CHAPTER I

INTRODUCTION

There has long been interested in the development of lithium-ion batteries for more efficiency and safety with potential usage in various applications. From the beginning, these batteries are composed of organic liquid electrolytes with high ionic conductivity. However, liquid electrolytes usually have low thermal stability, high flammability, toxic, restrictive electrochemical stability window, and no hindrance to dendrite expansion. The major challenge to these problems is to achieve a long battery life (charge-discharge cycle) with high conductivity (Tarascon, 2001; Quartarone, 2011; Manthiram, 2017).

Molecular simulations at fully atomistic scale of polymeric materials have been developed since 1980s to investigate molecular and material properties (Kotelyanskii, 2004). Most early works had been focused on synthetic polymers with structurally simple and nonpolar polyolefins. The earlier methods were often simplified by the models such as "united" atoms to reduce the computational cost. A method to generate amorphous polymeric materials at fully atomistic scale was first reported for atactic polypropylene glasses (Theodorou, 1985). In general, atomistic simulation of polymeric materials requires accurate conformational statistics for generation of initial guess structure and readily equilibration afterward. Thus, the crucial step for polymer simulations is to find a way to generate the realistic molecular model especially for chain conformation and interatomic correlation function.

The rotational isomeric state (RIS) models of PVF and PVC had been derived from ab initio electronic structure calculation. The RIS calculation predicted a higher chain stiffness (larger characteristic ratio) for PVC than PVF chain at all meso diad content. PVF and PVC chains were then coarse-grained by grouping each monomer unit into one bead and mapped onto the second nearest diamond (2nnd) lattice. The fully atomistic models of amorphous PVF and PVC structures can be obtained through the reverse-mapping procedure to restore the missing atoms followed by energy minimization. To validate these atomistic models, some molecular and material properties of amorphous structures were determined and compared with experimental data including conformational statistics, solubility parameters and the static structure factor.

Polymer surface is an essential part of various technological applications (Feast, 1987). Their importance covers many issues in designing high-performance materials including wettability and contact angle, interactions and reactions at surfaces, tribology, adhesion and adsorption, and surface modification (Mittal 1 and 2, 1983). There have been numerous past studies on the structures and properties of polymer surfaces (Garbassi, 1994) and a better understanding should provide the great capacity to alter the chemical structure of polymer chains to improve surface properties to meet specific purposes (Stamm, 1992). Properties of polymers near the surfaces can be remarkably different from the bulk structures including local density, conformation, chain size/shape, and bond/chain orientation which can be varied at different positions from the surface (Forrest, 1992). The role of chain stiffness on structural and molecular properties for the free surface of polymer melts was examined by Monte Carlo (MC) simulations of the coarse-grained (CG) polyethylene-like chains on the second nearest neighbor diamond (2nnd) lattice. Polyethylene-like model by multiplying the statistical weights with the chain stiffness parameter (k) to represent more flexible (k = 0.0 and 0.5) and stiffer (k = 1.5 and k = 2.0) chains than normal polyethylene (k = 1.0). For the melt-vacuum surfaces of stiffer chains, bulk densities become lower with broader surface profiles. For more flexible chains, monomers at the end/middle position are more segregated/depleted near the surface. The chain stiffness arising from barriers to bond rotation and structural constraints are closely related to the macroscopic properties of polymers. For computer simulation, the degree of local flexibility can be adjusted by manipulating the intramolecular energetics can affect the molecular and structural properties of polymer surfaces. In principle, the simulation of fully atomistic models should provide the most detailed information as one can consider the specific chemistry of polymer chains.

The first SPE was reported in the 1970s using poly (ethylene oxide), PEO (Fenton, 1973; Wright, 1975). For ionic conductivity in alkali metal-PEO complexes, it has been proposed that metal ions work as charge carriers in the non-crystalline phase of the polymer host. Ionic diffusion occurs through the formation and dissociation of the coordination structure between cations and oxygen atoms in PEO (Ratner, 1988). The disadvantage of PEO is a very low metal ion transportation caused by the crystallization and trapping effects due to the strong coordination between the PEO backbone and metal ions (Capiglia, 1999; Zhang, 2014; Itoh, 2017;). In addition, the poor mechanical, thermal stability and semi-crystalline property of PEO reduce its efficiency as SPEs. Although inorganic salt can be dissolved well in PEO, the ionic conductivity of SPEs is 10^{-8}-10^{-5} Scm^{-1}, still lower than 10^{-3} Scm^{-1} for practical applications.

Therefore, the role of the intermolecular interaction related to the chain packing in the condensed phase, which can be intimately associated with polymer crystallization. The role of the intermolecular interaction related to the chain packing in the condensed phase, which can be intimately associated with polymer crystallization. Monte Carlo (MC) simulations of coarse-grained (CG) polyethylene (PE)-like models with different non-bonded interaction parameters between monomer beads were proposed to study the effect of intermolecular interaction on polymer crystallization from the molten state. It is also very important for technological application because more than 60% of industrial polymers are semi-crystalline materials and their functional properties are closely connected with polymer morphologies. Crystallization of flexible chains, with many intrinsic bond conformations, contains complex dynamics over broad lengths and time scales, spanning from large-amplitude molecular motions to atomic-scale rearrangements to optimize crystal order.

