Self-Organization of Rod−Coil Molecules into Nanoaggregates: A Coarse Grained Model

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ABSTRACT: Triblock rod−coil oligomers with bulky coil blocks were previously utilized to create self-organized mushroom-shaped nanoaggregates. The boundary effects in such small aggregates and the steric repulsions due to close packing of bulky coil blocks lead to highly perturbed, nonideal systems. We describe here a coarse grained model to understand the properties of such systems. This model is based on enumeration of chain conformations on a lattice to calculate entropy loss due to aggregation. We studied the contribution of chain architecture and crystallization enthalpy on equilibrium properties such as size, size distribution, and thermodynamic stability for a mushroom-shaped constrained structure. In agreement with previous theoretical work for other finite architectures, our study verified that aggregate size is determined by the competition between entropic and enthalpic contributions from different blocks. Most importantly, polydispersity of the nanoaggregates was found to decrease as bulkiness of the coil block structural unit is increased and also as surface energy of the rod block crystal is increased. These results suggest that branched coil architectures such as dendrons could be utilized to further improve the structural properties of the aggregates.

Introduction

Designing nanoscale objects with distinct and permanent shapes is one of the main objectives of contemporary chemistry and nanotechnology. Even though it is possible to reach the high molar mass range with conventional polymer synthesis, these objects are usually not conformationally well-defined. On the other hand, nature shows us wonderful examples of macromolecules with well-defined three-dimensional structures, such as proteins. Clearly, the ability to synthesize such structures in the laboratory (with non-peptidic chemistry) would be extremely useful for many reasons. Understanding and controlling the formation and packing of such structures could offer, for example, new materials with unique properties,[1] identify artificial enzymes, or lead to nanoobjects to engineer the behavior of cells (artificial receptors, ligands, pore plugs). Self-organization is a rapid pathway from small molecules to supramolecular nanometer-sized objects.[2] It can be defined as the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by noncovalent bonds which could be either specific or nonspecific.[2,3] One of the main challenges of this strategy is to learn how to control the spontaneous formation of such objects by encoding size and shape information into the precursor molecules. The thermodynamic stability of such aggregates is determined by the nature of the noncovalent interactions involved. Clearly, the energy gap between the global minimum and all other minima will be critical in obtaining shape-invariant objects such as proteins.[4]

Self-organization of rod−coil and coil−rod−coil molecules into aggregates and phase diagrams for the melt state of such molecules have been extensively studied both theoretically[5−11] and computationally.[12−15] The difference in the flexibility of building blocks leads to microphase separation and determines their phase diagrams.[16,17] The driving force for the rod blocks to aggregate (for favorable enthalpic contributions) against the aggregation resistance of flexible coil blocks (not to lose their entropy) creates a frustrated system.[6−9] Semenov and Vasilenko[5] have studied nematic to smectic-A transition for rod−coil molecules and obtained phase diagrams that include bilayer and interdigitated monolayer structures. Williams and Fredrickson[9] proposed the "hockey puck" structure for the melt state of rod−coil molecules where the coil block is much longer than the rod block and analyzed the finite size system effects on chain stretching. Rod−coil molecules have also been proposed as candidates for obtaining noncentrosymmetric structures. ABC type coil−rod−coil molecules and mixtures of ABC triblock and AB diblock molecules were proposed as candidates for obtaining ferroelectric smectic phases.[6,18] The latter has been experimentally realized in a recent study.[19]

Our group has published the first experimental observation of noncetrosymmetric objects formed by self-organization of triblock rod−coil molecules.[1] Prior to our report, there had been theoretical predictions that suggest rod−coil molecules as a good candidate to create discrete objects.[6,9] The precursor molecule for formation of noncentrosymmetric objects is referred to as a triblock rod−coil molecule, since two of its blocks are conformationally flexible and one block is rigid. The first flexible block has bulky repeats (e.g., styrene) and has a very low degree of polymerization. A tube around the molecule in its extended conformation (covering the van der Waals radius of the monomers) would have a larger cross section along this block compared to the other two, because of bulky repeats. Furthermore, this atactic block is not crystallizable and increases the solubility of rod−coil molecules. The second block is a flexible spacer group which links the bulky coil block to the rod block. In terms of cross section this group has the smallest

