

Pattern formation in a dendrimer model

Zheng Yu Chen and Chengzhen Cai

Guelph-Waterloo Program for Graduate Work in Physics and Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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A dendrimer is a hyperbranched macromolecule that is grown from a central core generation by generation. We demonstrate through Monte Carlo simulations of a dendrimer model in two dimensions that when the terminal monomers and the interior monomers interact through an effective Flory-Huggins parameter χ , an angularly dependent domain structure forms in the molecule for sufficiently large χ . Based on the simulation data, we further show that the formation of the domain pattern is a smooth crossover, not a phase transition, from a mixed structure. [S1063-651X(98)10701-8]

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It is well known that the blending of two immiscible polymer species, A and B , usually results in a polymer-polymer phase separation at a macroscopic scale with a distinct phase boundary between the A - and B -rich phases. In systems consisting of polymers that contain thermodynamically incompatible blocks connected by covalent bonding, microscopic structures may be stabilized, forming different phase domains. One of the well-studied examples is the mixture of diblock copolymers with covalent bonds between the incompatible blocks; the system exhibits a large variety of microscopic structures as the relative block lengths and the Flory-Huggins parameters vary [1]. A second example is systems of binary mixtures of grafted polymer chains, in which two types of immiscible linear homopolymers, A and B , are randomly end grafted onto a surface; when the numbers of A and B molecules are same, the polymer chains of the same type splay laterally to form clusters, so that their free ends form stripe domains with alternating A - and B -rich regions next to each other [2–4]. Another example is the system of grafted, Y-shaped copolymers on a flat surface in which the Y-shaped copolymer is composed of an arm of a homopolymer chain A , and another arm of an incompatible homopolymer chain B jointed by a short stem which tethers the entire molecule to a surface. Recently it has been shown that such systems may exhibit well-defined domain structures along the surface of the grafting plane [3–5]. Moreover, a fourth example is the system of grafted diblock copolymers in a selective solvent, in which the diblock copolymers self-assemble into an ordered layer of pinned micelles [6,7].

Is there a similar pattern-formation phenomenon and possibly an accompanied phase transition in a *single* starburst dendrimer molecule? A starburst dendrimer is a hyperbranched molecule stemming from a central core, as illustrated by the sketch in Fig. 1 [8–20]. In a G -generation starburst dendrimer molecule, the zeroth generation is the central core which branches into f arms containing P monomers (“spacers”) each, with each end of the previous generation further branching into $f-1$ arms containing the same number of spacer monomers. Terminating at the G th generation, the dendrimer has a regular branched, starburst structure. The dendrimer sketch in Fig. 1 is a four-generation dendrimer containing $f=3$ functional branching points with $P=2$ spacer monomers in each linear portion [21]. Most of the

recent models used for investigating the conformational properties of dendrimers assume that all monomers are thermodynamically identical, and most theoretical studies have focused on the radial distribution of the monomer density as a function of the radius from a common center (the center of mass or the branching center) [22–32]. Recently, attention has also been paid to investigating the segregation of the three dendrons rooted from the center [29]. Here we do not intend to model any molecules specifically. Rather, we address a more general question in this Brief Report: would any microstructure form inside a codendrimer as a consequence of the difference in the chemical composition of the terminal-interior parts, and, if it would, what spatial symmetry would exist?

We shall generally label the interior monomers (open circles in Fig. 1) the A monomers, and the terminal ones (filled circles) the B monomers, and assume that the Flory-Huggins parameter that describes the interaction between the

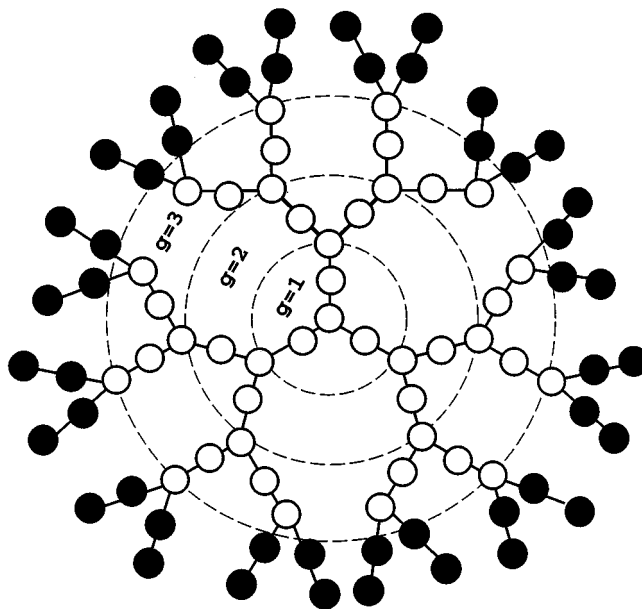


FIG. 1. A four-generation dendrimer model with $f=3$ and $P=2$. The filled and empty circles represent monomers of different types B and A , respectively.

