Supporting Information for:

Influence of a Nanoparticle on the Structure and Dynamics of Model Ionomer Melts

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Colloid Potential vs. LJ Potential:

If one uses a simple Lennard-Jones (LJ) potential shifted radially (where the shift factor accounts for the size of the NP), with the same interaction strength as for monomer-monomer interactions, then monomers near the surface experience less total cohesive interaction strength than those in bulk, as discussed in the main text. In initial tests, we implemented such a potential and found that ions did not adsorb to the NP surface even for the sticky NP case (for which NP interaction well depths were set as though the NP was a sticker bead). To more fairly set the NP-monomer interaction strengths to allow for the same overall effective cohesion as for monomer-sized particles, the strength of the NP-monomer interaction should depend on the size of the NP (accounting for how many monomer-monomer interactions are replaced by an NP-monomer interaction). This size effect is naturally included in the colloid potential described in the main text, which more accurately describes the interaction between two particles of disparate sizes. Below, we compare results of our initial tests using the shifted LJ potential with the results using the colloid potential (as in the main text).

Specifically, examples of the two potential forms at two interaction strengths are given in Figure S1. The well depth is given by ε_{ij} for the LJ potential, and by the Hamaker constant ($24\pi\varepsilon_{NP}\rho_{NP}\sigma^3$) for the colloid potential. For $\varepsilon_{NP\text{-}B}$ = 1kT, the corresponding Hamaker constant is $A_{NP\text{-}B}$ = 67.1kT (refer to main text). It can be seen that the colloid potential is slightly more attractive than the shifted LJ potential for the $\varepsilon_{NP\text{-}B}$ = 1kT case, and has a larger effective diameter. For the case when $\varepsilon_{NP\text{-}S}$ = 2.0 (NP-Sticker interaction strength when the NP is assumed to have sticky interactions), the Hamaker constant $A_{NP\text{-}S}$ is approximately 134kT, thus, the well depth is significantly increased for the colloid versus the shifted LJ potential.

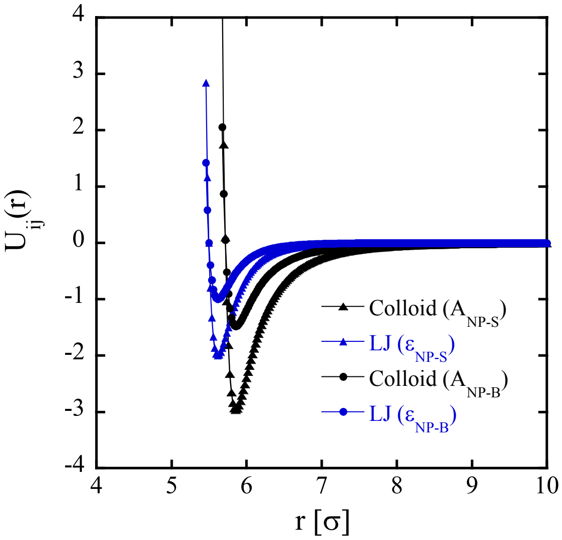

Figure S1: Colloid and LJ potentials for two different interaction strengths, as labeled

Figures S2 and S3 show snapshots for sticky NP systems simulated using the shifted LJ potential; even at high ion densities, the aggregates are depleted from the NP surface, in contrast to the colloidal potential results presented in the main text.

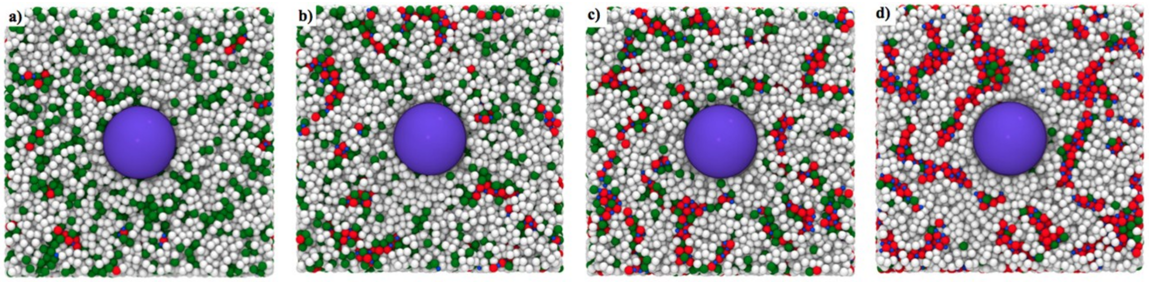

Figure S2: Snapshots of $N_{bb} = 3$ system neutralized to (a) 10%, (b) 25%, (c) 50%, and (d) 75% with a sticky NP, where the NP interaction with monomer beads and counterions is through a shifted LJ potential