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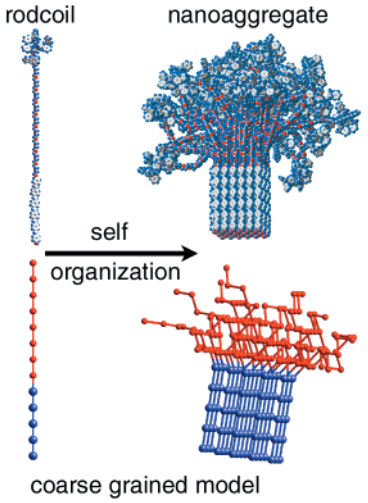

Figure 1. Rod−coil molecules form nanoaggregates by self-organization (top). Coarse grained representation of the rod−coil molecule and the aggregate used in the calculations (bottom). The coil and rod beads are represented by red and blue colors, respectively.

and most likely plays a major role in the stability of supramolecular objects. Oligoisoprene and oligobutadiene have been the most common chemical building blocks for the spacer block in work carried out in our laboratory. The third block is a crystallizable rod segment, and its large enthalpy of crystallization provides the driving force for aggregation. Unlike the first and second blocks, which are structurally diverse, the rod block has the structural precision of a chemical compound. Some of the rod segments investigated contain biphenyl ester groups[1,20,21] or phenylenevinylene structural units[22] and most would be insoluble and infusible structures without covalent attachment of coil segments.

The discrete objects formed by the self-organization of rod−coil molecules have a mushroom-like shape (Figure 1), where the coil groups form the cap and the rods crystallize to form the stem. Interestingly, these noncentrosymmetric aggregates form from solution simply by solvent evaporation. As evident from transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS), these aggregates pack into layered films. A variety of experiments[1,23,24] provide data for the noncentrosymmetric nature of these aggregates, which is most likely a result of the nanophase separation of different blocks of the molecule and preferred parallel packing of the rod blocks into the crystal. Depending on the chemical structure of the triblock molecules, the aggregates have average dimensions in the range 2−12 nm as observed by TEM.[25] Even though all of the molecules studied have the same triblock architecture, the chemical structures as well as the relative lengths of the rod and coil blocks are different. Comparison of these nanostructured materials reveals remarkable differences in aggregate shape, size, and polydispersity.

The molecules considered here are much shorter than classical block copolymers. Because of the extremely small size of the self-organized nanoaggregates, finite size effects[8,10,26] are much more pronounced. Unlike the proposed finite size aggregates with nematic or smectic cores,[6,9] the mushroom aggregates have a crystalline core, stretching the coil blocks even further. In this study, a coarse grained model was developed to understand the effect of molecular design parameters on the self-organization of rod−coil molecules. Rather than exploring the entire phase diagram, which has been thoroughly studied,[5−10] we will concentrate on the thermodynamic properties of the mushroom-shaped constrained structure. The equilibrium properties of these objects are analyzed with a lattice model. This model is based on lattice enumeration of chain conformations to calculate entropy loss due to packing of coil blocks into finite size aggregates. We assumed that there is an energetic penalty for antiparallel packing of rod molecules, which makes the mushroom-like packing favorable over a hockey puck structure, and therefore the calculations are done only for noncentrosymmetric packing of rod−coil molecules. This assumption is based on our experimental results on rod−coil molecules. A variety of rod−coil molecules with completely different chemistry but the same triblock architecture have been shown to from noncentrosymmetric aggregates.[1,20−22,27] At this point there is no fundamental understanding of the forces that lead to parallel packing of the rods into this mushroom-shaped structure. In the absence of a penalty for antiparallel packing it is highly possible that the equilibrium structure could be an interdigitated bilayer or a hockey puck shaped aggregate with two caps, which would be more favorable for entropic reasons. We also assumed that neighboring aggregates are far enough to relax any additional perturbations. The relation between the nature of the molecular precursor and aggregate properties as well as their stability were examined using this model. The precursor features of interest include architecture of the coil block and the enthalpy of crystallization for rod segments, and aggregate properties analyzed are size and size polydispersity.

Model and Method

In the coarse grained representation of the nanoaggregate, the rod−coil molecule is composed of beads connected via rigid bonds (Figure 1). The model separates the entropic and enthalpic contributions to the free energy, such that the coil beads contribute only to the configurational entropy, whereas rod blocks provide the enthalpic component. The coil block is modeled as freely jointed chains; in other words, there are no torsional or angular restrictions among these beads. The coil beads act like hard spheres; that is, the nonbonded energy between two coil beads is infinite if any two beads occupy the same lattice site and zero otherwise. Therefore, the enthalpy term in the free energy expression for coil beads vanishes, and the contribution from the coil block is purely entropic. The conformational flexibility of the coil blocks depends on the size of the nanoaggregates. It was shown previously that as the length of the coil block in a rod−coil copolymer decreases, self-organized objects grow to larger dimensions. A morphological change from zero-dimensional aggregates (all dimensions finite and small), to stripes, and to two-dimensional films can be observed.[28,29] By using a bulky coil block, the growth of the crystalline core can be limited to much smaller dimensions. In these finite size aggregates flexible coil blocks can splay around the crystalline core to reduce steric repulsions among bulky coil blocks.

