CHAPTER V

CONCLUSION

This thesis investigates multiscale computer simulations were applied to examine molecular determinants that can control structural properties of the host polymers in electrolyte application. To improve the ionic conductivity of polymer electrolytes, some possible paths are proposed to modify the repeating units to adjust the intrachain stiffness and intermolecular interaction that can affect conformational characteristics, molecular dimension, chain perturbation near the surface, crystallization, upon cooling from the melts, atomistic amorphous structures and the degree of ionic dissociation in polymerized ionic liquids.

The First part is multiscale molecular simulations of two polymer hosts for gel electrolytes: PVC and PVF. This part illustrates a multiscale molecular modeling method to generate and equilibrate PVC and PVF models at their amorphous state. The method starts from quantum chemistry calculation to derive the statistical weights of the rotational isomeric state (RIS) model. PVC and PVF chains were then mapped to the coarse-grained (CG) model using the modified RIS model onto the 2nnd lattice. The mapping of PVC and PVF chain can be done by grouping each monomer to one CG bead. The average non-bonded interactions were estimated using the discretized Lennard-Jones (LJ) potential. Coarse-grained PVC and PVF at the bulk density were then generated and readily equilibrated by lattice Monte Carlo simulation. The on-lattice properties were determined including chain conformational statistics and molecular mobility (rotational and translational modes). Dynamics of PVF is faster than PVC about one order of magnitude. The equilibrated PVC and PVF structures from the 2nnd lattice were then reverse-mapped to fully atomistic models. Chain dimension, conformational statistics, structural and thermodynamic properties were determined for both neat PVC and PVF structures. All these results are comparable well with experiment data.

The second part is film stiffness, The effect of chain stiffness on structural and molecular properties of the free surfaces of polymer melts was studied by MC simulation of CG polyethylene-like models. The effect of chain stiffness on structural and molecular properties of the free surfaces of polymer melts was studied by MC simulation of CG polyethylene-like models. For polymer surfaces with more flexible chains, higher bulk densities with sharper surface profiles are obtained. Near the surface, end-bead monomers are more segregated for more flexible chains while middle-bead monomers are more depleted. As a function of chain stiffness, bulk densities become higher and accompanied by sharper surfaces. In general, both bonds and chains adopt random orientation in the structures but tend to have anisotropic orientation near the surface, especially more pronounced for stiffer chains. The molecular dimension has a more compact shape for more flexible chains because of a larger fraction of gauche conformation. Near the surface, chains are more flattened for stiffer chains, especially in the perpendicular direction to the surface. In the bulk region, more flexible chains adopt a larger amount of gauche conformation and have denser structures as evidenced by higher/lower intramolecular/intermolecular energies. In the surface region, however, chains tend to gain more trans conformation and the structures become less dense as indicated by lower/higher intramolecular/intermolecular energies.

The third part is the role of the intermolecular interaction related to the chain packing in the condensed phase, which can be intimately associated with polymer crystallization. Lattice Monte Carlo simulation has been developed to determine the effect of intermolecular interaction of CG PE-like chains on the structural formation during an initial stage under stepwise cooling from the molten state. The conformational characteristics, the bond and molecular orientation, structural packing, intra- and intermolecular bond order parameters were evaluated. The growth of structure formation is generally faster, and the chains can have better-ordered orientation for chains with intermolecular interaction parameters close to the normal PE. The PE-like chains with too attractive or too repulsive intermolecular interaction exhibit poorer crystallization characteristics as chains can adopt a lower amount of trans conformation and have more difficulty in forming the ordered structures. For PE-like polymers with too repulsive interaction, larger fluctuations of the magnitudes of the conformational state and the order parameter are evidenced. For PE-like polymers with too attractive interaction, chains still adopt some amount of gauche conformation at lower temperatures with less degree of chain ordering. Thus, only PE-like chains with intermolecular interaction parameters close to the normal PE can exhibit the ordered structures with a large degree of trans conformation and chain orientation in the ordered structure formation under stepwise cooling from the molten state.

The final part is MD simulation of detailed structures and ion transportation of polymerized ionic liquid/ionic liquid blends. To summarize for the overall results from above, we reported molecular dynamics simulations of the structure, dynamical and ion transport properties of imidazolium-based polymerized ILs blended with IL electrolytes by GROMACS 2020.1 package. Our study is interested in the hypothesis that the addition of ionic liquids to polyILs can improve of accelerating the polymer/ion dynamics and simultaneously encourage mobile ions to the overall conductivity. To illustrate polymerized cations at the classical level within the framework of the OPLS-AA force field model, we tackled force field evolution be circumspect for intramolecular interactions with the take part of quantum mechanical calculations. Afterwards, atomistic molecular dynamics simulations at different IL concentrations were conducted to examine the mechanisms underlying ion transport in polyIL-IL blends. We illustrated results for the structural peculiarities, polymer dynamics, ion transport mechanisms, glass transition temperature (T_g), transference numbers, the ideal ionic conductivities and compared the behavior of polyIL–IL blends at different of ILs concentrations by MD simulation and experiment (T_g and conductivity). All properties above, indicating that are agreed between simulations and experiment results.