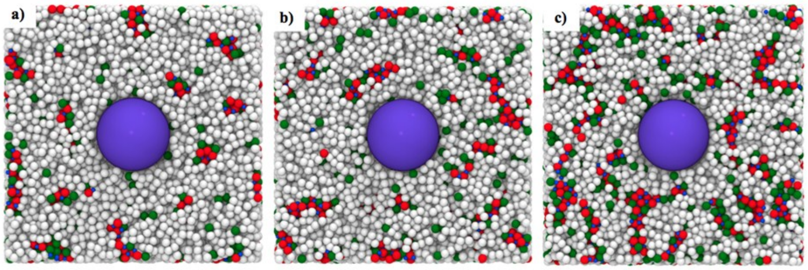

Figure S3: Snapshots of (a) $N_{bb} = 7$, (b) $N_{bb} = 5$, and (c) $N_{bb} = 3$ systems neutralized to 50% with a sticky NP, where the NP interaction with monomer beads and counterions is through a shifted LJ potential

To show the difference in effective interactions with NP size, we present snapshots and pair correlation functions for systems with the same strength of NP-monomer interactions (of shifted LJ form) but changing NP size, in Figure S4. In particular, the first "neutral" NP-Ion radial distribution function peak positions are at 3.5σ, 2.75σ, and 2.5σ from the contact (the NP radius plus a monomer radius) for the NPs of diameters 7.5σ, 10σ, and 12.5σ, respectively. This implies that the aggregates are organizing more closely to the larger NPs though they all have the same interaction strength. Meanwhile, if the colloid potential is used as in the main text, the ionic aggregate ordering around the NP is similar across this diameter range.

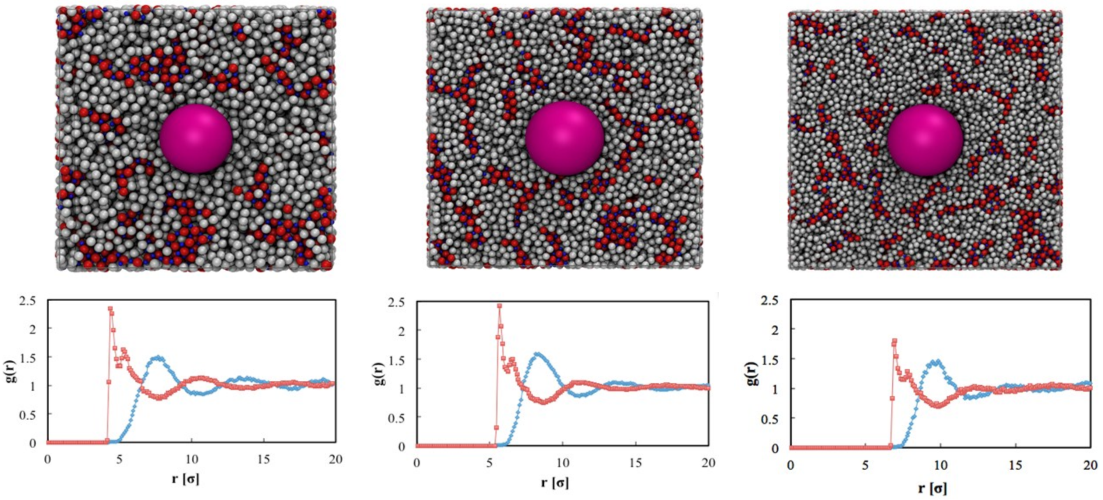

Figure S4: Snapshots and corresponding NP-Backbone (red) and NP-Ion (blue) radial distribution functions for the N_{bb}3-75%Na system with a "neutral" NP, where the NP interaction with monomer beads and counterions is through a shifted LJ potential with the same NP-monomer interaction strength as for monomer-monomer interactions and the NP diameter is 7.5σ (left), 10σ (middle), and 12.5σ (right)

Dynamics of Pure Ionomer vs. Ionomer Nanocomposite:

To ensure the particle loading does not significantly impact overall material properties of our systems (as we wish to consider low loadings), we compute the average mean squared displacement (MSD) and polymer end-to-end vector autocorrelation (ACF_{ee}) function for N_{bb}3-50%Na and N_{bb}3-75%Na with a sticky NP and compare to these quantities for a pure system (without a NP). These two systems are expected to be the most sensitive to the NP loading, as they have the highest ion contents. This is reported in Figures S5 and S6. As expected for such low NP loading fraction, after averaging across all polymers in the simulation box, the average properties of the NP systems are similar to the analogous pure ionomer systems.

