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Micelles and networks formed by symmetric triblock copolymers in dilute solutions that are poor solvents for the terminal blocks

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Summary

A simulation for symmetric triblock copolymers in dilute solution shows a rich variety of structures when the solvent produces a net attractive interaction between the terminal blocks. Depending on the strength of this interaction, the system can form transitory aggregates, large independent micelles, or branched structures in which bridging soluble internal blocks connect dense particles formed by the aggregation of insoluble terminal blocks. The formation of the branched structure with the ABA triblock copolymer can be seen under conditions where the corresponding AB diblock copolymer would provide steric stabilization for a polymer colloid.

Introduction

Symmetric triblock copolymers, which are represented by the abbreviation ABA, form a variety of structures in dilute solution in solvents that interact differently with the two types of blocks. The simpler system is provided by a solvent that interacts preferentially with the two blocks located at the ends of the chain. In this system, the triblock copolymer can form micelles that have much in common with the micelles formed by the diblock copolymer, AB. In the micelle, the bonded end of each soluble block is constrained to lie very near the surface of the dense core formed by the insoluble block. In contrast, the free end of the soluble block may wander away from this interface up to a distance that is defined by the maximum extension consistent with maintenance of acceptable bond lengths and angles between successive bonds.

A richer variety of structures can be envisioned in a solvent that interacts preferentially with the internal block in the symmetric triblock copolymer. This communication provides an initial description of a simulation that can demonstrate the dependence of these diverse structures on the sizes of the two types of blocks, the concentration of the symmetric triblock copolymer, and the energetics of the interaction of the blocks with one another and with the solvent. This simulation is an extension of the one that is used to study the steric stabilization of polymer colloids by diblock copolymers (1).

Experiments have convincingly shown the existence of some of the structures that can be seen in the simulations. In particular, there is good evidence for the aggregation of some (2–5), but not all (6–8), symmetric triblock copolymers in media that interact preferentially with the internal block. Some of the systems that did not exhibit aggregation show intramolecular association instead (6,7). Persuasive evidence for the formation of micelles in these systmes is provided by the recent work of Balsara *et al* (5). Another type of architecture that has been the subject of speculation is a branched structure comprised of insoluble beads connected by bridges provided by the soluble internal block (3).

The simulations reported here provide support for all of these conclusions and speculations. Depending on the energetics of the pair-wise interactions, the system can (a) exhibit no stable aggregates, (b) aggregate into distinct micelles, or (c) form a branched structure that has as its limit a network that extends infinitely in three dimensions.

Simulations

The simulation was performed using a simple modification of the procedure developed for the study of steric stabilization of polymer colloids by diblock copolymers (1). It is performed on a cubic lattice of dimensions 22 x 22 x 22. Periodic boundary conditions were employed. Lattice sites cannot be doubly occupied. In the simulations described here, the volume fraction of the copolymer is 0.0376. Each copolymer contains 20 beads, distributed as 5 beads in each of the two blocks of A at the ends, and 10 beads in the single internal block of B. The remainder of the beads on the lattice are assumed to be occupied by solvent. An interaction energy denoted by ϵ_{XY} was assigned to each situation where components X and Y occupy nearest neighbor sites, but are not bonded to one another, and

$$\epsilon'_{XY} = \frac{\epsilon_{XY}}{kT} \tag{1}$$

The simulations reported here correspond to all ϵ'_{XY} being equal to zero, with the exception of ϵ'_{AA}, which can assume values that are negative.

Reptation moves were used to convert the system from configuration i to configuration $i+1$. Acceptance of a proposed move is governed by the prohibition of double occupancy of a site by two beads of a copolymer, the ϵ'_{XY}, and the Metropolis rules (9). Since we are interested in properties of the system at equilibrium, our adoption of reptation for the conversion of one configuration of the system into another does not imply that the dynamics (which is not the subject of the simulation) is controlled by reptation. The initial configuration for each simulation was generated from a set of parallel chains by conducting 10^6 iterations with all pairwise interaction energies set equal to zero. The random configuration so generated was then run to equilibrium using the desired energetics. Equilibrium was obtained within 10^8 iterations.

Results and Discussion

A snapshot of the simulation was taken at intervals of 5×10^5 iterations. For the athermal system, in which all pair-wise interactions energies are zero, two or more chains are sometimes observed to be in incidental contact in a particular snapshot. However, in the absence of an attractive potential to stabilize the chains involved in these collisions, they dissociate during the next 5×10^5 iterations.

When the energetics are modified to correspond to $\epsilon'_{AA} = -0.25$, aggregates are more commonly seen than was true in the athermal case. Figure 1 is a two-dimensional projection of the block copolymers as seen in a typical snapshot taken after equilibration. Since the snapshot is for the fundamental cell of dimensions 22 x 22 x 22, chains that cross the boundary of the cell appear as disconnected fragments in the Figure. A few small aggregates form and dissociate during the course of the simulation. Unassociated chains are always present. Some of the symmetric triblock copolymers that participate in an aggregate have both of their terminal A blocks in the core, but a more typical situation is a chain with a single A block contributing to the transitory aggregate while its other A block is free in solution. The system also may contain intramolecular aggregates, formed by chains in which the A blocks at either end associate with themselves as a consequence of the formation of a hairpin loop by the soluble internal block.

