Abstract

An understanding of dynamics in single-ion conducting (SIC) polymers, such as ionomers with ionic groups covalently bonded to the polymer backbone, is needed to design these polymers for use as electrolytes. In melt SICs, the ions tend to self-assemble into nanoscale ionic aggregates, and the morphology of these aggregates affects both the ion and chain dynamics. I will describe the ionic aggregate morphologies and ion dynamics in atomistic molecular dynamics (MD) simulations of precise polyethylene-based SICs with two different chemistries. In both cases, we find that the ionic aggregates form percolating clusters provided the polymers are neutralized with a sufficiently high fraction of cations. The structure factors calculated from the simulations are in good agreement with x-ray scattering. The mechanisms for ion transport in these atomistic simulations are the same as those found in previous coarse-grained MD simulations. In systems with isolated ionic aggregates, ions move through a process of aggregates merging, rearranging, and breaking up. In systems with percolated ionic aggregates, ions "shuttle" along the ionic aggregate. From recent coarse-grained simulations, we find that the diffusion constant for ions in systems with percolated ionic aggregates is inversely proportional to the cation-anion association lifetime. Collectively, the simulations provide guidance for design rules to improve ionic conductivity in SICs.