of Dendrimer–Polyelectrolyte Complexes

Authors:

Keywords: dendrimers, polyelectrolytes

Abstract: We carry out a systematic analysis of static properties of the clusters formed by complexation between charged dendrimers and linear polyelectrolyte (LPE) chains in a dilute solution under good solvent conditions. We use single chain in mean-field simulations and analyze the structure of the clusters through radial distribution functions of the dendrimer, cluster size, and charge distributions. The effects of LPE length, charge ratio between LPE and dendrimer, the influence of salt concentration, and the dendrimer generation number are examined. Systems with short LPEs showed a reduced propensity for aggregation with dendrimers, leading to formation of smaller clusters. In contrast, larger dendrimers and longer LPEs lead to larger clusters with significant bridging. Increasing salt concentration was seen to reduce aggregation between dendrimers as a result of screening of electrostatic interactions. Generally, maximum complexation was observed in systems with an equal amount of net den

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Article Title: Coarse-Graining in Simulations of Multicomponent Polymer Systems

Authors: Coarse-Graining; Multicomponent Polymer Systems

Keywords: simulations

Abstract: We investigate the mapping required between the interaction parameters of two different coarse-grained simulation models to ensure a match of the long-range structural characteristics of multicomponent polymeric system. The basis for our studies is the recent work of Morse and workers, which demonstrated the existence of a mapping between the interaction parameters of different coarse-grained simulation models which allows for a matching of the peak of the disordered state structure factor in symmetric diblock copolymers. We extend their results by studying a variety of systems, including, asymmetric diblock copolymers, symmetric triblock copolymers and diblock copolymer-solvent mixtures. By using the mapping deduced in the context of symmetric diblock copolymers, we observe excellent agreement for peak in the inverse structure between both two popular coarse grained models for all sets of polymeric systems investigated, thus providing strong support to the transferability of the mappi

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Article Title: Directed self assembly of block copolymers using chemical patterns with sidewall guiding lines, backfilled with random copolymer brushes

Authors: Gunja Pandav, William J. Durand, Christopher J. Ellison, C. Grant Willson and Venkat Ganesan

Keywords: self-assembly; lithography;

Abstract: Recently, alignment of block copolymer domains has been achieved using a topographically patterned substrate with a sidewall preferential to one of the blocks. This strategy has been suggested as an option to overcome the patterning resolution challenges facing chemoepitaxy strategies, which utilize chemical stripes with a width of about half the period of block copolymer to orient the equilibrium morphologies. In this work, single chain in mean field simulation methodology was used to study the self assembly of symmetric block copolymers on topographically patterned substrates with sidewall interactions. Random copolymer brushes grafted to the background region (space between patterns) were modeled explicitly. The effects of changes in pattern width, film thicknesses and strength of sidewall interaction on the resulting morphologies were examined and the conditions which led to perpendicular morphologies required for lithographic applications were identified. A number of density multi

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Article Title: Interactions and Aggregation of Charged Nanoparticles in Uncharged Polymer Solutions

Authors: Gunja Pandav, Victor Pryamitsyn, Venkat Ganesan

Keywords: Particle-polymer mixtures; aggregation; clustering

Abstract: We employ an extension of the single chain in mean field simulation method to study mixtures of charged particle and uncharged polymers. We examine the effect of particle charge, polymer concentration and particle volume fraction on the resulting particle aggregates. The structure of aggregates were characterized using particle-particle radial distribution functions and cluster size distributions. We observe that the aggregation between particles increase with increasing particle volume fraction and polymer concentration, and decreasing particle charge. At intermediate regimes of particle volume fraction and polymer concentrations, we observe the formation of equilibrium clusters with a preferred size. We also examined the influence of multibody effects on the structure of charged particle-polymer system. Our results indicate that the effective two-body approximation overpredicts the aggregation between particles even at dilute particle concentrations. Such effects are implicated to be a co

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Final Project Report

Background: Recently, polymer electrolyte membrane materials have emerged as attractive candidates for devices such as batteries, fuel cells and for applications such as water purification membranes. Unfortunately, electrolyte membrane materials possessing high ionic conductivities often tend to lack the requisite mechanical strength for applications. In this context, significant interest has arisen in the use of ordered phases of multicomponent block copolymers, in which one or more of the blocks (glassy) serves to furnish mechanical strength to the membrane while the other "functional" (rubbery) block facilitates transport of ions and permeants. Inspired by the successes in the context of polymer electrolytes, other studies have extended this general idea to design alcohol separation membranes, fuel cells etc.

