Molecular simulation study of self-assembly of tethered V-shaped nanoparticles

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(Received 17 July 2008; accepted 23 October 2008; published online 23 December 2008)

We use Brownian dynamics to investigate the self-assembly of single end tethered, laterally tethered, and double end tethered V-shaped nanoparticles. The simulation results are compared with model bent-core molecules without tethers and polymer tethered nanorods to elucidate the combined effects of V-shaped geometry and the immiscibility between the V-shaped nanoparticles and the tethers on the self-assembled structures. We show that the V-shaped geometry significantly alters the phase diagram of tethered nanoparticles and further that the immiscibility between particles and tethers leads to structures not previously predicted for bent-core molecules. Examples of mesophases predicted include honeycomb, hexagonally packed cylinders, and perforated lamellar phases. © 2008 American Institute of Physics. [DOI: 10.1063/1.3025918]

I. INTRODUCTION

Polymer-functionalized nanoparticles have been proposed as promising building blocks for the bottom-up fabrication of nanostructures.¹ Recent experimental studies suggest that precise control over positioning polymeric chains onto the surfaces of nanoparticles will become viable in the near future. For example, Pan et al.² synthesized tethered gold nanorods and nanospheres by nucleotide hybridization. DeVries et al.³ tailored the surface of spherical metal nanoparticles with self-assembled surfactants, inducing active poles to which they attached N-mercaptoundecanoic acid. Nie et al.⁴ synthesized cetyltrimethylammonium bromide ((C₁₆H₃₃)N(CH₃)₃Br) (CTAB)-coated Au nanorods with thiol-terminated polystyrene chains of molecular weight Mₙ = 12 000 attached at two ends. Simulations predict that the thermodynamic immiscibility between nanoparticles and their polymeric tethers will produce a collection of ordered structures, similar to those occurring due to microphase separation in block copolymers and surfactants.¹,³–⁶ However, in contrast with block copolymers and surfactants which consist of only flexible components, the local packing of hard nanoparticle “blocks” or “headgroups” gives rise to additional orientational ordering within the self-assembled mesostructures. While theoretical progress has been less developed due to the complicated entropic interactions between such asymmetric building blocks,¹¹–¹⁵ computer simulations provide a potential means to tackle the problem. Using mesoscale simulations, Zhang et al.¹ showed the distinct local packing configurations that could be formed from tethered rods, disks, triangles, and hexagons in complex three-dimensional (3D) morphologies. Horsch et al.⁶,⁷ predicted that end tethered nanorods can form chiral, twisted, hexagonally packed cylinders which are the consequence of the competition between energetic and entropic effects. They further predicted that laterally tethered nanorods would form novel bilayer sheetlike structures at high packing fraction.⁸ It is therefore suggestive that geometrical anisotropy, in terms of aspect ratio and symmetry, is an important factor that substantially affects the phase behavior of tethered nanoparticles.⁷,¹⁶

It has been argued that nanoparticle systems may form self-assembled structures that mimic those found in molecular liquid crystals.¹⁷,¹⁸ Molecular liquid crystals exhibit many exquisitely ordered phases that arise from packing considerations. One such molecule that has received particular attention because it is achiral yet forms chiral phases has a rigid V-shape unit; it is also known as a “banana” or bent-core molecule. In 1996, Niori¹⁹ was the first to experimentally demonstrate that these molecules form various unprecedentated liquid crystalline phases. Columnar rectangular ribbons (B₁),²⁰–²⁴ chiral tilted smectic (B₂),²⁴–²⁹ twist grain boundary (B₄),²⁶,³⁰–³² and polar splaying, undulated layers (B₇)²¹,²⁸,³³ are popularly reported mesophases formed by these molecules. Depending on the chemical nature of the molecules as well as their bending angle and terminal chain length, different temperature-dependent phase transitions have been observed. Owing to its unique geometry, bent-core molecules exhibit spontaneous chiral structures and switchable polar ordering that are not inherent to linear molecules. Of particular interest is the spontaneous development of superstructural chirality which can be employed in a variety of optical and electronic applications including photonic band gap materials³⁴ and, more recently, negative refractive index materials.³⁵–³⁹

