Spontaneous Curvature of Dense Cylindrical Core-Shell Structures formed by Dendrite-like Polymers in Selective Solvent: A Computer Simulation Study

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Abstract

Using the bond fluctuation model we have examined a 3D bottle-brush polymer with dendrite-like side chains. The backbone and the inner parts of the side chains are considered to be chemically indistinguishable and form the cylindrical core. The outer parts of the side chains form a cylindrical shell. Three different situations are considered with respect to the solvent conditions of both the core and the shell. When the core experiences poor solvent conditions and the shell good solvent conditions to keep the polymer from collapsing, the polymer displays conformational behavior significantly different from both other cases that behave like a persistent chain. It turns out that the bond angle correlation data is fitted quite well using a theoretical model that includes both stiffness and curvature and which has been developed in our previous publication on spontaneous curvature in adsorbed comb copolymers. If both curvature and stiffness could be increased it may be possible to obtain ring closure depending on solvent conditions or temperature.

Introduction

The conformational properties of comb copolymers consisting of a flexible backbone to which side chains are densely grafted at regular distances have formed the subject of many publications in the last decade [1–34]. The competition between the intrinsic backbone flexibility and the excluded volume of the side chains results in a stiffening that can be sufficiently pronounced to speak of a cylindrical bottle-brush. The foundation of the theoretical analysis of cylindrical bottle-brush molecules was laid by the papers by Birshtein and coworkers [1] and Fredrickson [3], while the first successful syntheses of these polymers were done by Schmidt and Tsukahara [4–6]. Experimental conformation of the stiffening of bottle-brush molecules into shape persistent cylindrical objects soon followed in the form of light scattering experiments [13].

Recently, the interest in comb copolymer brushes involves not only the conformational properties due to the excluded volume of the side chains, but also the influencing of these properties by imposing different chemical properties for the backbone and the side chains as well as by changing
solvent conditions [28–30, 33, 35–38]. In this way it has appeared possible to alter the shape of the polymer brush or to induce intra molecular phase separation.

In our current study, we employ the bond fluctuation model (BFM) to investigate bottle brush polymers with dendrite-like side chains. The side chain segments near the surface of the bottle brush are of different chemical composition than the rest of the side chain material and the backbone. The object is to obtain a cylindrical core shell structure. We consider three different cases. One case is the athermal case in which the conformational behavior of the polymer is governed by architecture and excluded volume only. In this case the core and shell are indistinguishable as no interactions other than excluded volume are present. In both other cases the polymer segments in the shell repel each other. The difference in both remaining cases is contained in the solvent conditions for the core segments: either moderate solvent just prior to the coil to globule transition for a linear homopolymer or poor solvent conditions beyond the coil to globule transition. The shell serves as a stabilization that is to keep the polymer from collapsing.

We will demonstrate that the poor solvent case differs from both other cases in that the conformational properties deviate significantly from the behavior of a simple persistent (wormlike) chain by using a bond angle correlation plot as well as scattering analysis. In our previous paper on spontaneous curvature in comb copolymers strongly adsorbed at a flat surface [39] we developed a theoretical model that includes both stiffness and curvature. Using this model we were able to fit the bond angle correlation data quite well. Surprisingly, the very same model seems to fit the bond angle correlation data in the present system. This may be explained by a large persistence length that causes the polymer, locally, to behave as a 2D system.

If both curvature and persistence could be increased it may be possible to obtain a system that exhibits ring closure depending on temperature or solvent conditions. The investigation of polymers for which conformational properties can be influenced in this way aims at the application of these in amongst others nano technology and medicine.
Simulation Model

The bond-fluctuation model (BFM) in 3 dimensions [40–43] was employed to perform the simulations. In the 3-dimensional BFM a polymer is modelled by a coarse grained representation consisting of a sequence of beads. For linear chains, when there is no topological stiffness, these beads allow for interpretation in terms of the Kuhn statistical segment size. Every bead occupies 8 lattice sites on a cubic lattice and during simulation the bond length between beads is allowed to vary. As originally described in the papers by Deutsch and coworkers [41–43] the allowed bond lengths are limited by excluded volume constraints and the requirement that entanglement is incorporated into the model. Hence, the original set of bond lengths has been determined to be

\[ b = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10} \]  

This set contains 108 possible bond vectors and allows for 100 different bond angles \( \epsilon \in [0, \pi] \). In contrast, 6 bond vectors with one length allowing for two angles appear in single site lattice models like the Verdier-Stockmayer model. As Deutsch and Dickman [41] demonstrated, the BFM approximates the continuum limit (in which there is no lattice) more closely than single site lattice models. Importantly, lattice models in general allow for more efficient simulations than off-lattice models [40], especially when interactions are taken into account [42].

