

Micellization between Copolyelectrolytes and Oppositely Charged Small Molecules in Dilute Solutions

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Summary

The interaction between AB diblock copolymers with small molecules, C, has been studied using molecular dynamics. In this experiment, the A molecules are neutral and the B and C molecules are oppositely charged. The charged molecules aggregate into clusters with the neutral A blocks surrounding the cluster forming micelles. The mean interparticle distance, $\langle r \rangle$, and equilibration time were measured while varying the size and charge ratio of the AB copolyelectrolyte.

Background

Recent research has shown that triblock copolyelectrolytes can form very ordered structures when in the presence of oppositely charged macromolecules.¹ The endblocks of these charged triblocks have been shown to aggregate into coacervate domains; midblocks fill the corona forming physical linkages in between coacervate domains. An analogous experiment would be to study diblocks copolyelectrolytes, which are not able to bridge, and should form micelles in solution. This can be studied by examining charged copolyelectrolytes mixed in with oppositely charged small molecules. These mixtures should form micelles in dilute solutions.

Simulation Methods

The model used to describe bonded and non-bonded interactions in this simulation is the Lennard-Jones chain. The following dimensionless potential energy function was employed:

$$U^* = \sum_{i < j, ij \text{ not bonded}} 4(r_{ij}^{-12} - r_{ij}^{-6}) + \sum_{i < j, ij \text{ bonded}} \frac{3000}{2} (r_{ij} - r_0)^2$$

To represent the charged interactions the screened Coulomb potential is used:

$$U(r_{ij}) = \lambda \frac{q_i q_j}{r_{ij}} \exp(-r_{ij} * \kappa)$$

Where λ is the electrostatic strength, κ is the inverse Debye length, q represents the sign of the charge for each molecule. In this simulation λ was set to 100 and κ has been set so that the electrostatic interaction between two monomers is $1e-4$ at one third of the box length.

The system was modeled using molecular dynamics in the canonical ensemble. To do this, the molecules were initially disturbed onto a cubic lattice within the simulation cell. The molecules were given initial random velocities, which were rescaled using the Berendsen thermostat. The potential energy was then minimized using a conjugate gradient analysis. The simulation was then allowed to run for 2,000,000 time

steps of 0.001 with periodic velocity rescaling. The mean interparticle distance, $\langle r \rangle$, was measured as an indicator of polymer aggregation. For all simulations the box length was set so that $\rho = N/V = 0.008$.

Results and Interpretation

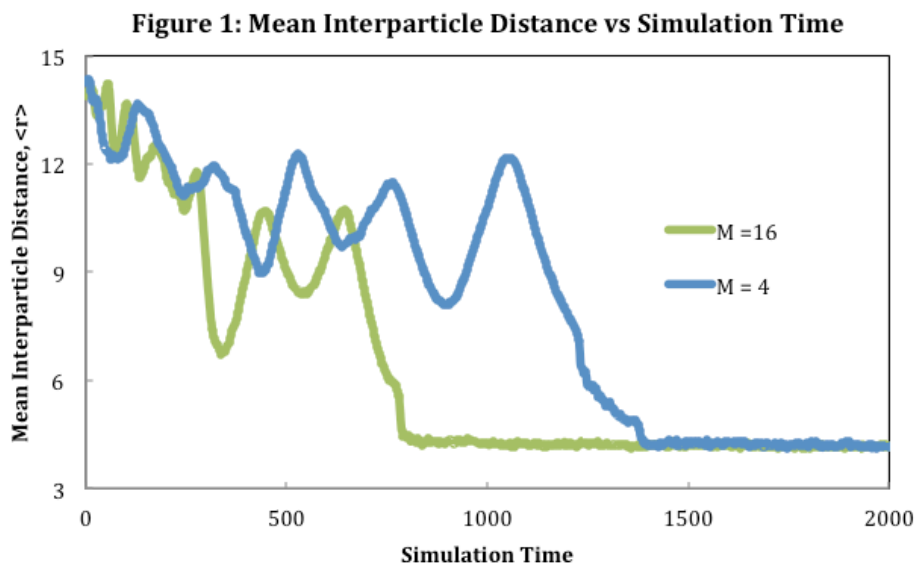


Figure 1: Mean interparticle distance as a function of time for various polymer lengths. In this simulation the charge fraction was held constant so 25% of particles in the polymer chain were charged. The number of atoms was held constant so that there were a total of 240 atoms within the simulation cell. Sharp decreases in this plot indicate that aggregation is occurring and polymer chains or clusters are combining. Sharp increases occur when individual clusters move apart from each other within the simulation cell.

