

Polymer chain conformations in ionic liquids

Ionic liquids are salts that are liquid at ambient temperatures. They have been studied extensively over the past decades as solvents for chemical transformation. Ionic liquids have several properties that make them potentially good solvents such as negligible vapour pressure, a wide liquid temperature range and exceptional thermal, chemical and electrochemical stability. Thousands of cations and anions can be combined to get virtually unlimited number of different ionic liquids. This provides an excellent platform for tuning properties for desired applications; ionic liquids are thus termed as “designer solvents”. However, the applications of ionic liquids are limited by their lack of two important properties: mechanical strength and structural integrity. These shortcomings can be minimised upon addition of polymers to ionic liquids. Polymer/ionic liquid composites have the structural integrity of polymers and ionic conductivity of ionic liquids, which make them suitable for applications like membranes for fuel cells and gas separations, ion conduction media for batteries, electroresponsive gels for actuators and artificial muscles, and high-capacitance dielectrics for plastic electronics and energy storage.

Although polymer-ionic liquid mixtures have been studied extensively for applications, little is known about the nature of polymer-ionic liquid interactions. Ionic liquids differ from conventional solvents as they comprise of mobile charged species capable of exerting long-ranged coulombic interactions, as opposed to only short-ranged dipolar interactions in molecular solvents. It is unclear whether these long-ranged interactions play an important role between polymer chains and ionic liquids. In other words, it is not known if polymers exhibit fundamentally different properties in ionic liquids, as compared to conventional molecular solvents. Our work aims to understand the behaviour of polymer chains in ionic liquids by determining conformations of the polymer chains.

The interactions between a polymer chain and solvent molecules strongly affect the conformation the chain adopts in solution. For example, polymer chains adopt a contracted conformation in poor solvents while adopting a more expanded conformation in good solvents. Thus, by studying the conformation of polymer coils in solution, we can learn about the polymer-solvent interactions. A commonly used parameter that quantifies polymer chain conformations is the Flory exponent ' ν ', that determines how the radius of gyration of the polymer coil, R_g (which is a measure of size of the coil), changes with the molecular weight (M). R_g obeys the power law: $R_g \propto M^\nu$, where ν is the Flory exponent. In a poor solvent, polymer coils are collapsed and ν is 1/3, while in a good solvent, the coils are more expanded and ν is 3/5. In solvents where polymer coils behave as random walks, ν is 1/2, and when polymers have linear rod-like conformations, ν is 1. Thus, the Flory exponent ν is a good indicator of the polymer conformation as well as the solvent quality. We can learn about the conformations of polymers in ionic liquids by determining the Flory exponent for the system.

To the best of our knowledge, no experiments have determined ν for any polymer-ionic liquid system. However, a handful number of simulation studies have been done, but they predict different values of Flory exponent using different simulation techniques. Yethiraj and coworkers have simulated the polymer poly(ethylene oxide) in the ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄]. Using atomistic simulations^[1], they predict that ν is 0.9 (which indicates nearly linear chains), but using coarse-grained simulations^[2], they predict that ν is 0.3

(which indicates collapsed chains). Thus, our goal is to experimentally determine the Flory exponent, ν , for PEO in [BMIM][BF₄].

A relatively accessible technique to determine ν is by conducting intrinsic viscosity measurements. Intrinsic viscosity $[\eta]$ is the ability of a substance to increase the viscosity of the solution. It is the rate of increase of relative viscosity (ratio of solution viscosity to solvent viscosity) with concentration of the solute, in the limit of low concentrations. The Mark-Houwink relation states that in the large molecular weight limit, the intrinsic viscosity increases with molecular weight as the power law: $[\eta] = KM^a$. K and a are the Mark-Houwink parameters, and a is related to ν by the relation: $a = 3\nu - 1$. By measuring the intrinsic viscosity for five different molecular weights of the polymer in the solvent, we can determine a by plotting $\log [\eta]$ versus $\log M$ and determining the slope.

We are currently studying solutions of PEO in [BMIM][BF₄] for low polymer concentrations. We have measured viscosities of these solutions using a parallel plate rheometer, and have determined the intrinsic viscosities for PEO-10 ($M = 10$ kg/mol) and PEO-20 ($M = 20$ kg/mol) to be 17.1 mL/g and 23.5 mL/g respectively. One can estimate of the solvent quality by comparing these values with the reported intrinsic viscosities of PEO in other solvents with known Flory exponents. For PEO-20, the intrinsic viscosities in good solvents ($\nu \sim 0.65$) range from 28 mL/g to 36 mL/g, while for theta solvents ($\nu \sim 0.50$) they range from 21 mL/g to 24 mL/g. For PEO-10, the intrinsic viscosity range in good solvents is 18 mL/g to 23 mL/g, while for theta solvents it is 15 mL/g to 17 mL/g. By comparing intrinsic viscosities from our measurements with the above reported values, we see that PEO in [BMIM][BF₄] lies in the theta solvent range. In the future, we plan to measure the intrinsic viscosities of three higher molecular weights of PEO in [BMIM][BF₄]: 75 kg/mol, 150 kg/mol and 250 kg/mol. We will then plot $\log [\eta]$ versus $\log M$ and determine the Mark-Houwink parameter a and the Flory exponent ν .

References

^[1] Mondal, J.; Choi, E.; Yethiraj, A. *Macromolecules* **2014**, *47*, 438–46

^[2] Choi, E.; Yethiraj, A. *J. Phys. Chem. B* **2015**, *119*, 9091-9097