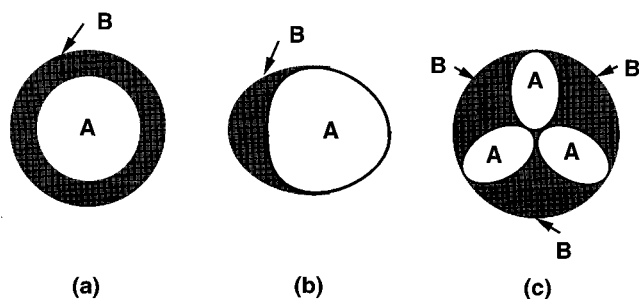


FIG. 2. Three probable segregation patterns in dendrimers. The dark area is the B -rich region and the white the A -rich region.

A and B monomers is χ . In Fig. 2, we sketch a few possible domain structures that the dendrimer could exhibit for large enough χ . The structure in Fig. 2(a) contains a strong segregation of the B monomers, represented by the dark area, toward the surface of the dendrimer (a “core-shell” structure), in which the spherical symmetry is retained. The structure in Fig. 2(b) contains A - and B -rich domains, separated by a probably curved boundary (an “egg-yolk” structure), in which twofold symmetry exists. The structure in Fig. 2(c) contains a more exotic pattern with threefold rotational symmetry (a “trillirium-flower” structure). In diblock copolymer brushes, instead of forming flat A - and B -rich layers parallel to the grafting surface, the brushes prefer to form a periodic stripe pattern with A - and B -rich stripes arranged along the surface of the grafting plane [3,4]. The latter structure has a higher entropy. Structurally, the dendrimer molecule considered here bears some resemblance to the system of a polymer brush grafted to a common spherical surface. Thus the core-shell structure, similar to the flat layer structure in diblock copolymer brush, is probably unfavorable to the entropic energy. As demonstrated below, for a two-dimensional dendrimer, we found that the structure in Fig. 2(c) is stable for sufficiently large χ . The stabilization of a certain structure is the result of competition between a reduction of the interface boundary and a maximization of the entropy. The structure in Fig. 2(c) would have a larger interface between the A - and B -rich domains, but a higher entropy in comparison to the structure in Fig. 2(a).

The analytic formulation for the dendrimer model sketched in Fig. 1 is difficult: there is no satisfactory mean-field model in the literature to describe a “homodendrimer,” i.e., a dendrimer containing identical monomers [22,28]. Therefore, we resorted to Monte Carlo simulations for the study. The actual model that we used was similar to the dendrimer sketched in Fig. 1: we only considered molecules with $P=2$. There are thus $N_A=6(2^{G-1}-1)+1$ monomers of type A , $N_B=6\times 2^{G-1}$ monomers of type B , and a total of $N=N_A+N_B=6(2^G-1)+1$ monomers in the molecule. The lengths of the bonds between the adjacent monomers were set to 1. To simulate the interaction between the A and B monomers, we simply used a step function potential, constructed in such way that any A - B pair that has a distance smaller than the force range of 0.9999 would experience a positive potential of magnitude ϵ_{AB} . The effective Flory-Huggins parameter is thus $\chi=\epsilon_{AB}/k_B T$, where k_B is the

Boltzmann constant and T is the temperature. More conveniently, χ was treated as an adjustable parameter in the simulations.

We further simplified our calculation by only considering two-dimensional dendrimers only. Our purpose is to demonstrate domain formations in dendrimers. Two-dimensional simulations make the task much easier. We will carry out three-dimensional simulation at a future time. The two-dimensional model itself can be used to model dendrons with central cores grafted along a common straight line, which would exhibit cylindrical symmetry. The steric repulsion between the monomers was modeled by considering an excluded-volume diameter d which was chosen to be smaller than the bond length. We adopted an algorithm that allows for bond crossing, subject to the monomer-monomer excluded-volume interaction. In each Monte Carlo step, a new configuration was obtained by using the pivot method [33], which rotates the whole portion of the molecule around a randomly chosen monomer as the center of the rotation. The new configuration was rejected if it contained overlapping monomers, and otherwise accepted after further verification of the acceptability based on the Metropolis criterion that accounts for the Boltzmann weight associated with the repulsion ϵ_{AB} . A five-generation molecule and a six-generation molecule were studied. Since the steric interaction is more severe in a two-dimensional space, the excluded-volume diameters were fixed at relatively small values: $d=0.2$ for both $G=5$ and 6 cases. The simulations were performed at different temperatures corresponding to various values of $\chi=\epsilon_{AB}/k_B T$. For each χ , 5×10^6 Monte Carlo steps were considered. In each simulation, a total of 5×10^5 initial Monte Carlo steps were used for thermal equilibration.