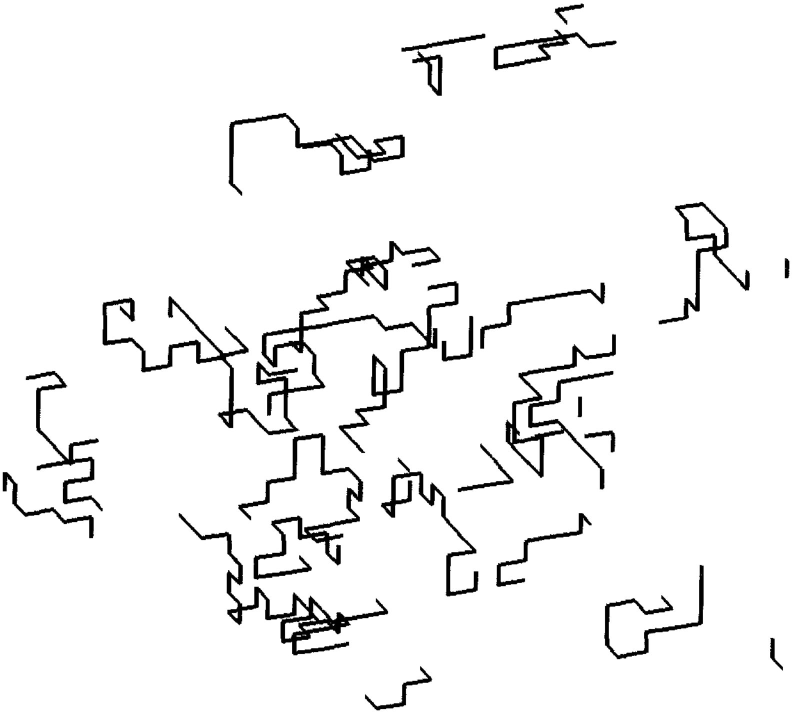

Figure 1. Two-dimensional projection of a representative snapshot of the system with pair-wise interactions corresponding to $\epsilon'_{AA} = -0.25$. The appearance of small fragments at the edges arises from the periodic boundary conditions; all copolymers contain twenty monomer units.

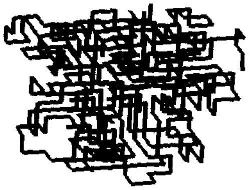

Figure 2. Two-dimensional projection of a representative snapshot of the system with pair-wise interactions corresponding to $\epsilon'_{AA} = -0.5$.

Intensification of the interactions, corresponding to $\epsilon'_{AA} = -0.5$, causes the chains to associate into a single aggregate within about 5×10^6 iterations. A two-dimensional project of this aggregate is depicted in Figure 2. This aggregate has the structure of a micelle, with a dense core comprised of the A blocks and a corona formed by the B blocks. In many of the snapshops, 2–4 of the terminal A blocks are free in solution. Several variations on this structure are seen in a minority (on the order of 10%) of the snapshots. In one variant, seen in 5–6% of the snapshots, one of the twenty chains is free and does not participate in the micelle formed by the remaining nineteen chains. Another variant, seen in 5% of the snapshots, contains one chain that forms an internal hairpin loop. More rarely the system will contain two micelles, one smaller than the other, and these two micelles are bridged by the soluble internal block of one of the symmetric triblock copolymers.

Simulations have been reported for the diblock copolymers with the same concentration (volume fraction 0.0376), same energetics (corresponding to $\epsilon'_{AA} = -0.5$), and same number of A and B beads (10 each) per chain (1). These diblock copolymers irreverisbly form the largest possible micelle under these conditions. No free unassociated chains were seen in the system comprised of AB diblock copolymers. Hence the drive toward the formation of the largest micelles is reduced when the architecture of the chains is changed from a diblock to a symmetric triblock in which the terminal blocks prefer to interact with themselves.

A further intensification of the interactions, corresponding to $\epsilon'_{AA} = -1$, leads to bridged structures of the type depicted in Figure 3. These structures develop in about 44×10^6 iterations. The Figure shows four seperate aggregates of A blocks that are held together by bridging B blocks. This particular snapshot contains three aggregates with eleven A blocks and one aggregate of 7 A blocks. Thus all 40 A blocks in the system participate in an aggregate, and the aggregates do not differ greatly in size. Three of the soluble internal blocks in this Figure provide bridges between aggregates, and the remaining 17 soluble blocks form loops in the corona of the aggregates. The conclusions from this particular snapshot are typical of other snapshots. Only about 1% of the snapshots contain an A block as a dangling end. There is always a preponderance of loops over network chains.

The corresponding system with diblock copolymers (same concentration, same energetics, and same number of A and B beads per chain) forms a sterically stabilized system with several independent micelles (1).

Conclusion

The simulation of symmetric triblock copolymers in an environment that promotes self-interaction of the terminal blocks reveals all of the types of structures that have been demonstrated experimentally, as well as structures that have been the subject of speculation. The control in the definition of the system that is possible in computer simulations will permit an accurate definition of the transitions between these different structures. It will also show how the change in the arrangement of the monomer units from an AB diblock copolymer to an ABA triblock copolymer can produce fundamental changes in the structures formed as a consequence of the aggregation of these chains.

Acknowledgments

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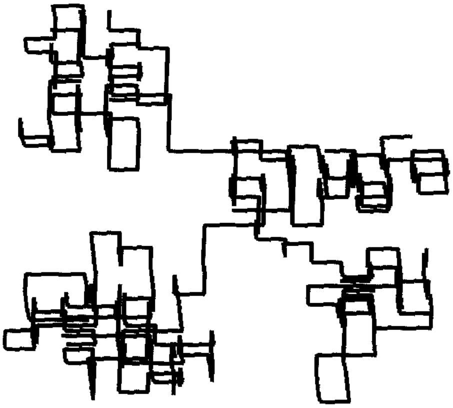

Figure 3. Two-dimensional projection of a representative snapshot of the system with pair-wise interactions corresponding to $\epsilon'_{AA} = -1$.

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