To model the interactions we introduce a stepwise potential between each bead pair in the system, excluding chain neighbors [35, 42, 43]:

\[ u_{ij}(r) = \begin{cases} \infty & r < 2 \\ \epsilon_{ij} & 2 \leq r \leq \sqrt{10} \\ 0 & r > \sqrt{10} \end{cases} \]  

The Latin indices distinguish possible bead types on the basis of their chemical nature.

As usual, the Monte-Carlo (MC) scheme in the context of the BFM consists of repeatedly choosing a random monomer in the system and trying to displace the monomer by one lattice spacing in a randomly chosen direction (taking into account excluded volume and bond vector con-
The scheme proceeds with the calculation of the energy change when the move appears possible. Finally, the Metropolis criterion dictates the transition probability: \( P = \min\{1, \exp(-\Delta E)\} \). Here \( \Delta E \) is the energy difference, in units of \( k_B T \), with respect to the previous state of the system. When the move is rejected, the previous state of the system is re-sampled instead of sampling the rejected state and the scheme is repeated.

The simulations are performed on an ‘infinite’ three-dimensional cubic lattice, as opposed to imposing periodic boundary conditions. This is advantageous when simulating single polymer chains. Usually, like in the melt, a finite lattice is used with periodic boundary conditions. However, in the case of simulating single chains precautions have to be made to warrant that monomers on the chain do not interact with monomers of a different periodic image.

The three-dimensional lattice as present in computer memory consists of 200x200x200 lattice sites. These are mapped onto the bead position vectors \( \vec{r} = (x, y, z) \mid 0 \leq x, y, z < 200 \). Position vectors outside this region are mapped back into the finite lattice, preserving their ‘real’ coordinate in memory as well. Effectively, a list (which may be empty) of beads is connected to each lattice site in the finite lattice, with monomers in the list belonging to different, non-overlapping, regions in real lattice space. In fact, it is like folding a road map with the size of the map growing and shrinking as required. The main advantage of this technique is that, as far as the polymer chain is concerned, the lattice has infinite size and undesirable interactions between periodic images are prevented independent of the size of the finite lattice in computer memory. This makes it possible to perform simulations of large systems even when memory restrictions are tight.

A representative set of conformations and connected physical properties was obtained in the usual way: A pre-prepared conformation of the system was brought into thermodynamic equilibrium by applying the MC scheme with a liberal amount of MC moves. Meanwhile, collective properties of the system, e.g. the radius of gyration of the molecule, were being monitored to check that these values eventually levelled out. In a system in thermodynamic equilibrium these values oscillate around a certain constant value. Multiple independent runs are performed to ensure that the system is not trapped in a local free energy minimum. After equilibration of the system, the MC scheme was continued and from the resulting set of conformations the physical properties of interest were calculated.
Results and Discussion

Originally, the system we set out to investigate was going to be a comb copolymer with diblock side chains. In this scenario the inner block, which is grafted to the backbone, experiences poor solvent conditions as does the backbone. The outer block experiences good solvent conditions and serves to create sufficient surface tension to keep the polymer from collapsing into a globule. Preliminary theoretical analysis indicated that if the outer blocks are short the polymer may become unstable with respect to bending. However, the first simulation results showed that the outer blocks did not succeed in preventing a collapse. In other words, compared to the collapse transition of a linear homopolymer, the collapse transition upon decreasing the solvent quality of the inner blocks and the backbone did not shift sufficiently to create a large enough window of stability. In this window of stability the battle between the core, that wants to collapse, and the shell, that wants to maintain the surface, may cause bending instability. To increase the size of the window of stability with respect to collapse we chose to use dendronized side chains instead of diblocks: Instead of one outer block, three outer blocks are grafted to the inner block.

The system under investigation consists of a backbone of 120 segments to which an equal amount of side chains are attached. The side chains consist of an inner block of length 10 and three outer blocks of length 3. The inner blocks and the backbone are considered to be chemically indistinguishable.

