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IONIC AGGREGATION AND COUNTERION DYNAMICS IN MODEL IONOMERS

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Introduction

Ionomers, polymers containing a small fraction of covalently bound ionic groups, have potential as solid, single ion conducting electrolytes in future batteries. However, the ions tend to form aggregates, making counterion diffusion unacceptably slow. A key materials design question is how molecular properties affect ionic aggregation and counterion dynamics. Recent experimental advances have allowed synthesis and extensive characterization of ionomers with a precise, constant spacing of charged groups.[1] Because the molecular architecture is controlled and these materials show increased ionic aggregate ordering versus their randomly spaced analogs, this set of experiments is ideal for direct comparisons with molecular simulations. While X-ray scattering and microscopy can reveal various properties of the ionic aggregates, a detailed microscopic picture of the structure and composition of the aggregates can at present only be determined from molecular simulations. The precise ionomers are ideal for study by simulation since the molecular architecture is known exactly. The focus of this work is a set of coarse-grained molecular dynamics (MD) simulations of model ionomers in the melt state. We investigate the effects of molecular architecture on the ionic aggregate morphology and ionic diffusion.

Experimental

We perform molecular dynamics simulations of coarse-grained ionomers using a bead-spring polymer model. A unit of 9 backbone beads is repeated 4 times per chain. The middle bead of the repeat unit is either charged (the ionene architecture) or is bonded to a charged pendant bead. Other polymer beads are uncharged, and an equal number of oppositely charged counterions are added. We use typical Kremer-Grest parameters; all beads interact through a repulsive Lennard-Jones (LJ) potential with $\varepsilon_{LJ} = 1.0$ shifted to zero at its minimum, and adjacent beads are connected by the FENE potential. The LJ diameter of all polymer beads is 1.0 σ while the counterion diameter is 0.5 σ and the cross interaction is additively mixed. All beads and counterions have unit mass. A bead of this model maps approximately to three CH_2 units in a polyethylene backbone. Long range electrostatics were fully accounted for with the particle-particle particle-mesh method in the LAMMPS MD code. The Bjerrum length $l_B/\sigma = 36$ (dielectric constant $\varepsilon_r = 4$) as in our previous work.[2] The system packing fraction $\eta_t = \left(\rho_{ci}\sigma_{ci}^3 + \rho_b\sigma^3\right)\pi/6$ was set to $0.7\pi/6 = 0.366$, in the range typical of polymer melts, where ρ represents number density and the subscripts *ci* and *b* stand for counterions and polymer beads, respectively. The cubic simulation box contained 800 polymers. Each simulation was equilibrated for 10^7 timesteps, and production runs were performed for an additional 10^7 timesteps.

The charged beads were placed either in the polymer backbone (ionenes) or as pendants on the backbone. Additionally, the polymers had either periodically (**Figure 1**) or randomly spaced (**Figure 2**) charged beads. The random ionomers were built by linking groups of type X, containing no charges, and groups of type Y that contain charges, randomly together as illustrated in **Figure 2**. To understand the range of ionic aggregate morphologies possible in real materials, we vary the spacing of charges along the chain as well as the degree of randomness.

Results and Discussion

Snapshots from the simulations of the various systems reveal significant differences in morphology. We previously found that the ionenes tend to form percolated ionic aggregates, which often span the simulation box in three dimensions.[2] In contrast, the pendant precise ionomers form discrete, compact aggregates with a relatively narrow size distribution, as shown in the snapshot in **Figure 3**. In this snapshot, only the charged beads and counterions are shown; the polymer is invisible for clarity. The aggregates are colored by size, with small clusters in red and large clusters in blue. We have now extended our simulations to include the random block ionomers. Once again we find a different morphology, as shown in **Figure 4**. The aggregates have a much larger size distribution in the random case. The smaller aggregates of the random pendant ionomers are roughly spherical, while the larger aggregates are more extended and resemble short thick strings of a similar width as the more spherical pendant ionomer aggregates.

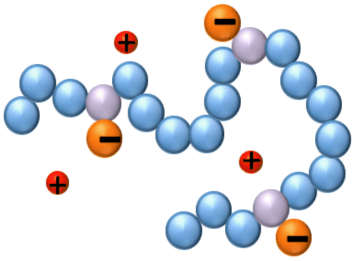

Figure 1. Sketch of coarse-grained, precise pendant ionomer.

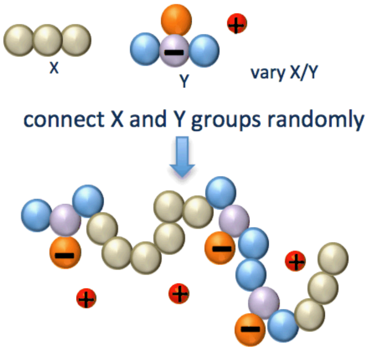

Figure 2. Sketch of random pendant ionomer.