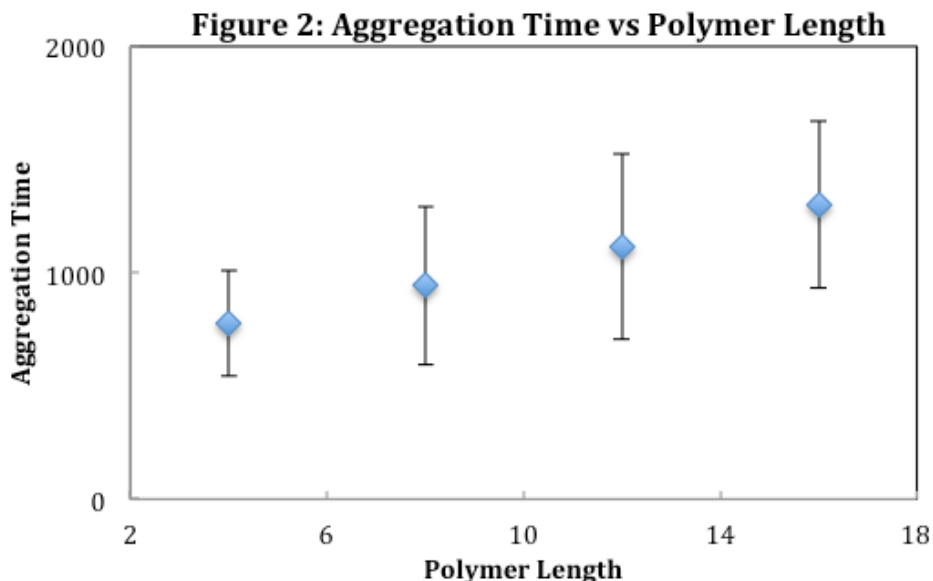


Figure 2: Aggregation time vs polymer length. In this simulation the charge fraction was held constant so 25% of particles in the polymer chain were charged. The number of atoms was

held constant so that there were a total of 240 atoms within the simulation cell. 3 simulations for each polymer length were averaged. Equilibrations clearly increase with increasing polymer lengths.

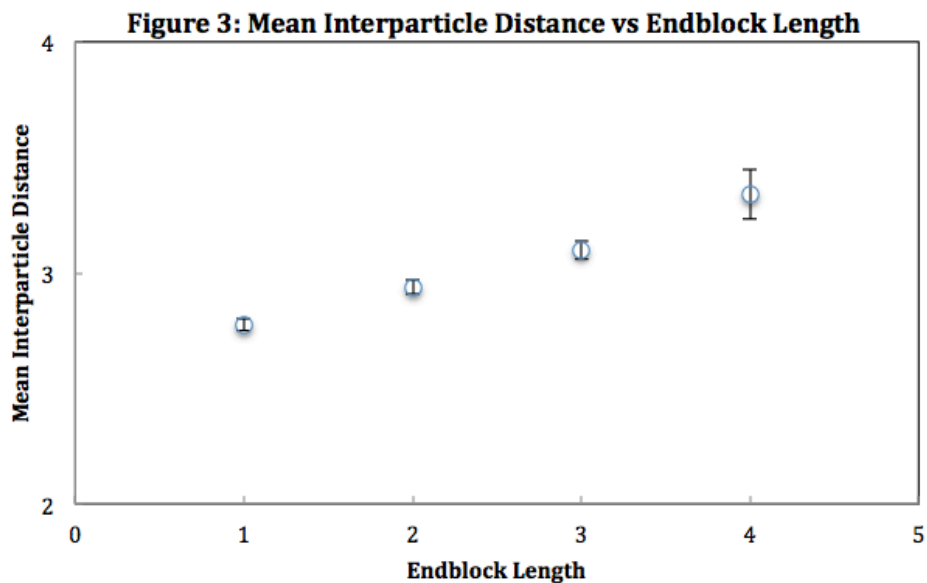


Figure 3: Equilibrium mean interparticle distance as a function of endblock length. The size of the neutral block was held constant at 4 monomers; the endblock length represents the number of the charged monomers in the polymer chain. The simulation was allowed to run for a total simulation time of 5,000, at the end the mean interparticle distance was measured. The values reported are the average of 5 runs for each endblock length. The number of polymer chains was held constant so that there were a total of 10 polymer chains within the simulation cell.