Molecular chirality and long-range polar interactions are proposed theoretically,¹²,¹⁴ computationally,⁴⁰–⁴³ and
exponentially\textsuperscript{26,38} to be two major factors leading to the spontaneous formation of chiral structure and helical morphologies in the $B$ phases of bent-core molecules. At mesoscopic length scales, however, these two ingredients are not easily experimentally reproduced. Alternatively, Xu \textit{et al.}\textsuperscript{44} proposed that steric interactions might be sufficient for chiral desymmetrization and that neither molecular chirality nor dipole-dipole interactions are necessary. In their Monte Carlo simulations, coarse-grained $V$-shaped molecules with soft repulsive interactions indeed exhibit a chiral smectic phase with a random interlayer polar distribution. Johnston \textit{et al.}\textsuperscript{45} demonstrated that bent-core molecules interacting via a Gay–Berne potential, which is essentially a directional Lennard-Jones (LJ) potential, assemble into a twist grain boundary phase. The simulated superhelical structure is in good agreement with previous experimental work in the literature. Dewar \textit{et al.}\textsuperscript{46} reported a tilted smectic $B$ phase with a coarse-grained bead-chain model and a LJ pairwise interaction. They argued that this “bumpy” model is physically relevant due to the fact that the bent-core units are normally made up of several aryl groups. Actual bent-core molecules, however, are synthesized with flexible terminal chains; these parts of the molecule have been often excluded in previous theoretical or computational work. Recently, Dewar and Camp\textsuperscript{47} studied systems of bent-core molecules with two short flexible tails, one at each end. They demonstrated that, as compared to previous rigid models, the flexible model led to enhanced fluctuations in the smectic-layer structures, which is in better correspondence with those in actual smectic liquid crystals. However, in their configurational-bias Monte Carlo simulations, they ignored steric interactions between tails on different molecules. The prior simulation studies of tethered nanoparticles described earlier suggest that these flexible segments may play an important role in the self-assembly of these molecules.

In this study, we investigate the self-assembly of polymer tethered $V$-shaped nanoparticles (TVNs). The simulation results are compared with both the model bent-core molecules without tethers and polymer tethered nanorods, a limit of TVNs in which the opening angle is 180°. Our study thereby elucidates the combined effects of $V$-shaped geometry and the immiscibility between the $V$-shaped nanoparticles and the tethers on the self-assembled structures. We show that the $V$-shaped geometry significantly alters the phase diagram of tethered nanoparticles and further that the immiscibility between particle and tethers leads to structures not previously predicted for bent-core molecules.

\section{II. MODEL AND SIMULATION METHOD}

We utilize minimal, coarse-grained models and Brownian dynamics (BD) to study the phase behavior of a solution of TVNs in three dimensions. Our minimal models, which are not restricted to any specific system but instead pertain to a general class of tethered nanoparticles, are developed based on empirical potentials that are successful in capturing the relevant physics of block copolymers, surfactants, and colloidal particles.\textsuperscript{48,49} A primary advantage of this approach is that the liquid crystal behavior of the $V$-shaped nanoparticles and the complex entropic interactions arising from the asymmetry between the rigid nanoparticles and the flexible polymer tethers are automatically incorporated. In this study, we aim to investigate the role of the number and position of tethers of fixed length, the opening angle of the $V$-shape nanoparticles, and the immiscibility between tether and particle on the resulting self-assembled morphologies.

\subsection*{A. Model}

The computationally efficient model of $V$-shaped particles that we study here consists of five beads with diameter 1.0$\sigma$, arranged rigidly in the shape of the letter “V.” The center to center distance between two adjacent beads in a particle is 1.0$\sigma$. The particles are connected to tethers via finitely extensible, nonlinear, elastic (FENE) springs.\textsuperscript{50} Previous simulations of tethered nanorods showed that rod roughness, which is controlled by the number of beads used to represent the particle, have little effect on the self-assembled structures.\textsuperscript{7} Additionally, this model closely relates to the previous simulations of bent-core molecules\textsuperscript{44,46} and recently synthesized colloidal particles.\textsuperscript{51,52} The opening angle of the $V$ group is set to be 140°, which is the angle normally attained for actual bent-core molecules and used in previous simulations.\textsuperscript{44–46} Flexible tethers are modeled as linear chains consisting of four beads of diameter 1.0$\sigma$ bonded together via FENE springs. The tether length is chosen to be roughly equal to the distance between two $V$ ends, allowing for direct comparison with moderate aspect ratio tethered nanorods.\textsuperscript{6,7} We consider three geometries of TVNs that are single end, double end, and laterally tethered as illustrated in Fig. 1.