Efficient algorithms have been developed for exact enumeration of the number of conformations for linear

chains on a lattice.[30−32] However, even for the short chains considered in this study, calculating the number of conformations for an aggregate of N molecules becomes extremely costly as N increases. The particle insertion method of Widom[33] and its successors have been widely used for direct calculation of thermodynamic quantities such as chemical potential from simulation in both molecular[34,35] and polymeric[36,37] systems. In these methods, assuming that all particles in the system experience the same interactions, a test particle is inserted into the system to calculate the excess chemical potential. For fast convergence of such an algorithm, a fundamental requirement is that the partition function should be dominated by a few conformations. In our model however all conformations contribute to the partition function equally since we have assumed that the coil beads have hard-sphere-type interactions. Furthermore, the system is not homogeneous such that the number of available conformations is highly dependent on the position of the molecule in the aggregate.

Here, the number of conformations (Ω_N) is calculated for different size aggregates (N) on a hexagonal lattice. For a single molecule with a given architecture, the number of conformations Ω_1 is calculated by exactly counting the acceptable conformations on the lattice, which do not violate the connectivity of beads and avoid bead overlap. It is assumed that the conformations of the coil are restricted to the half space above the top surface of the crystalline rod core. The entropy of aggregates with more than one molecule is calculated as follows. Assume an aggregate of size N with Ω_N conformations. If another molecule is added to the aggregate, the number of conformations for the new aggregate, Ω_{N+1}, can be calculated as

$$\Omega_{N+1} = p_{N+1}\Omega_1\Omega_N \tag{1}$$

where p_{N+1} is a correction factor for the overlapping conformations in the sets Ω_N and Ω_1. This correction factor is dependent on the position of the newly added molecule and the architecture of the molecule. The correction factor p_{N+1} is calculated by inserting a new molecule to an N-molecule aggregate. One conformation is chosen from each one of the sets, Ω_N and Ω_1, randomly. Using these conformations, an aggregate of $N + 1$ molecules is generated, and this conformation is tested for any overlapping beads. If there are no overlapping beads, then this conformation belongs to the set Ω_{N+1}. This process is similar to the test particle insertion method of Siepmann[36] which is an implementation of Widom's method to short chains. However, in our case the $N + 1$ chain is inserted to a predefined position, since we are interested in calculating the correction factor p_{N+1} which has a unique value for the $N + 1$ position in the aggregate. The correction factor p_{N+1} is estimated as the ratio of the number of successful trials to the total number of trials, where 10^4 total trials are performed for each new molecule added to the aggregate.

Using eq 1 recursively, starting from the exact number of conformations for a single molecule Ω_1, the number of conformations for an aggregate of size N can be obtained as follows:

$$\Omega_N = (\Pi_{i=1}^{N} p_i)(\Omega_1)^N \tag{2}$$

where $p_1 = 1$ since all the conformations are accepted for a single molecule aggregate. After Ω_N is obtained, the Boltzmann equation can be used to obtain entropy per molecule for an aggregate of size N,

$$S = \frac{k}{N}\ln(\Omega_N) = k\left(\frac{\ln(\Pi_{i=1}^{N} p_i)}{N} + \ln(\Omega_1)\right) \tag{3}$$

Unlike the coil block, the rod block is completely rigid, such that all the beads are aligned in a straight line. The rod block contributes only to the enthalpic part of the free energy expression, since it is infinitely rigid and therefore has zero entropy. The enthalpy of the crystal can be expressed in terms of its bulk and surface energies. Since the rods form a two-dimensional crystal, the enthalpy per molecule for an aggregate composed of N molecules can be expressed as follows:

$$H = \frac{2\pi r E_s - \pi r^2 E_b}{N} \tag{4}$$

where E_s and E_b are positive constants corresponding to the surface and bulk energies per molecule. Assuming $r \simeq \sqrt{N}a/\sqrt{\pi}$ for a two-dimensional crystal, where a is the lattice constant for the crystal, one obtains