Ion Distributions in Diblock Copolymer Lamella

We have been pursuing an "inverse coarse-graining" approach which uses soft coarse-grained interaction potentials to create the equilibrium configurations of self-assembled morphologies, and then reintroduce (progressively, if needed) finer scale details. In earlier work, we demonstrated the manner in which the parameters in the coarse-grained simulations can be chosen such that they correspond to some appropriate coarse-grained macroscopic interactions characterizing the polymer monomers or segments of the finer scale model and implemented on a bead-spring polymer melt test system.

In the present period of effort, we extended the above developments to achieve a full scale reverse mapping of atomistic simulations. Figure 1(a) displays the mass density profiles of various components of the block copolymer as a function of distance along the box. The density profiles of PS and PEO are characteristic of phase-separated block copolymers. The ion-doping was introduced at random with equal probabilities on any site in the box. However, at the end of about 15 ns, it can be clearly seen that the ions are redistributed in such a way that most of the Li^+ ions aggregate in the PEO domain compared to that of the PS domain. Such trends can be attributed to the partial negative charges in the oxygen atoms in the PEO domain. The PF_6^- ions follow a density profile similar to that of the Li^+ ions. Figure 1(b) displays a snapshot of the equilibrated Li- PF_6 doped PS-PEO system.

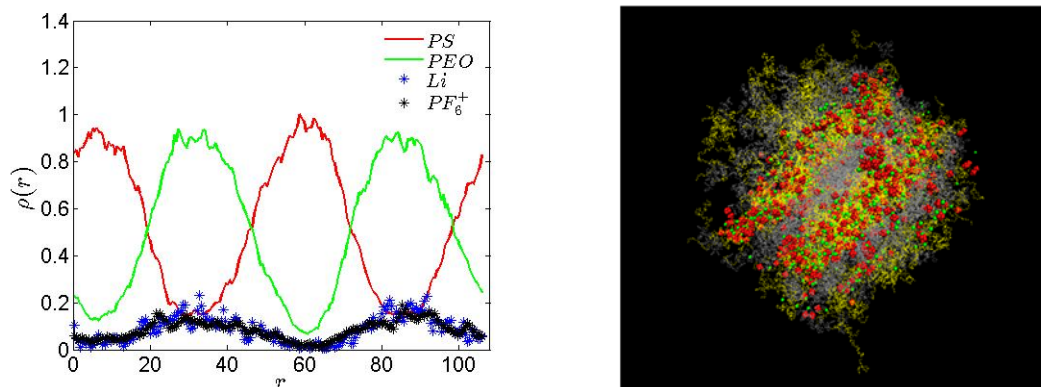


Figure 1: (a) Mass density profiles as a function of distance along the box. The mass densities of Lithium ions are scaled by the ratio of masses of Lithium to PF_6^- to appear visible in the plot. (b) Snapshot of the equilibrated block copolymer system.

Lithium Coordination with PEO Molecules.

From the discussion pertaining to Figure 1, it was clearly demonstrated that the ions preferentially segregate into the PEO phase. Here, we characterize the coordination of Li^+ ions with the specific EO atoms based on the placement of the latter groups along the chain and contrast the results for BCP with homopolymers.

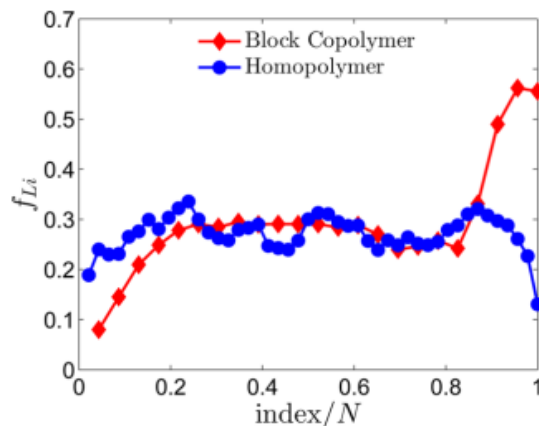


Figure 2. Normalized fraction of lithium ions bound to each oxygen atom of the chain relative to the total number of lithium ions in the PEO phase

Towards the above objective, we computed the fraction of the number of cations (f_{Li}), defined as the number of cations that are within the first coordination shell of each EO atom ($r \leq 2.4 \text{ \AA}$) relative to the total number of coordinated cations in the copolymer (or homopolymer) system, as a function of EO monomer index along the chain. We indexed EO atoms starting at the link position, with the terminal oxygen in the PEO block. In Figure 2, we display f_{Li} as a function of the EO atom positions along the chain. For the case of homopolymers, the distribution of lithium ions across different oxygens are seen to be almost uniform, with a slight dip near the end of the chains arising from end-effects accompanying the small MW chain. In contrast, in the case of block copolymers a stronger heterogeneity can be seen, with a larger fraction of lithium ions binding with the EO segments toward the end of the PEO chain accompanied by a depletion in binding characteristics with the EO monomers in proximity to the PS-PEO link positions. Such differences arise because the oxygen atoms corresponding to the EO units near the link position are localized near the interfacial region of the lamella accompanied by a lower density of lithium ions (Figure 1). In contrast, the oxygen atoms toward the end of the chain are concentrated toward the bulk of the PEO domain which is characterized by a higher density of lithium ions (Figure 1).