To account for solvent selectivity, we assume that the solvent is poor for the nanoparticles and good for the tethers for all cases unless otherwise indicated. The effective interaction between solvophobic $V$-shaped particles is therefore modeled by a 12-6 LJ potential between the individual beads of the particles, truncated and shifted to zero at $r_{\text{cut}}=2.5\sigma$, to incorporate short-range attraction and excluded volume:
The nonbonded interaction between solvophilic tethers is modeled by the purely repulsive Weeks–Chandler–Andersen (WCA) potential between tether beads. WCA is essentially a LJ potential truncated and shifted to zero at its minimum:

\[
U_{\text{WCA}}(r) = \begin{cases} 
4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + 4\epsilon \left[ \left( \frac{\sigma}{r_{\text{cutoff}}} \right)^{12} - \left( \frac{\sigma}{r_{\text{cutoff}}} \right)^6 \right], & r < r_{\text{cutoff}} = 2.5\sigma, \\
0, & r \geq r_{\text{cutoff}} = 2.5\sigma.
\end{cases}
\]

The thermodynamic immiscibility between nanoparticles and tethers is represented by using the repulsive WCA potential for nanoparticle-tether interactions. In our simulations, the potential energy well depths are chosen to be identical for nanoparticle-nanoparticle, nanoparticle-tether, and tether-tether interactions, \(\epsilon_{\text{NP-NP}} = \epsilon_{\text{NP-T}} = \epsilon_{\text{T-T}} = \epsilon\). The natural units for these systems are the diameter of a bead, \(\sigma\), the mass of a bead, \(m\), and the LJ well depth \(\epsilon\). The time scale is defined as \(\tau = \sigma(m\epsilon)^{-1/2}\) and the dimensionless temperature is \(T^* = k_B T/\epsilon\). The number density is defined as \(\rho = N/V\), where \(N\) is the total number of beads and \(V\) is the box volume.

B. Simulation method

The BD simulation method is widely used in the study of block copolymers, surfactants, and colloidal particles. In BD, each bead is subjected to conservative, random, and drag forces, \(F^C_i\), \(F^R_i\), and \(F^D_i\), respectively, and its motion is governed by the Langevin equation:

\[
m_i \ddot{r}_i = F^C_i + F^R_i + F^D_i.
\]

Here \(m_i\) and \(r_i\) are the bead mass and position, respectively. The conservative force \(F^C_i\) is determined by the gradient of the pairwise potentials between a bead and its neighbors. The random and drag forces represent the bombarding effects of solvent molecules on a bead. The random force \(F^R_i\) is independent of the conservative force and satisfies the dissipation fluctuation theorem:

\[
\langle F^R_i(t) \rangle = 0,
\]

\[
\langle F^R_i(t) F^R_j(t') \rangle = 6\gamma k_B T \delta_{ij} \delta(t-t').
\]

The drag force is related to the bead velocity \(F^D_i = -\gamma v_i\), where \(\gamma\) is the friction coefficient and \(v_i\) is the bead velocity. We choose the friction coefficient \(\gamma = 1.0\) to limit the ballistic motion of a bead in a time step to approximately 1.0\(\sigma\). The combination of the random and drag forces serves as a nonequilibrium-conserving thermostat for the system and helps minimize numerical round-off errors that can accumulate during long simulation runs. Since the steady-state solution of the Langevin equation yields the Boltzmann velocity distribution, BD reproduces the canonical (NVT) ensemble. The rotational degrees of freedom of V-shaped particles are incorporated using the equations for rotation of rigid bodies with quaternions. We employ the velocity Verlet scheme to integrate the equation of motion of tether beads and to advance the rotational motion of the V-shaped particles with a time step \(\Delta t = 0.005\tau\).