The well-known "ionomer peak" in the scattering is present in all the simulations. The peak is significantly more intense for the pendant ions with a long periodic spacing of charged beads, which form roughly spherical aggregates. We find, in agreement with recent experiments,[1] that increasing the spacing between the ions along the chain moves the ionomer peak to lower wavevector. Moving from the precise to random ionomers broadens the ionomer peak and also moves it to lower wavevector. These trends are shown in the counter ion-counter ion structure factors plotted in **Figure 5**.

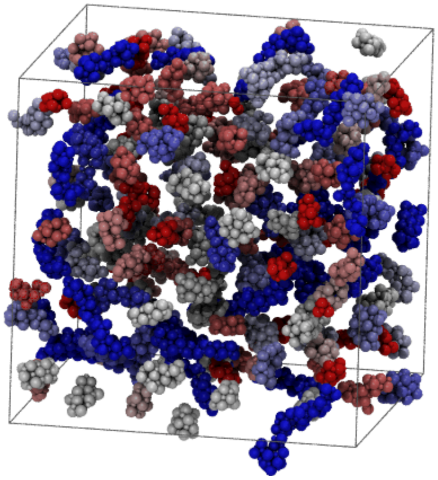

Figure 3. Snapshot of the precise pendant ionomers with a spacing of 9 beads between each charged group, at $\varepsilon_r = 4$. Only counterions (smaller spheres) and charged beads (larger spheres) are shown. Aggregates are colored from red to white to blue in order of increasing number of ions in the aggregate.

Preliminary results indicate that the counterion diffusion is faster in the percolated systems than in the less percolated ones. In particular, the diffusion is faster in the ionenes than in the pendant ionomers. Depending on the degree of randomness in spacing of charged beads along the chain, counterion diffusion can increase or decrease versus that of the precisely spaced materials.

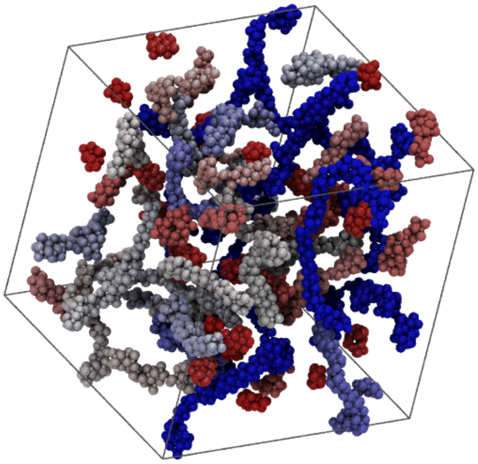

Figure 4. Snapshot of the random block, pendant ionomers with a spacing of 9 beads between each charged group, at $\varepsilon_r = 4$. Color scheme as in **Figure 3**.

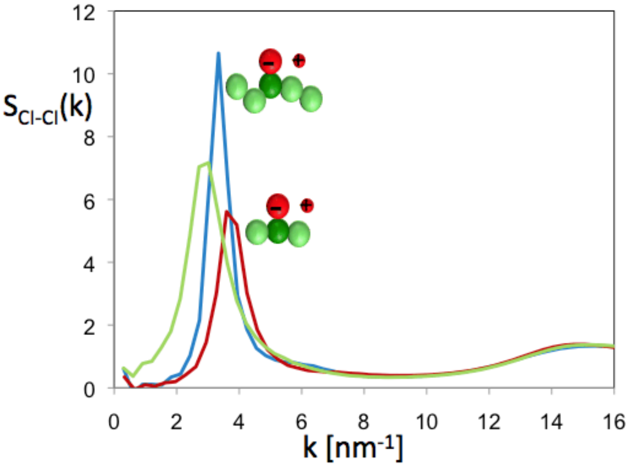

Figure 5. Counter ion-counter ion partial structure factor as a function of wavevector from the simulations. The curves are for precise pendant ionomers with 3 beads per charged group (red), precise pendant ionomers with 5 beads per charged group (blue), and block random pendant ionomers with an average of 5 beads per charged group (green). The mapping to units of nm^{-1} assumes $\sigma = 0.4$ nm.

Conclusions

In conclusion, we have performed coarse-grained MD simulations of model ionomers with a variety of molecular architectures. All model systems formed ionic aggregates, and the low wavevector ionomer peak in the scattering is present in all cases. The peak is significantly more intense for pendant ions with a long periodic spacing of charged beads, which form roughly spherical aggregates. This morphology is in qualitative contrast to the extended aggregates of ionenes that show increased counterion diffusion. Randomness in the architecture leads to more stringlike aggregates, with larger size distributions than for the precise pendant ionomers. Depending on the degree of randomness in spacing of charged beads along the chain, counterion diffusion can increase or decrease versus that of the precisely spaced materials. Thus, details of the ionomer architecture have a strong effect on aggregate morphology, which in turn affects counterion diffusion and hence conductivity.

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References

(1) Seitz, M. E.; Chan, C. D.; Opper, K. L.; Baughman, T. W.; Wagener, K. B.; Winey, K. I. *J. Am Chem. Soc.* **2010**, *132*, 8165.

(2) Hall, L.M; Stevens, M. J.; Frischknecht, A.L. *Phys. Rev. Lett.* **2011**, *106*, 127801.