

Multiscale Modeling of Polymer Electrolytes

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I. INTRODUCTION

Polymers are a ubiquitous class of macromolecules, which have numerous biological and industrial applications. The ability to accurately model and simulate polymers demonstrates fundamental knowledge, and provides predictive capabilities. This review will focus on the application of polymers as an electrolyte medium and, more specifically, how to simulate polymer dynamics.

A commonly studied polymer known to be ionically conductive is poly(ethylene oxide) (PEO). When simulating a polymer system a first step generally involves defining the systems initial conditions (e.g. the positions of all the atoms). Due to the many degrees of freedom polymers exhibit, defining a low energy initial structure is not a trivial matter, certainly not as easy defining a unit cell for a periodic crystal solid [citation]. Ideally, one would define the smallest representative system possible to minimize computational costs. What chain length is necessary for a representative polymer system?

That turns out to be a very important and complicated question, which may have multiple answers depending on the polymer system and the properties of interest (i.e. equilibrium structure and/or dynamics). Considering LiTFSI dynamics in a PEO system, a complication is that multiple ionic transport mechanisms exist, and are present at varying levels depending largely on the degree of polymerization [citation].

One mechanism of cation transport that has been established is the diffusion of a polymer chain with coordinated ions; this is referred to as vehicular transport. This mechanism dominates when polymer chains are short and entanglement effects can be ignored [citation]. The second mechanism occurs when thermal fluctuations cause a change in the local environment around a cation, resulting in increased free energy. The cation then diffuses to a location with lower free energy [citation]. For the purposes of this review, vehicular transport is not a considered to be a suitable mechanism due to issues at the electrolyte electrode interface; thus the emphasis is placed on long chain polymers.

Another important metric when considering polymer electrolytes is ionic conductivity. Figure 1 demonstrates that short chain PEO (>1 kg/mol MW) is more ionically

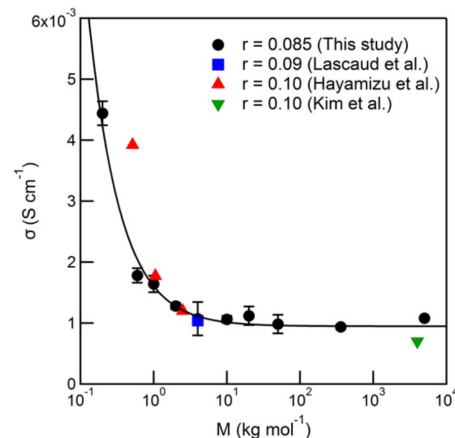


Fig. 1. A comparison of PEO/LiTFSI conductivity from several studies at 349 ± 1 K and $r=0.085-0.10$. Adopted from [citation]

conductive than long chain PEO. This seems to suggest that vehicular transport is a more efficient transport mechanism. However, PEO by itself does not possess the mechanical properties necessary to prevent certain failure modes such as dendrite growth in lithium metal batteries [citation]. AB block copolymers have been suggested to combine a mechanically rigid ionically insulating phase with an amorphous ionically conducting phase [citation]. Contrary to the homopolymer electrolyte, Figure 2 shows that PS-*b*-PEO LiTFSI is more conductive at higher molecular weights. Revisiting the question of chain length, it appears that in order to faithfully represent ion dynamics in a PS-*b*-PEO system PEO needs to have a molecular weight of at least ~ 5 kg/mol or roughly 80 monomers (560 atoms) calculated using a monomer and reference volumes from Eitouni and Balsara. This requirement excludes any consideration of the PS block, which likely acts as an anchor. In a highly entangled system the bulky side groups of PS will create more drag resulting in slower polymer chain diffusion, and forcing the ionic transport mechanism towards fluctuation driven diffusion.

Does the PS block need to be considered? If the polymer system is microphase separated into a lamellar structure one could make the argument that the ions are contained in the conducting PEO phase not interacting with the PS. Indeed experiments have shown that

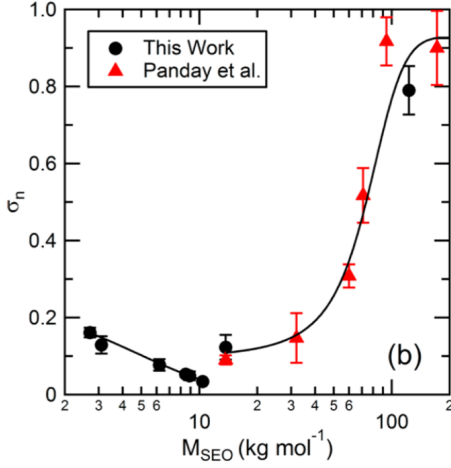


Fig. 2. Normalized conductivity, σ_n , versus total molecular weight, MSEO, at 90 °C. Adopted from [citation]

ions dislike the PS phase [citation]. Nevertheless, recent findings have indicated that disordered structures are more conductive than microphase separated structures [citation]. Inevitably in a disordered structure there will be more ion contact with the PS block, which makes ignoring it harder to justify.