We sampled the phase diagram of monolayer V-shaped nanoparticles at nine different number densities \(\rho\) ranging from 0.1 to 0.9, corresponding to volume fractions from 0.005 to 0.47. The systems are initially athermal, where all interactions are treated with the repulsive WCA potential, and at high temperature \((T^* = 1.6)\) and low concentration. The simulation box is gradually rescaled until the target concentration is reached. At the target concentration, the systems are equilibrated until the fluctuation of the potential energy falls below 5% over several million time steps. To ascertain that any observed phases are not affected by our finite box size, we simulated systems with \(N_p = 200, 600, 1000, 1200, 2000, 3000\) building blocks for a fixed number density. We then repeat the simulations with different cooling paths to help avoid kinetically trapped structures at certain concentrations and to ascertain that the predicted structures are independent of the thermodynamic path. Using this procedure, we obtained metastable states only when trying to produce perforated lamellar phases with single end TVNs for small system sizes, e.g., with \(N_p = 200\) and 600 building blocks. For larger systems and all other structures, we always achieve equilibrium structures regardless of the cooling schedule. The simulations presented in this work were performed with an in-house code and represent approximately 5000 hours of central processing unit time on Power G5 2.0 GHz processors.

III. RESULTS AND DISCUSSION

A. Single end tethered V-shaped nanoparticles

The phase diagram of single end TVNs is similar to that of tethered nanorods, reproducing all phases except the tetragonally perforated lamellar phase. Similar to end tethered nanorods, we observe micelles ordered in a body-centered cubic (bcc) mesophase structure, hexagonally packed cylinders, hexagonally perforated smectic layers, and smectic layers as the volume fraction of the building blocks increases (Fig. 2). Although the bend in the nanoparticle geometry does not substantially change the mesophase classification, it does change the local packing of the particles within the aggregates, as follows.
creases, the micelles are ordered into a bcc morphology as the asphericity parameter, which is defined as the ratio of the micelle interaction. The asphericity parameter is close to zero, indicative of a spherical micelle. In contrast with the micelles predicted for single end TVNs at $T^*=0.8$ and $\rho=0.3$, the majority of micelles consist of 35–65 particles. Table I shows that at $\rho=0.2$ and $T^*=0.8$, the majority of micelles consist of 35–65 particles where the asphericity parameter is close to zero, indicative of a spherical shape. In contrast with the micelles predicted for single end TVNs, snapshots of these spherical micelles in Fig. 3(b) show that the tethers tend to extend radially from the center of the micelle, resulting in an isotropic intermicelle interaction.

1. BCC spherical micelles (M)

For number densities from 0.1 to 0.3 for $T^* \leq 0.8$ single end TVNs aggregate into micelles. As concentration increases, the micelles are ordered into a bcc morphology [Fig. 3(a)]. To quantify the shape of the micelles, we compute the asphericity parameter $A_3$ which is defined as $A_3 = \frac{1}{2} \sum_{i<j} (R_i^2 - R_j^2) / \left( \sum_{i<j} R_i^2 \right)$, where $R_i^2$ is the eigenvalue of the gyration tensor of each micelle and the average is performed over all micelles in the size range. The asphericity parameter $A_3$ may vary from zero for a spherical micelle to unity for a rod-shaped micelle. Table I shows that at $\rho=0.2$ and $T^*=0.8$, the majority of micelles consist of 35–65 particles where the asphericity parameter is close to zero, indicative of a spherical shape. In contrast with the micelles predicted for single end TVNs, snapshots of these spherical micelles in Fig. 3(b) show that the tethers tend to extend radially from the center of the micelle, resulting in an isotropic intermicelle interaction.

2. Hexagonally packed cylinders (H)

For $0.3 < \rho < 0.56$, hexagonally packed cylinders are formed for $T^* < 1.2$ [Fig. 4(a)]. Hexagonally packed cylinders are theoretically predicted and experimentally observed for bent-core molecules, block copolymers, and other shape amphiphiles such as end tethered nanorods, tethered nanospheres, and tethered nanocubes. Although there are random defects along each cylinder, the packing of the nanoparticles within each cylinder is similar to that predicted for the rectangular columnar phase ($B1$) of bent-core molecules, in which the V-shaped nanoparticles nest together in cross section with the polar direction perpendicular to the cylinder axis [Fig. 4(b)]. Nonetheless, while the nested packing of V-shaped nanoparticles is strongly energetically favored, it also induces an entropic penalty that can be mitigated either by nanoparticles tilting with respect to the interfacial normal, increasing the distance between tether anchor points, or switching the anchor points randomly from one side to another. Additional entropy is achieved by randomly alternating the polar direction of bundles of nested nanoparticles to reduce the tether overcrowding [Fig. 4(c)]. This suggests that it is the immiscibility of tethers and particles, which is absent in previous simulations of bent-core molecules, that results in additional orientational order within each cylinder. Moreover, Fig. 4(c) also indicates that the nanoparticle-tether junctions are ordered locally into a hexagonal packing, and thus are restricted to planar inter-