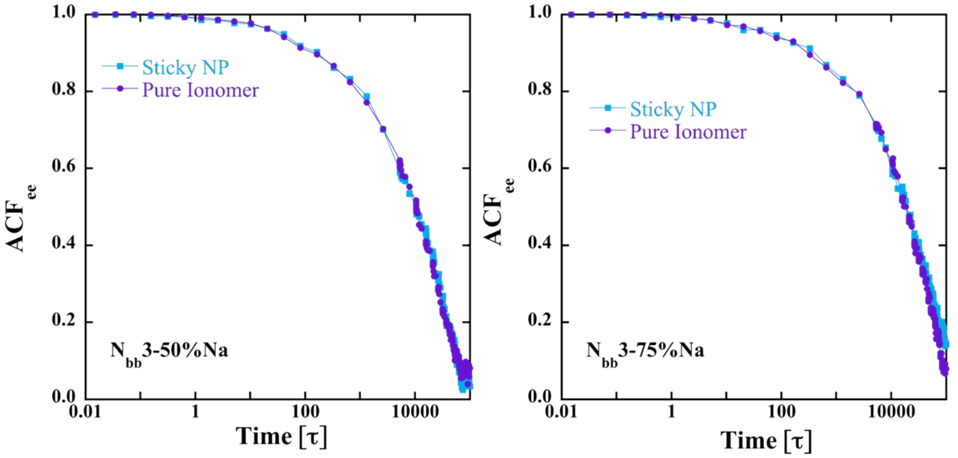

Figure S5: Polymer ACF_{ee} calculated as $\langle \vec{R}_{ee}(t) \cdot \vec{R}_{ee}(0) \rangle$, normalized by the average value at time 0, for different systems as labeled

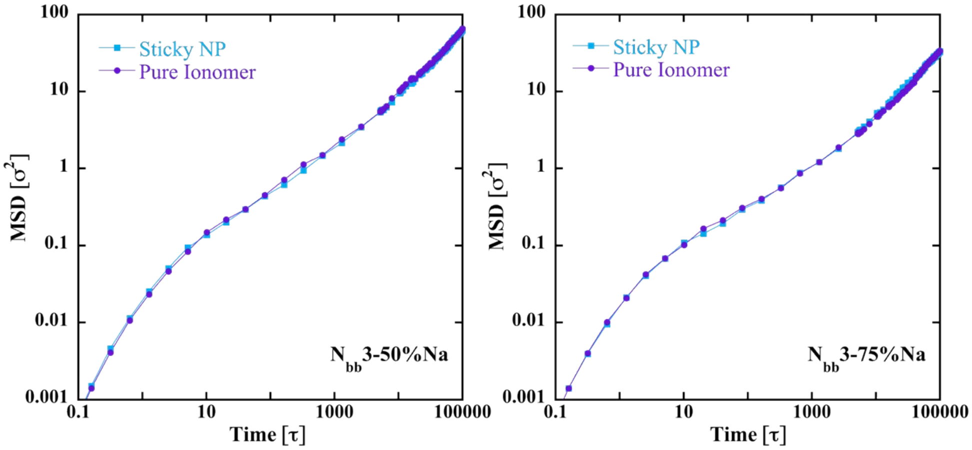

Figure S6: MSD of the polymers' centers of mass for different systems as labeled

Structure Factor:

We computed the Ion-Ion structure factor, $S_{ion-ion}(k) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle e^{-ik\cdot(r_i - r_j)}\right\rangle$, where the sum is over all ions, for the pure melt and for a system with a neutral NP, as given in Figure S7. We find a slight increase in the ion structure factor intensity for systems with the neutral NP, because the aggregates move away from the NP and slightly increase the ion density in the rest of the box.

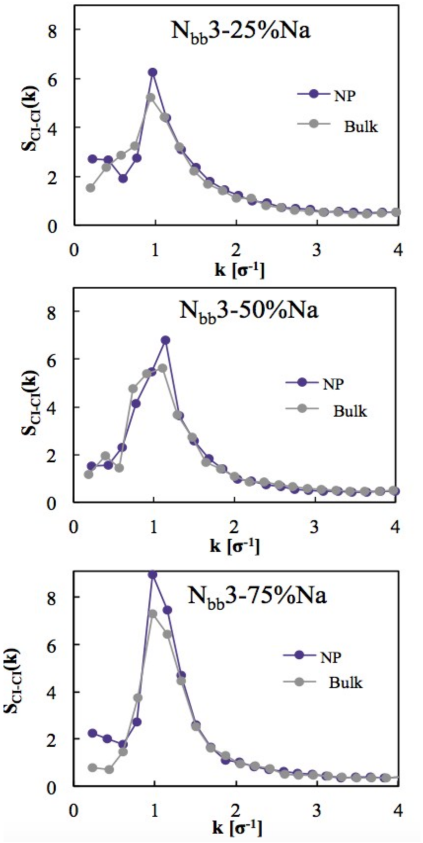

Figure S7: Ion-Ion structure factor for three systems with and without the NP, as labeled

Bond ACF:

We calculate the bond vector autocorrelation function for two shells of thickness 2σ, as well as the bulk, and report it in Figure S8. It is seen that the dynamics returns to bulk behavior in the second shell; we only report dynamics in the first shell in the main text.

