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Simulations of ionic aggregate morphology and dynamics in ionomer melts

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Ionomers are attractive as single-ion conducting polymer electrolytes, which would be safer and have higher efficiency than currently-used liquid electrolytes. However, ionomers do not have sufficiently high conductivities for practical application. An understanding of the relationships between ionomer chemistry, morphology, and ion transport is needed to design ionomers with improved conductivity. To investigate the morphology formed by aggregates of the ions, we have performed molecular dynamics simulations of a series of polyethylene-based model ionomer melts, in which the spacing between functional groups is precisely controlled. The simulations provide new insights into the shape, size, and composition of ionic aggregates. In particular, we observe a wide variety of aggregate morphologies, ranging from small spherical aggregates to string-like shapes and large percolated networks. The structure factors calculated from simulation agree well with X-ray scattering data. Depending on the morphology, the simulation and experimental scattering curves can be well fit with either a modified hard sphere or a newly-developed modified hard cylinder model. To reach long enough simulation times to follow ion transport in these systems typically requires coarse-grained models. We apply a static electric field to the system to extract the ion mobility and conductivity as a function of ionomer morphology. The coarse-grained simulations show that systems with percolated aggregate morphologies have higher ion mobilities.

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