<table>
<thead>
<tr>
<th>Micelle size</th>
<th>Asphericity parameter</th>
</tr>
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<tbody>
<tr>
<td>35–40</td>
<td>0.02 ± 0.019</td>
</tr>
<tr>
<td>40–45</td>
<td>0.02 ± 0.014</td>
</tr>
<tr>
<td>45–50</td>
<td>0.02 ± 0.017</td>
</tr>
<tr>
<td>50–55</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>55–60</td>
<td>0.02 ± 0.015</td>
</tr>
<tr>
<td>60–65</td>
<td>0.03 ± 0.011</td>
</tr>
</tbody>
</table>
faces which prohibit a relative twist between adjacent nanoparticles. This explains why single end TVNs do not exhibit a smooth and uniform twist along the cylinders as predicted for end tethered nanorods. 7

3. 3D hexagonal perforated lamellae (HPLs)

For 0.56 < ρ ≤ 0.7, we observe a morphology intermediate between columnar and lamellar phases [Fig. 5(a)]. As ρ increases from that of the cylinder phase, the repulsion between aggregates induces a morphological change toward a higher interfacial surface to volume ratio. When quenching a disordered system, we observe that the nanoparticles first form interconnected tubes with the tethers extending outside. As T decreases further, the interconnected tubes merge and rearrange into sheets to maximize the distance between repulsive aggregates and minimize interfacial areas. Because the sheets are formed by the combination of tether-coated interconnected tubes, they are perforated by the tethers already occupying the merged space. Packing the nanoparticles into sheets is energetically favorable for the nanoparticles but is entropically unfavorable for the tethers. The entropic penalty induced by the high grafting density of the tethers can then be alleviated by the following factors. First, the nanoparticles pack with tether anchor points distributed randomly on both sides of the sheet. Second, the perforations in each sheet are ordered into a hexagonal lattice as shown in Fig. 5(b), which allows for a uniform distance between neighboring perforations, and hence reduces the entropic penalty caused by packed nanoparticles between perforations. Finally, the perforations are arranged between sheets in a 3D ordering to maintain the constant and lowest concentration of tethers at each perforation. Since the perforations in layers closely relate to the excluded volume interactions between the tethers, these 3D structures have not been predicted for bent-core molecules in previous simulations where the terminal chains were ignored. 54, 56

We did not observe the tetragonally perforated lamellar phase as predicted for tethered nanorods in Ref. 6, even within the same window of number densities. As pointed out in Ref. 6, the key factor that gives rise to the tetragonally perforated lamellar phase is that the nanorods must align with the sheet normal. This orientation is clearly impossible for bent rods.

4. Lamellar phase (L)

At 0.8 ≤ ρ ≤ 0.9 we observe a lamellar phase at temperatures at and below Tc = 1.4. As compared to end tethered nanorods 6 which form lamellar phases at Tc ~ 4.0, the packing of V-shaped particles into layers is more difficult, requiring alignment along two axes versus one axis. Consequently, at high density, ordered phases appear at lower temperatures as compared with tethered rods. With Np = 2000–3000 building blocks, we observe three independent layers as shown in Fig. 6(a). Here the intralayer fluctuation is much less than in the lamellar phase formed by tethered nanorods 6 because the V-shaped nanoparticles nest within each other to achieve optimal packing, thereby providing additional stability within each layer. Moreover, as indicated by the split second peak of the two-dimensional nanoparticle-nanoparticle distance correlation function [Fig. 6(b)], the nanoparticles within each layer pack into a regular hexagonal lattice 46 with tether anchor points alternated randomly on both sides to reduce the grafting density of tethers. Edge-on views of the layers [Fig. 6(a)] show that the nanoparticles exhibit a uniform tilt with respect to the interfacial normal, maximizing the distance between tether anchor points, and thus allowing the tethers to have more free volume. For 0.9 ≤ Tc ≤ 1.4, the tilt angle varies from 29° to 31°, which is consistent with previous simulations 46 and experimental observations. 26, 29 Interestingly, owing to their two-dimensional geometry, the tilting V-shaped nanoparticles result in a well-defined handedness within each layer, which is unavailable for the smectic phase in tethered nanorod systems. Figure 6(c) reveals that V-shaped nanoparticles within a sheet tilt to allow for an efficient packing of adjacent spherical beads. To quantify the handedness of each layer, we measure the average chiral order parameter with the rms average chiral fluctuations: 44