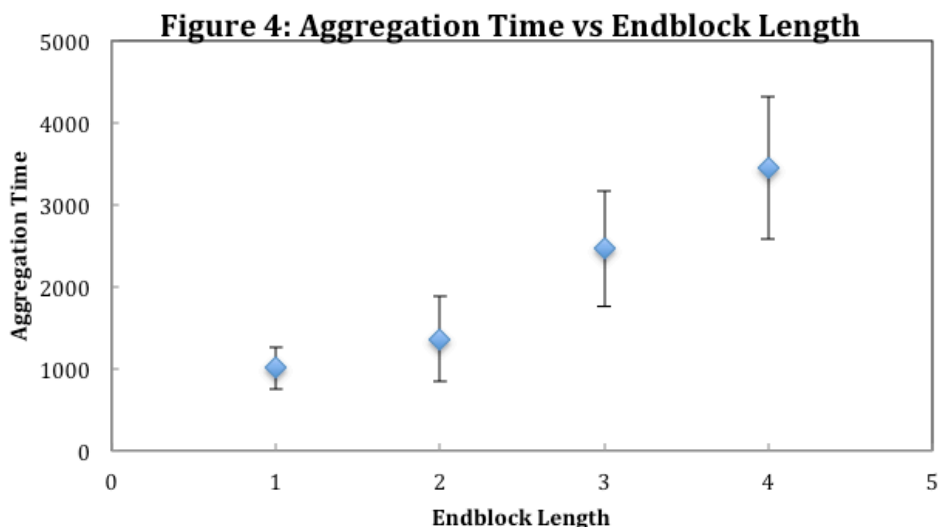


Figure 4: Aggregation time vs charge fraction. The size of the neutral block was held constant at 4 monomers; the endblock length represents the number of the charged monomers in the polymer chain. 5 runs for each length were allowed to run until the mean interparticle distance matched the value obtained at which point the aggregation time was recorded. The number of

polymer chains was held constant so that there were a total of 10 polymer chains within the simulation cell.

Figure 1 illustrates the mean interparticle distance of all units in the simulations as a function of simulation time. Sharp decreases in this plot indicate that aggregation is occurring and polymer chains or clusters are combining. Sharp increases occur when individual clusters move apart from each other within the simulation cell. Eventually, all clusters aggregate into 1 larger cluster. This final aggregation time takes longer as the polymer length increases as shown in figure 2. In figure 2, the total charge fraction was held constant at 25% of the polymer length, as the polymer length is increased from 4 to 16 monomers while keeping the total number of monomers constant; there is a linear increase in the simulation time.

In figure 3 and 4 the size of the neutral block and the numbers of chains were held constant such that the charge fraction increased from 20% to 50% of the polymers length. Increasing the size of the charged block leads to bigger clusters as shown in the increase in the mean interparticle distance reported in figure 3. Because the overall number of atoms increases with increasing polymer length there is a significant increase in the final aggregation time with increasing the polymers charge fraction as shown in figure 4.

There are several potential deficiencies in the model used. First, the model is highly coarse grained, and intermolecular interactions between atoms are not accurately addressed. Also, single atoms represent the charged molecules with point charges located in the center of each atom; this does not truly represent the correct electrostatics, as dipoles are not accounted for and the behavior of these charged molecules are restricted to that of charged spheres. If this approach were to be improve a much more atomistic model would be employed; however this would increase the computational expense dramatically.

Caption

This movie shows the aggregation of 24 charged block copolymers with a stoichiometric amount of oppositely charged small molecules. Each polymer chain consists of 8 monomers, 6 of these neutral and 2 charged. In this simulation, neutral monomers represented by white atoms, bound charged monomers by blue atoms, and red atoms represent the oppositely charged small molecules. During the course of the simulation the charged molecules aggregate forming micelles with the neutral polymer chains surrounding the charged core.

¹ Hunt, J. N., Feldman, K. E., Lynd, N. A., Deek, J., Campos, L. M., Spruell, J. M., Hernandez, B. M., et al. (2011). Tunable, High Modulus Hydrogels Driven by Ionic Coacervation. *Advanced Materials*, 23(20), 2327–2331.