II. POLYMER MELTS

Simulating a dense melt of amorphous long chain polymers is challenging because of the many degrees of freedom that exist. Backbone molecules are generally free to rotate about their torsion angles, and as a result finding an equilibrium structure can take an exceeding long time [citation]. When using brute force molecular dynamics (MD) or primitive Monte Carlo (MC) schemes relaxation time of an entangled polymer melt with polymers of length N scales as $\sim N^3$ [citation]. Realistic computation times are around $\sim N^4$, so MD with full atomistic detail is only tractable for short or medium chain polymer melts. Recently, Abbott et al. developed a 21-step MD algorithm for growing and equilibrating dense amorphous polymer melts of medium length ($N \sim 45$) [citation]. Basic MC schemes (e.g. trial move rotates a torsion angle) suffer from low acceptance rates in high-density melts when volume exclusion is considered. There are advanced MC techniques such as double bridging shown in Figure 3 that reduce the time to reach equilibrium [citation]. Although, it is unclear how such an algorithm would work with an AB diblock copolymer.

III. COURSE GRAINING

In order to devise a computational manageable problem spatial or temporal course graining can be utilized to

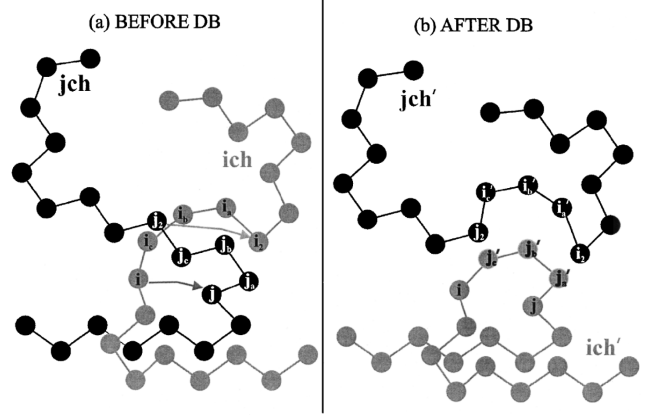


Fig. 3. Schematic of the double bridging (DB) move. (a) Local configuration of the two chains prior to the DB move. Trimer (j_a, j_b, j_c) is to be excised from jch , and trimer (i_a, i_b, i_c) from ich . (b) Local configurations of the two new chains after the DB move. Trimer (j'_a, j'_b, j'_c) connects i and j in ich' . Trimer (i'_a, i'_b, i'_c) connects i_2 and j_2 in jch' . Adopted from [citation]

reduce the dimensionality of the system. Figure 4 shows one strategy for spatially course graining PS. Course graining allows for much larger systems to be studied ($N = 500 - 1000$). As expected there is a price to pay for smearing out atomistic detail. Course grained polymer melts generally get structures right, but dynamics are accelerated and some thermodynamic properties are challenging to get right [citation].

IV. MULTISCALE MODELING

The wide range of length and time scales involved with long chain polymer processes necessitates a multi-scale modeling approach. For example at the microscopic level, bond vibrations occur on the picosecond time scale and angstrom length scale. The segment length of a monomer is typically around a nanometer (nm) and related dynamics are tens of picoseconds. Depending on surroundings typical end-to-end distances for polymers are 10–100 nm, and equilibration takes 10–100 nanoseconds. At the mesoscopic scale, an entangled polymer system of characteristic length 1–100 microns relaxation takes micro to milliseconds. [citation]

A number of different approaches have been developed to address these time and length scale issues [citations]. In general, relaxation of long chain polymer melts requires spatial course graining. After equilibrium is reached atomistic detail can be mapped back on to the course grained model for further analysis. The details of how this is accomplished are still up for debate. In any case, it is clear that atomistic detail would need to be brought back into the model to study ion dynamics.

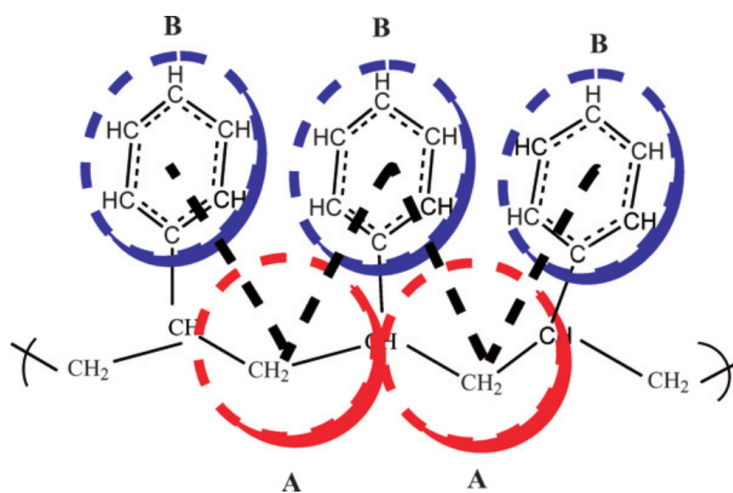


Fig. 4. Coarse-grained mapping scheme for PS: one monomer is mapped to two different CG beads (σ_A 4.1 Å, m_A 27 amu and σ_B 5.2 Å, m_B 77 amu). CG bonds are shown with thick dashed lines. Adopted from [citation]