$$H = \frac{2\sqrt{\pi}aE_s}{\sqrt{N}} - a^2E_b = \frac{E_s'}{\sqrt{N}} - E_b' \tag{5}$$

where E_s' and E_b' are constants with energy units. Combining eqs 2 and 4, the free energy per molecule is obtained from

$$F = H - TS \tag{6}$$

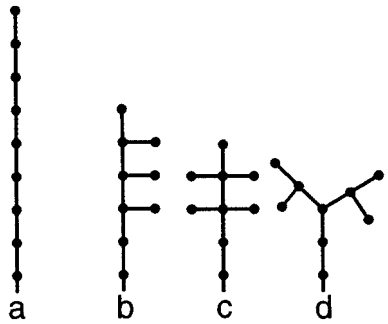

Figure 2. Different coil architectures, which represent the chemical and architectural modifications in the coil block.

Results and Discussion

Experimentally, a variety of triblock rod−coil molecules with different chemical groups and block lengths have been synthesized in our laboratory. In our model these differences are represented by changes in the connectivity of the coil beads (Figure 2). Four different molecules are considered, all of them with nine coil beads but with varying connectivity ranging from the linear connectivity in molecule **a** to the dendritic connectivity in molecule **d**.

For the enthalpic contribution to the free energy, two different rod blocks with the same bulk energy (E_b') but different surface energies (E_s') were considered in this study. Since we are interested only in a qualitative analysis of molecular variables, E_b'/k_BT (k_B is the Boltzmann constant and T is the temperature) is set to zero and $E_s'/k_BT = 5$ and $E_s'/k_BT = 10$ values are used.

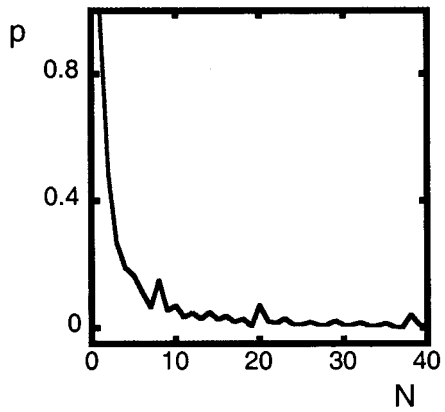

Figure 3. Correction factor for entropic loss due to addition of each new molecule to the aggregate. Only the results for the linear coil architecture (molecule **a** in Figure 2) are shown.

The surface term dominates for small aggregate size but quickly loses its effect as aggregate size increases (eq 4). At the extreme limit of infinite aggregate size the surface term vanishes. However, experimental results suggest the aggregate size is small enough so that surface and bulk energy terms are equally important. Even though both cases converge toward the bulk energy as aggregate size increases, the higher surface energy case converges much more slowly.

To calculate the entropic contribution, the correction factors p are calculated for each of the four different coil architectures. Figure 3 shows the variation of p for each new molecule added to the aggregate for a linear coil architecture. As mentioned before, p is position-dependent, and the peaks correspond to the first molecules added to form a new ring around the first molecule for hexagonally packed rod blocks in two dimension. The maximum error in any p is less than 0.32% where each correction factor p is calculated from 10^4 trials. For any given aggregate size the entropy of the aggregate is obtained using eq 3. In eq 3 the second term is the logarithm of the number of conformations for a single chain and depends only on the coil architecture. However, the first term is dependent also on the number of molecules in the aggregate and is the correction factor for the perturbation on chains as a result of close packing. This correction factor, which represents the decrease in entropy per chain, is plotted in Figure 4 for all four different coil architectures. The maximum error in entropy for any of the calculated aggregate sizes is less than 0.0013%. The entropy per molecule decreases with increasing aggregate size, since the molecules are conformationally more restricted in bigger aggregates. The slope of the entropic reduction is smallest for the linear coil architecture (molecule **a**) and increases as the head region of the coil architecture becomes bulkier (molecules **c** and **d**). This provides an effective way of disrupting the growth of the aggregates and therefore lowers the polydispersity of the aggregate size. This finding correlates well with the experimental results for rod−coil molecules incorporating a bulky triphenylamine (TPA) coil group which has a much larger cross section compared to the original styrene coil.[22] These TPA rod−coil molecules have a remarkably low polydispersity compared to any other rod−coil molecule synthesized so far in our group.