$$\overline{\chi} = \frac{1}{M} \sum_{i=1}^{M} \chi_i$$
Here \( \chi_i \) is the chiral order parameter of a V-shaped nanoparticle which is defined as \(^4\)

\[
\chi_i = \left( \frac{1}{M} \sum_{i=1}^{M} (\chi_i - \bar{\chi})^2 \right)^{1/2}.
\]

Here \( \chi_i \) is the chiral order parameter of a V-shaped nanoparticle which is defined as \(^4\)

\[
\chi_i = [(\mathbf{m} \times \mathbf{n}_i) \cdot \mathbf{p}_i](\mathbf{m} \cdot \mathbf{n}_i).
\]

Here \( \mathbf{m} \) is the local sheet normal, and \( \mathbf{n}_i \) and \( \mathbf{p}_i \) are the end-to-end vector and unit polar vector of the nanoparticle, respectively. At equilibrium, for all layers, the average chiral order parameter is remarkably greater than the rms average chiral fluctuations, indicative of a well-defined chirality. For example, for the snapshot shown in Fig. 6(a) we obtain \((\chi; \chi_{\text{rms}}) = (-0.41 \pm 0.006; 0.04 \pm 0.011)\), \((0.39 \pm 0.008; 0.09 \pm 0.018)\), and \((-0.42 \pm 0.004; 0.04 \pm 0.001)\) for each layer, respectively. Although the current results are reminiscent of the chiral smectic \( C \) phase \((B2)\) formed by bent-core molecules, we hypothesize that the chirality varies randomly from layer to layer because adjacent layers are only weakly coupled by the excluded volume interactions between the tethers. \(^4\) This can be attributed to the absence of directionally favored interactions to help guide the interlayer correlation as in the simulations of Johnston \textit{et al.} \(^5\)

**B. Laterally tethered V-shaped nanoparticles**

The previous simulations of Horsch \textit{et al.} \(^8\) showed that laterally tethered nanorods form stepped ribbons and two kinds of bilayer sheets with different crystalline interlayer packings of symmetries \( P_2 \) and \( C_{mm} \), respectively, in a solution good for the tethers and poor for the nanorods; the bilayer sheet mesophases have been recently confirmed experimentally. \(^5\) The interaction between tethers are mod-

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**FIG. 6.** (Color) (a) Lamellar phase (L) formed by \( N_p=2000 \) single end TVNs at \( T^* = 1.3 \) and \( \rho = 0.8 \). (b) Nanoparticle distance correlation within the layer shown in the inset. The blue ends are without tethers. (c) Local packing of the bumpy V-shaped nanoparticles within a sheet.

**FIG. 7.** (Color online) Phase diagrams of (a) laterally TVNs and (b) laterally tethered nanorods. [Adapted from M. Horsch, Z. Zhang, and S. C. Glotzer, \textit{Nano Letters} \textbf{6}, 2406 (2006)]. Black filled circles indicate disordered states. Symbols indicate ordered mesophases. Left: interconnected tubes (I) and lamellae (L). Right: elongated micelles (EM), stepped ribbons (R\(_{C_{mm}}\)), \( C_{mm} \)-packing lamellae (L\(_{C_{mm}}\)), and \( P_2 \)-packing lamellae (L\(_{P_2}\)).
are formed for 0.2
the structure with tethers removed.

we observe a decrease in the disorder-order tem-
perature of the lamellar phase
removal.