The normalized density profiles of monomer A and monomer B for the case of $G=5$ are shown in Figs. 3(A) and 3(B), respectively, in three-dimensional plots for several values of the effective χ . The height represents the density and the basal plane represents the two-dimensional space considered. The first three peaks near the core of the A -monomer density profile correspond to the locations of the first three monomers branched off from the center; these peaks are always present. The first plot of Fig. 3(B) shows that there is a weak angular dependence for $\chi=0$, where the three directions in which the B monomers concentrate are directly coupled to the directions of the three peaks in Fig. 3(A), viewed from the center. There is a weak segregation of the three branches, which is a phenomenon suggested earlier by Mansfield [34], and discussed recently by Murrat and Grest [29]. The last set of plots in Figs. 3(A) and 3(B) is for $\chi=0.3$. Apart from the three peaks associated with the first generation, the density profile for the A -type monomers now shows a more interesting structure; there are three minima and the three stronger maxima in the plot. The density profile for the B monomers shows three strong peaks where the B monomers concentrate. Note the locations of these maxima correspond to the locations of the minima in the A -monomer plot. Also appearing near the center is a three-fold deep well, complementary to the maxima in the plot for the A -type monomers. This demonstrates that A - and B -rich domains will form for strong χ , or, in reality, at low temperatures. The middle plots in Figs. 3(A) and 3(B) are for the case of $\chi=0.1$, which is approximately the crossover point when the demixing starts to take place.

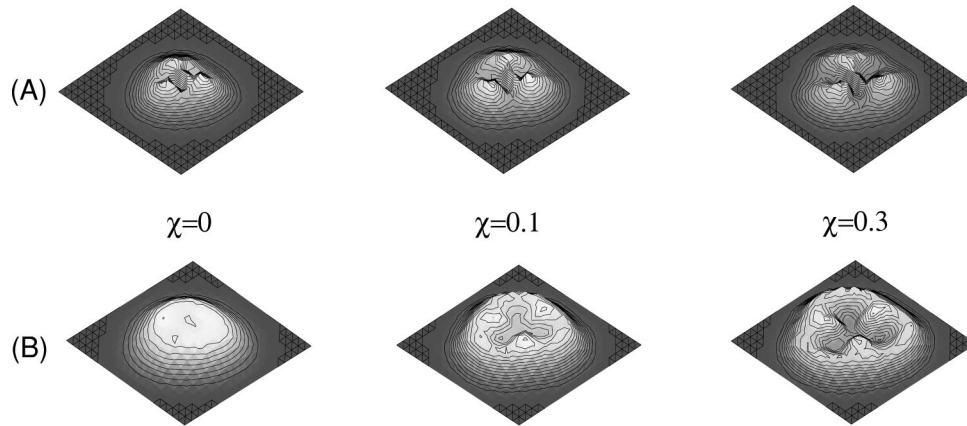


FIG. 3. The average density plots of A (the first row) and B monomers (the second row) for $G=5$ and 3 values of the parameters: $\chi=0, 0.1$, and 0.3 . The dark, gray, and white colors represent densities varying from the lowest to the highest.

When χ increases from 0 to 0.3, the weak maxima of the angular distribution function for the B monomers (not shown) disappear completely, and three new strong maxima start to appear at angles complementary to those of the earlier ones. In an attempt to describe quantitatively the angular dependence of these domain structures, we considered the order parameters

$$S_A = \frac{1}{N_A} \sum_i \langle \cos 3\theta_i \rangle, \quad (1a)$$

$$S_B = \frac{1}{N_B} \sum_j \langle \cos 3\theta_j \rangle \quad (1b)$$

for the A and B monomers, respectively. The indices i and j go over those of the A and B monomers, and N_A and N_B is the number of the A and B monomers, respectively. The angle θ is measured from the central core with respect to one of the three strong peaks of the A monomer density. Figure 4 shows the order parameters as functions of the effective χ parameter. For small χ , both the order parameters S_A and S_B have positive values, indicating a mixing of the A and B