The free energy per molecule is obtained using eq 6 for $E_s'/k_BT = 5$, and the free energy curves for different architectures are shown in Figure 5. The curvature of

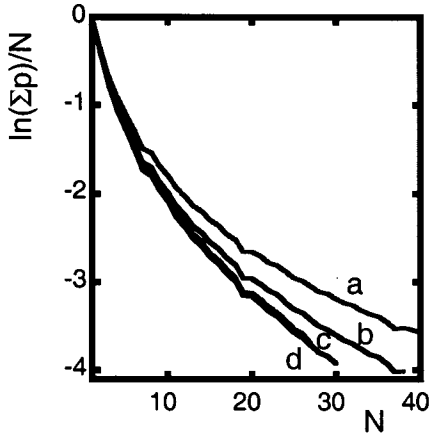

Figure 4. Reduction in the entropy of an aggregate as a function of aggregate size (N) for all four different coil architectures. Molecules with bulkiest coil blocks (molecules **c** and **d**) provide the most effective way of stopping the aggregate growth.

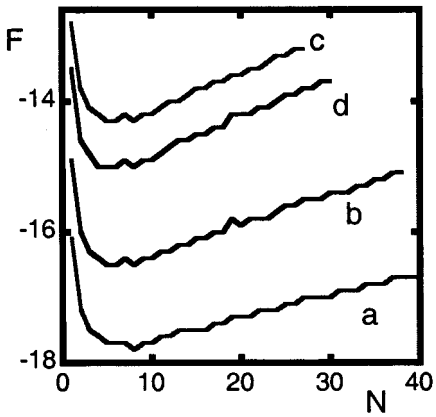

Figure 5. Free energy per molecule as a function of number of molecules per aggregate (N) for four different coil architectures. Molecules **c** and **d** yield a more well-defined minimum in the free energy curve.

the free energy curves increases as the bulkiness of the coil block increases. This suggests that in thermal equilibrium one would observe a higher polydispersity for a linear coil architecture, and the polydispersity would decrease as the coil group becomes bulkier. However, a linear coil architecture offers the most stable structure, because for a constant number of beads it has more conformational flexibility.

Another factor that will affect the equilibrium properties of nanoaggregates is the enthalpy of rod blocks. In Figure 6, a comparison of high ($E_s'/k_BT = 10$) and low ($E_s'/k_BT = 5$) surface energy rod clusters is shown for the dendritic coil architecture (molecule **d**). Molecules with high surface energy favor larger aggregate size, and therefore increasing E_s' shifts the free energy minimum toward larger N values. Moreover, a high E_s' also makes aggregate sizes smaller than the average size highly unfavorable. Experimentally, it has been observed that two rod−coil molecules with the same coil block but with different rod block yield surprisingly different results. Replacement of a rod composed of two biphenyl and two phenylenevinylene groups with a rod containing five phenylenevinylene groups changes the aggregate shape from circular to more elongated stripe-like morphologies.[27] The stripes have remarkably uniform width compared to the relatively polydisperse circular aggregates.

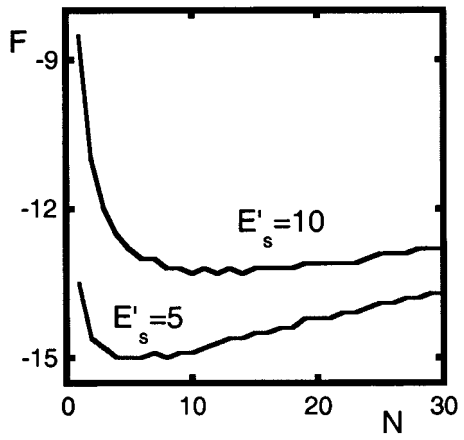

Figure 6. Free energy per molecule for high ($E_s'/kT = 10$) and low ($E_s' = 5/kT$) surface energy rods for the dendritic architecture. Higher surface energy would eliminate the small aggregates in the aggregate size distribution.

Conclusions

In this study we analyzed the key factors in self-organization of rod−coil molecules into nanoaggregates. Our results suggest in agreement with previous theoretical work that competition between entropic loss resulting from aggregation and enthalpic decrease due to crystallization yields finite-size nanoaggregates. Most importantly, we find that steric repulsions controlled by coil segment chemical structure can enhance the entropic cost of aggregation and this way control nanostructure size. Our work also suggests that polydispersity in aggregate size could be controlled through proper design of precursor molecules. Both high surface energy of rod block upon aggregation and bulkiness of coil structural units were found to be effective at reducing the polydispersity of nanostructure dimensions. Experimental findings support the model's predictions on polydispersity when very bulky units are used in the flexible segments of rod−coil molecules.

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