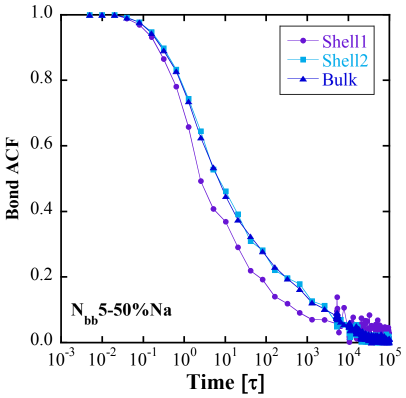

Figure S8: BACF for a N_{bb}5-50%Na at different distances from the NP surface, as labeled

Homopolymer Dynamics:

The bond autocorrelation function was calculated (see main text for details) for a homopolymer system of chain length N = 35 as a function of distance from the NP. It is seen from Figure S9 that the introduction of a NP increases the interfacial dynamics only very slightly; this is due to free volume effect caused by the presence of an interface (the NP interrupts monomer-scale packing, causing faster relaxation).

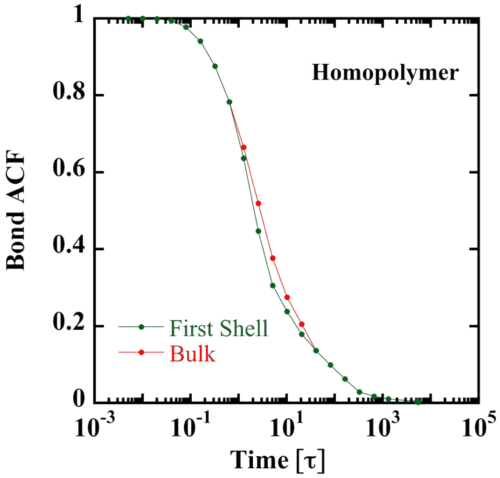

Figure S9: BACF for a homopolymer (N = 35) near and far from the NP surface, as labeled

Effect of NP Size:

To add to the related series of snapshots found in the main text, Figure S10 shows snapshots from the N_{bb}5-50%Na systems with NPs of three different diameters. All systems have the same polymer volume fraction.

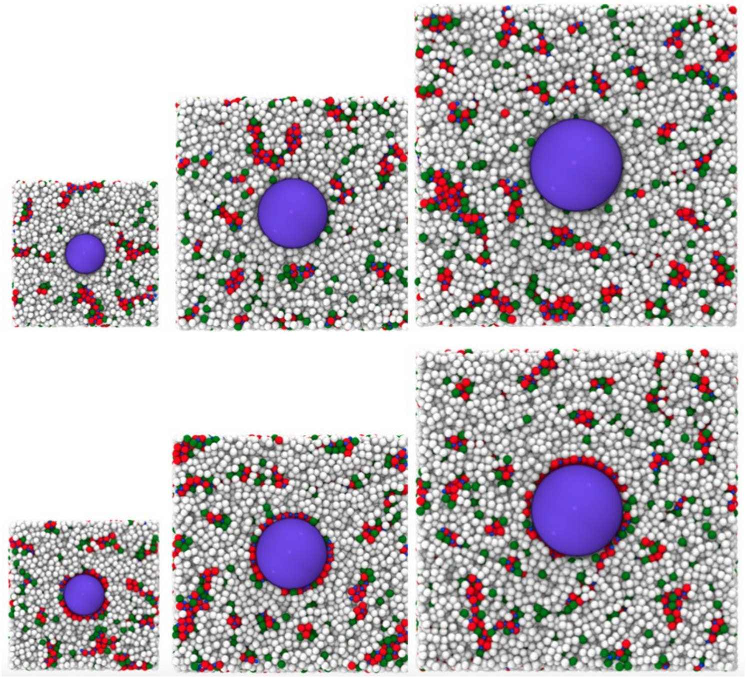

Figure S10: Snapshots from N_{bb}5-50%Na systems with NPs of diameters of 7.5, 10, and 12.5σ from left to right; top row is for neutral NP and bottom row is for sticky NP interactions