Ion – Polymer Coordination.

Further to understanding the coordination of ions along the backbone of the chain, comparisons between various radial distribution functions in the ion-doped, self-assembled PS-PEO block copolymer system and ion-doped PEO homopolymer system were effected. Figure 3(a) presents the RDF for the coordination between EO atoms and the Li^+ cations, wherein a peak, corresponding to the averaged van der Waals radii of the lithium–oxygen atoms is seen at $r = 1.9 \text{ \AA}$ in both homopolymers and block copolymers. Interestingly, the averaged strength of coordination of Li–EO is seen to be larger in the BCPs compared to pure PEO homopolymer melts. However, upon closer examination, the intensity of Li–EO peak in the PEO domain is seen to be almost identical to the results for pure PEO homopolymer melt. In contrast, the strength of Li–EO coordination is found to be much higher in the PS domain. Such trends can be rationalized by identifying that there exists a smaller number of EO atoms in the PS domain compared to that in the PEO

domain. Hence, the cations in the PS domain are more strongly bound to the available EO atoms whereas such association is more evenly distributed in the PEO domain owing to the larger number of EO atoms.

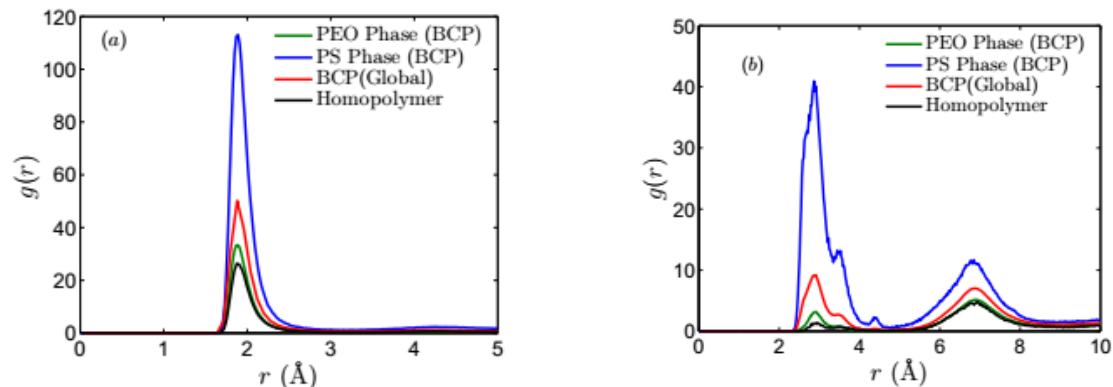


Figure 3: Radial distribution functions for (a) Li–O and (b) Li–PF₆ in PEO and PS domain separately. For comparison, the global averaged RDF in BCP and homopolymer are also shown.

Figure 3(b) displays the global and domain specific RDFs between cations and anions. Similar to the lithium–oxygen RDF displayed in Figure 3(a), the cation–anion coordination is also seen to be enhanced in the PS domain compared to that in the PEO domain. To understand such results, we note that in the PS domain the potential partners for the Li⁺ ions constitute the PF₆[−] ions and the smaller number of EO atoms present therein. In contrast, in PEO domain, there is a larger concentration of EO atoms, and therefore the binding of cations is expected to be stronger with the anions in the PS domain compared to that in the PEO domain. Such a coordination behavior causes the averaged (global) cation–anion RDF of BCPs to display a stronger peak compared to its homopolymer counterparts.