Complex 3D morphologies
structures the V-shaped nanoparticles form a network of in-
connected tubes without any specific order. These com-
plex structures result from the competition between the V-shaped nanoparticles attempting to maximize their contacts, but there is no long-range order because their alignment is randomly disturbed by the tethers attempting to maximize their free vol-

we ran five simulations with different cooling paths at each concentration. The average nanoparticle distance correlation (not shown) and the system potential energy at the target temperature indicate that these structures are stable and reproducible. Though we have not been successful in determining if these structures have any specific periodic ordering, the existence of this mesophase demonstrates that a bend in the nanoparticle shape can lead to a substantial change in the phase behavior of laterally tethered nanorods.

b. Lamellar phase (L) We find a lamellar phase at number densities from 0.5 to 0.9 at $T < 0.9$ [Fig. 8(b)]. The lamellar phase here is completely different from the tilted smectic phase formed by either end tethered V or end teth-
ered nanorods in that the V-shaped nanoparticles lie in the plane of each layer. In that respect, the morphology is more similar to that observed for laterally tethered nanorods, although here the particles do not form bilayer sheets. However, the observed morphology is similar to lamellar structures that are experimentally observed and theoretically predicted for lateral rod-coil block copolymers. Figure 8(b) shows that within a sheet the V-shaped nanoparticles fit together locally to maximize their contacts, but there is no 2. Attractive tethers

To model the attraction between tethers we use the LJ potential between tether beads instead of the WCA potential used in the previous case. Interestingly, we observe the honeycomb structures as shown in Fig. 9 over a wide range of number densities from 0.3 to 0.8. The honeycomb structures are in agreement with those experimentally observed for lateral rod-coil block copolymers where the incompatibility between rods and coils plays a vital role in the microphase
separation of the system. Simulation snapshots reveal that the tethers pack into hexagonally packed cylinders and the V-shaped nanoparticles form a connected network (Fig. 9). The radius of the cylinders approximates the average end-to-end distance of the tethers. It is therefore evident that a change in the interaction between the tethers results in a complete change in the phase behavior of the system.

C. Double end tethered V-shaped nanoparticles

The phase diagram of double end TVNs with attractive V particles and repulsive tethers is sketched in Fig. 10. As compared to single end TVNs, we also observe cubic ordered micelles, elongated micelles, and hexagonally packed cylinders; however, no smectic phases are found presumably because of the high volume fraction of the tethers.

1. BCC spherical micelles (M)

For 0.1 < ρ ≤ 0.3, we observe micelles as $T^* \approx 0.8$ as shown in Fig. 11(a). At sufficient concentrations, the micelles form a bcc morphology. The average number of V-shaped nanoparticles in each micelle is smaller than the micelles formed by single end tethered nanoparticles presumably due to the larger excluded volume of the tethers attached at both ends of the V-shaped nanoparticles. Figure 12 shows the remarkable difference in the average size of the micelles formed by single end tethered and double end tethered nanoparticles. We use the asphericity parameter to quantify the micelle shape and find that the micelles are also spherical. For example, at $\rho=0.3$ and $T^*=0.5$, we obtain $A_5 = 0.02 \pm 0.018$, indicative of spherical shape. Additionally, simulation snapshots [Fig. 11(b)] reveal that within a micelle the nanoparticles assume a twist between neighbors to compensate for the elastic strain in the tethers.

2. Long micelles (LM)

For $0.3 < \rho \leq 0.4$, elongated micelles are formed at $T^* \approx 1.0$ [Fig. 13(a)]. As the concentration of the system increases, the micelles expand to accommodate more V-shaped nanoparticles. We observe that the micelles are stretched into rodlike aggregates because of the nanoparticles attempting to nest together to minimize energy and the tethers attached at their two ends attempting to maximize their free volume [Fig. 13(b)]. One consequence of this is that the micelles grow into irregularly twisted ribbons of which an example is shown in Fig. 13(c). We again use the asphericity parameter to quantify the micelle shape and an example of the asphericity parameter as a function of the micelle size is given in Fig. 14. The asphericity parameter of large micelles ap-
proaches unity, indicative of rodlike shapes. Although the micelle size is nonuniform, we observe that the micelles are nematically ordered. Similar to the tethered nanorod system, the nematic order here results from the anisotropic interaction between micelles, which, because of their rigid cores, behave like rods.