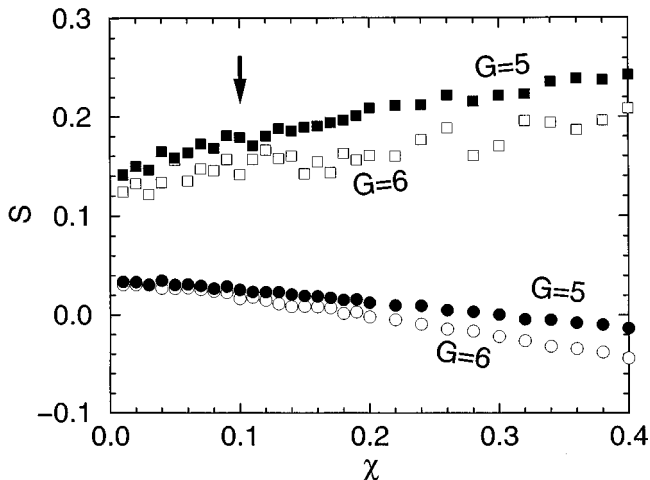


FIG. 4. The order parameters S_A (squares) and S_B (circles) as functions of χ . Filled symbols are for the case of $G=5$, and the open symbols for the case of $G=6$.

monomers and a weak segregation of the three branches due to binding constraints. As χ increases, S_B starts to decrease, indicating a trend for the A - B demixing. The turning point is around 0.1, based on observations of a series of plots similar to those in Fig. 2, when the B -rich domains start to establish clearly.

So far we have not discussed the nature of the pattern formation from a phase transition perspective. The S_B curve changes smoothly as χ increases. There is no indication of a sudden change of the value or the slope of the S_B curve near $\chi=0.1$, where we started to observe the pattern formation. To confirm further that this process is really a smooth cross-over and not a phase transition, we also collected information on the scaled heat capacity from our simulations, which is calculated by measuring the energy fluctuations

$$C/k_B = (\langle E^2 \rangle - \langle E \rangle^2) / k_B^2 T^2. \quad (2)$$

Figure 5 displays the C/k_B curve as a function of the effective parameter χ . In view of the smoothness of these curves, we concluded that there is no evidence that the process of pattern formation in this dendrimer model is a phase transi-

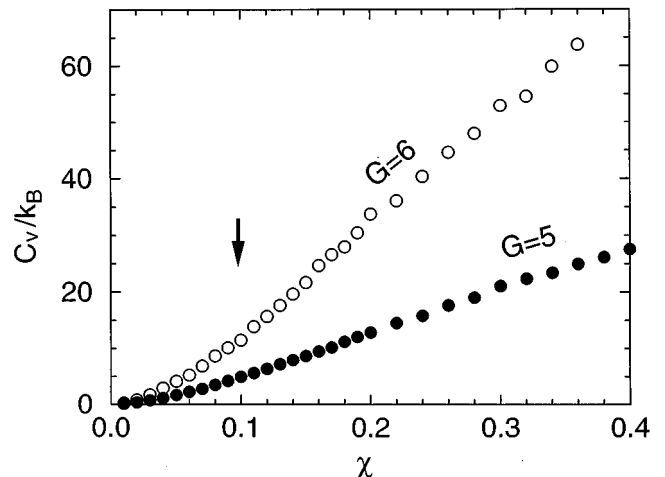


FIG. 5. Scaled heat capacity C/k_B as a function of χ . The filled symbols are for the case of $G=5$, and the open symbols for the case of $G=6$.

tion. In comparison, the formations of various diblock copolymer microstructures are usually associated with first order phase transitions [1]. Though the “ripple” phase transition is suggested to be second order in grafted Y-shaped copolymers [3], there has not been any observation that confirms this prediction in similar systems [2–4].

An interesting extension of this study would be to consider selective solvents for the *A* and *B* monomers. A poor solvent for the *B* monomers would effectively introduce attractions between *B* monomers, thereby producing a more concentrated distribution of the *B* monomers. The problem is that once the *B* monomers start to collapse into a dense region, the *A* monomers would also begin to gather in order to avoid the *B*-rich region. The intrinsic branching center could be pushed away, and symmetry breaking would take place.

The interplay of structural constraints, entropy maximization, and interface reduction could produce even richer patterns. Clearly, further studies are desired for these cases. Since we have restricted the monomers to move in a two-dimensional space, the question concerning the possibility of pattern formation in a three-dimensional dendrimer still remains. The threefold symmetry observed in this study could be replaced by other types of demixing symmetries for a three-dimensional dendrimer. One possibility is the formation of a three-dimensional structure similar to the sketch in Fig. 2(B).

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