Ion motion in polymerized ionic liquids

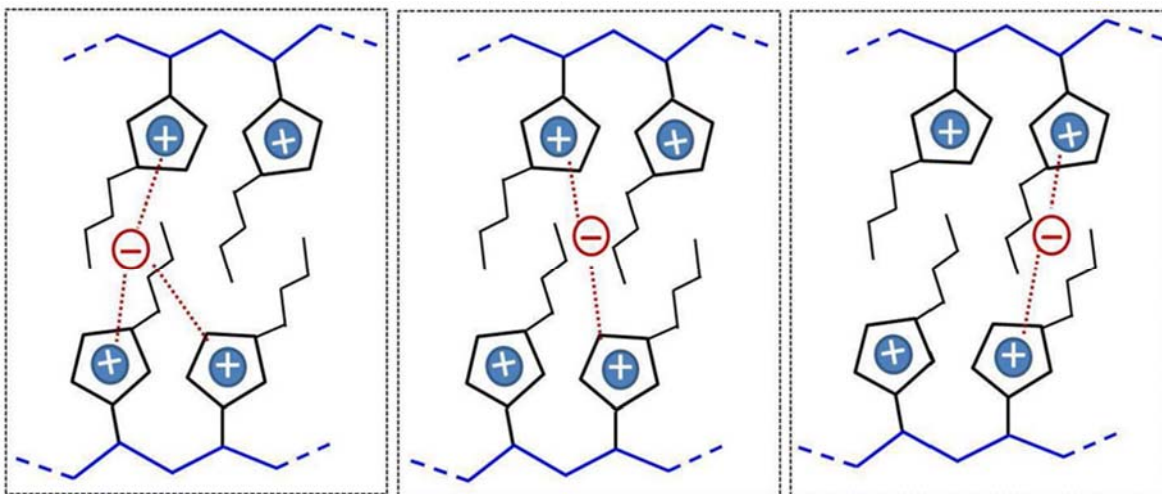
Recently, significant interest has arisen in ionic liquids (ILs) for a variety of applications such as gas storage, photovoltaics, heat transfer fluids, energy storage and batteries.^{4–8} Such an interest stems from the novel physical properties of ILs such as low vapor pressure, high thermal stability and nonflammability. In particular, ILs possess excellent ionic conducting properties at ambient temperatures, and are being explored for battery applications as an additive to polymer-salt binary electrolytes, which often possess requisite mechanical strengths but lack the desired room temperature conductivities. In this context, polymerized ionic liquids (polyILs) have emerged as a new class of novel polymer electrolytes consisting traditional ionic liquid (IL) monomers as their repeating units.^{9–12} PolyILs combine unique physicochemical and conductivity characteristics of ILs and noteworthy mechanical stability of solid polymer electrolytes. Moreover, in conventional salt doped polymer electrolytes, the high mobility of the anions causes them to accumulate at the electrode-electrolyte interface, resulting in concentration polarization, which increases the internal resistance. In contrast, polyILs are in the category of single ion conducting electrolytes in which the cations/anions are the sole mobile species, and therefore exhibit transference numbers close to unity and help eliminate concentration polarization.

In recent work, we used atomistic molecular dynamics to study the molecular mechanisms underlying ion transport in poly(1-butyl-3-vinylimidazolium-hexafluorophosphate) electrolytes blended with varying concentration of 1-butyl-3-methylimidazolium-hexafluorophosphate ionic liquids. Towards this objective, we developed the force field parameters for the intramolecular potentials by considering *ab-initio* quantum mechanical calculations.¹³ The force constants for the harmonic bonds and angles were evaluated from the

calculation of Hessian normal mode frequencies at the same level of theory by employing force field plugin available through visualizing molecular dynamics (VMD) package.

The diffusion coefficient of BMIM^+ and PF_6^- ions were calculated from the corresponding mean squared displacement curves, and was found to decrease monotonically with increasing polyIL:IL ratio at all the temperatures investigated. In an effort to rationalize our simulation results, we used a number of measures to characterize the coordinate behavior and time scales involved in the transport and pairing of the cation and the anion of the ionic liquid. Based on our MD simulations, we identified that the ability of polymerized ionic liquid electrolyte to influence structural relaxation of ion-pairs and aggregation is the key mechanism for the transport of ions.

To understand how the anions diffuse in the polyIL electrolytes, we analyzed various hopping events exhibited by anions. For this purpose, we decomposed all possible transport events into primarily three main categories: (a) Anion hopping events along polymer backbone by means of the formation and breaking of ion-pairs with polymerized cations, (b) Anion hopping events between different polymer chains, and (c) Anion hopping from polymer chains to free medium and vice-versa. We quantified the hopping event analysis by calculating the probability of anion association with N number of chains as well as n number of polymerized cationic monomers. We recall that in the absence of polymer chains the anion diffusion is achieved by means of ion-pair formation and breaking. Our results indicated that similar ion association prevails at polyIL:IL=25:75 due to the availability of large number of non-polymerized cations compared



to polymerized cationic monomers. As the polyIL:IL ratio increases, there was a clear transition of anion associations from *zero* chains to higher number of chains. At intermediate polyIL:IL ratios of 50:50 and 75:25, a given anion prefers to associate more likely with *two* polymerized cationic monomers of the same polymer chain. Interestingly, the anion association with *three* monomers is also seen to be equally probable at polyIL:IL=75:25 ratio. This suggests an anion transport mechanism being occurred via formation and breaking of the non-polymerized cation-anion pairs to polymerized cation-anion pairs.

In future work, we propose to build on the above preliminary results and combine with the recent “coarse-graining” and “fine-graining” simulation methodologies discussed in the context of background. Using such a combination of techniques, we seek to probe the mechanisms underlying *ion motion in block copolymerized polymer ionic liquids*, which has recently attracted significant interest.