3. Hexagonally packed cylinders (H)

As the concentration of the system increases, nematically ordered elongated micelles grow and merge to form cylinders. We observe a hexagonally packed cylinder phase as the number density is increased from 0.4 to 0.8 and \( T^* \approx 1.2 \) [Fig. 15(a)]. Although the hexagonally packed cylinder phase is commonly seen in nanoparticle-polymer systems, it is not usual in bent-core molecule systems. In the columnar phases formed by bent-core molecules, the columns form a rectangular lattice and within each column the molecules are proposed to pack in parallel such that their polar direction is either parallel (B1) or perpendicular (B1rev) to the cylinder axis. Gorecka et al. reported the first examples of hexagonally packed columnar phases (Colh) for polycatenar bent-core molecules. They further predicted that the cross section of each column consists of four molecules organized into a starlike shape. In our cylinder phase, however, the V-shaped nanoparticles are not only favored to nest together to maximize their contacts but they also tilt with respect to the interfacial normal to increase the distance between tether anchor points, leading to a twist between nanoparticles in each cross section [Fig. 15(b)]. An example of a cylinder in Fig. 15(c) shows that the twist in the cylinders is more irregular and randomly disturbed than that in the case of single end TVNs apparently due to the higher density of the tethers. Because the repulsive tether-coated cylinders are effectively repulsive to each other, the hexagonal lattice is entropically favored to maintain a constant spacing between neighbors.

It is interesting to note that, despite the similarity between our model double end TVNs and the model molecules used in Ref. 47, we do not observe any smectic-layer structures. This can be attributed to the exclusion of the dipole-dipole interaction between the V groups and the inclusion of the excluded volume interaction between the tethers in our simulations. Double end TVNs are an example of ABA triblock copolymers in which the B group has a rigid bent shape. Therefore, we expect their mesophases to be similar in part to those known for ABA triblock copolymers. Depending on the relative volume fraction of A and B copolymers, self-assembled structures can range from spherical micelles, cylinders, 3D bicontinuous, perforated lamellas, and lamellas. In our simulations, a double TVN is analogous to an \( A_2B_2A_4 \) triblock copolymer where lamellar structures are suppressed presumably due to the high relative volume fraction of tethers, which dominates entropic effects. We further postulate that in order for the double end TVNs to assemble into smectic phases as in bent-core molecules the tethers should be significantly shorter than the rigid nanoparticle. We have examined model building blocks with the tethers consisting of two beads (e.g., the \( A_2B_2A_2 \) configuration) to test this hypothesis. Preliminary results indicate that lamellar structures are eventually formed at sufficiently high concentrations (e.g., \( \rho=0.8 \)) (Fig. 16). Further investigation of this geometry will be the focus of future work.

IV. CONCLUSION

We present here the phase diagrams of TVNs with three different geometries. We have demonstrated that building block architecture significantly affects both the mesophase behavior and local packing of self-assembled structures.
While the phase behavior of single end TVNs has much in common with end tethered rods, the local packing within the mesophases is distinguished by the neat packing of the V-shaped nanoparticles. Most interesting is the spontaneous chiral symmetry breaking occurring due to the emergent chirality of V-shaped nanoparticles in lamellar phases, which is unavailable for linear nanorods. For laterally TVNs, the bent-shape geometry completely changes the phase behavior as compared to that of laterally tethered linear rods, resulting in a previously unreported interconnected structure as well as a lamellar phase. By changing the interactions between tethers from repulsive to attractive, we observe a completely different morphology, the honeycomb structure, over a wide range of concentrations. Meanwhile, the bulkiness of immiscible tethers in the double end TVN, a mesoscale analog of bent-core molecules, is shown to suppress the formation of lamellar structures. Instead we observe a hexagonally packed V-shaped nanoparticles. Most interesting is the spontaneous chiral symmetry breaking occurring due to the emergent V-shaped nanoparticles, is shown to suppress the formation of smecticlike phases as previously computational work reported—would not be adequate to produce any long-range ordered structures such as the twist grain boundary (B4) or tilted smectic (B2) phases with bent-core molecules.

ACKNOWLEDGMENTS

T.D.N. would like to thank C. R. Iacovella for helpful discussions. This work was supported by the Air Force Office of Scientific Research under MURI Grant No. FA9550-06-1-0337. T.D.N also acknowledges the Vietnam Education Foundation.