Polymer electrolytes are an attractive option to substitute liquid solutions due to their thermal stability and high flexibility (Hallinan, 2013). Polymer electrolytes can be divided into two groups: solid and gel electrolytes. Solid polymer electrolytes (SPEs) are electrolytes in which alkali salts can be dissolved in the appropriate polymers. The host polymers play a role in the diffusion of alkali ions through the local movement of chain segments. The first SPE was reported in the 1970s using poly (ethylene oxide), PEO (Fenton, 1973; Wright, 1975).

Ionic liquids (ILs) have been studied as solvents for polymerization reactions. Most recently, ILs have been shown to be good solvents for radical polymerizations due to their superior properties compared to conventional liquid electrolytes, are organic salts in the liquid state at room temperature. ILs contain cations and anions with low melting temperatures and exhibit high ionic conductivity with good electrochemical stability (Holbrey, 1999; Olivier-Bourbigou, 2010; Lei, 2017). Polymer-in-salt gel membranes have been prepared straightly by polymerization of vinyl monomers in ILs and by polymerization of ILs integrating polymerizable functions. It looked like a formation of IL-polymer gels, such as are explained by Watanabe and Mizumura (Watanabe, 1996), resulting from the plasticizing effects of the IL on the polymer matrix. The togetherness of some ILs with polymers can be advantageous in polymer processing to build plasticized materials. ILs are capable of holding imidazolium or pyridinium cations are identical to some conventional plasticizers, containing an aromatic core and pendant alkyl groups (Cadogan, 2000; Ohno, 2001). Other advantages of ILs depend on their non-flammability and non-volatility which are good for battery applications (Correia, 2018).

The so-called polymer ionic liquids (PILs) are a new subtype of polymer electrolytes that have advantageous properties over simple ionic liquids, such as non-flammability, wide electrochemical windows. and chemical stability. Therefore, it can be used as a promising material for the next generation solid-state battery (Ohno, 2001; Mecerreyes, 2011; Sangoro, 2014; Qian, 2017; Forsyth, 2019; Zhang, 2020). PILs contain charged groups with an ionic liquid structure in the main and/or side chains, which is weakly coordinated with opposite charges counterions. One of the major challenges for the application of polymers such as PIL as electrolytes is to create highly conductive while maintaining strong mechanical properties (Shaplov, 2018; Rochow, 2020; Yoshizawa-Fujita, 2021). Consequently, understanding the structures and dynamics of PILs and counter ions with their correlations is necessary in designing PIL-based materials with better performance.

1.1 Research objectives

1.1.1 To describe the conformational statistics and determine the conformational-dependent properties of vinyl polymer chains using the refined rotational isomeric state (RIS) model based on quantum chemistry calculation.

1.1.2 To generate the atomistic models and to predict material properties of amorphous structures of vinyl polymers and polymerized ionic liquids.

1.1.3 To investigate the role of chain stiffness effect and intermolecular interaction on surface properties and crystallization by Monte Carlo (MC) simulation of polyethylene-like model

1.1.4 To gain more understanding about the structure and property relationship of polymerized ionic liquids based on both experiments and molecular dynamic (MD) simulation.

1.2 Scope and limitation

1.2.1 Molecular simulation

1.2.1.1 **Quantum Chemistry:** for more accurate calculation of the optimized structure and conformational energies of two vinyl polymers (polyvinyl fluoride, PVF and polyvinyl chloride, PVC).

1.2.1.2 **Rotation Isomeric State (RIS) model** for the description of conformational statistics of two vinyl polymers (PVF and PVC). The statistical weights will be refined using quantum chemistry calculation and will be used in the Monte Carlo simulation for the multichain system at the bulk state.

1.2.1.3 **Monte Carlo (MC) simulation**

- For the initial generation and equilibration of amorphous bulk structures of two vinyl polymers (PVF and PVC). Fully atomistic models can be recovered by the reverse-mapping procedure to restore all atoms followed by geometry optimization using the forcefield-based method.

- Coarse-grained “Polyethylene (PE) - like” models on the second nearest neighbor diamond (2nnd) lattice with the chain stiffness parameter (k) to represent more flexible (k = 0.0 and 0.5) and stiffer (k = 1.5 and k = 2.0) chains than normal PE (k = 1.0). And the role of the intermolecular interaction related to the chain packing in the condensed phase, which can study the effect of intermolecular interaction on polymer crystallization from the molten state.

1.2.1.4 **Molecular Dynamic (MD) simulation** to determine the structures and dynamics of polymerized ionic liquids at the atomic scale. This MD technique may be able to give insight about the underlying mechanism of ion mobility and the estimation of theoretical diffusion coefficients of ionic species.

1.2.2 Experiments

In this research is studied to work on both molecular dynamics simulations and experimental studies of polymerized ionic liquids (Pbvim-TFSI) and polymerized ionic liquids-ionic liquids blends (PbvimTFSI-BmimTFSI). Identification transport effects of such blends and consequently specify the feature by which conductivity can be tuned by the addition of pure ILs to polyOLs. Particularly interesting feature is whether the phenomena of “decoupling” from mechanical properties of transport properties monitored in polyIL systems also broaden to their blends with ILs. And to diagnose the mechanisms underlying ion transport of polyIL–pure IL blends. A final purpose underlying our study was to deliberate the conductivity and transference number characteristics of polyIL–pure IL blends and attempt to comprehend the dependence of each property on the blending proportions.