The system is investigated under three different conditions. One of these is the case where the core (backbone and inner block of the side chains) is experiencing poor solvent and the shell is experiencing good solvent conditions. Poor solvent conditions are obtained by introducing an attractive potential between the segments belonging to the core. For the model employed, \( \theta \)-conditions for a linear homopolymer are reached for an potential strength of \( \epsilon = -0.235 \) and the coil-to-globule transition takes place near \( \epsilon = -0.29 \). The poor solvent conditions for the core correspond to a value \( \epsilon_{\text{core}} = -0.33 \). For the shell a repulsive potential is introduced \( \epsilon_{\text{shell}} = 1.2 \) that effectively serves to increase the excluded volume of the segments in the shell. The second system differs from the first only by a different core potential \( \epsilon_{\text{core}} = -0.26 \). This value is beyond the \( \theta \)-point but
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still well before the coil-to-globule transition. We shall refer to this case as the moderate solvent case. The third system is the athermal case. Here the behavior of the system is governed only by its topology and excluded volume.

In our previous article on spontaneous curvature of comb copolymers strongly adsorbed at a flat surface [39] we introduced a model that included both a persistence mechanism and curvature. The main prediction that followed from this treatment was that curvature should be visible as a deviation from normal persistent behavior in an investigation of the bond angle correlation function of the backbone. For a persistent worm-like chain it holds that $\langle \cos\theta(s) \rangle \propto \exp(-s/\lambda)$. Here $\cos\theta(s)$ is the cosine of the angle between two tangents to the backbone that are $s$ monomers apart [9, 11, 13, 14, 17]. The brackets denote a thermodynamic average. A plot of the logarithm of $\langle \cos\theta(s) \rangle$ versus $s$ should yield a straight line with a slope equal to minus the inverse of the persistence length. In our analysis of the 2-dimensional comb copolymer the prediction was made that in the presence of curvature $\langle \cos\theta(s) \rangle = \exp[-s/\lambda] \cos(Cs)$. Here $C$ is the mean curvature and it corresponds to the distance in beads along the backbone for which, in the mean, two tangents to the backbone are perpendicular.

In the 3-dimensional case the treatment becomes mathematically more engaging, as bending does not necessarily take place in a plane. However, if the persistence length $\lambda$ is of the same order of magnitude, or even larger, than $C$ it may be expected that the 2-dimensional model serves as a good approximation for the 3-dimensional case for values of $s$ not exceeding $C$.

Figure 6.1 shows a bond angle correlation plot for all three cases. The dashed line is a theoretical fit using $\lambda = 36$ and $C = 44$. It is immediately apparent that the poor solvent case behaves quite differently from both other cases which show simple persistent behavior. Upon decreasing the solvent quality the persistence length increases. For the athermal case the persistence length equals $\lambda = 21$, in intermediate solvent $\lambda = 25$ and the fitted line for poor solvent corresponds to $\lambda = 36$. However, on small length scales the backbone becomes more folded as apparent from the mean of the cosine of the bond angle $\langle \cos\theta(1) \rangle$. For the athermal case its value is 0.48, for intermediate solvent 0.41 and for the poor solvent case 0.35. For the poor solvent case the fitted persistence length and the curvature are of the same order of magnitude. In this case it may be expected that, for small values of $s$,
the 2-dimensional theory may fit the data reasonably well. Nevertheless, the quality of the fit is striking which appears to indicate that indeed the polymer has become unstable with respect to bending.

A different way of characterizing the conformational properties of the polymer is by investigating the scattering function. In our previous work on spontaneous curvature in 2 dimensions the presence of curvature gave rise to distinct peaks in the scattering data. In the 3-dimensional case there is an extra orientational angle over which averaging takes place. Any statistically significant bending takes place in a multitude of different orientations rather than in the plane as is true for the 2-dimensional case. As such, any peaks may be smoothed or averaged out. Figure 6.2 shows the Holtzer plots of the athermal case as well as the poor solvent case. For a worm like persistent chain the Holtzer plot goes through a maximum after which it levels out to a horizontal plateau for length scales smaller than the Kuhn statistical segment size. The height of the plateau equals $\frac{\pi}{l}$, where $l$ denotes the contour length per segment, and is proportional to the linear mass density. The athermal system behaves as expected. The Holtzer plot levels off at approximately $qS(q) \approx 1.5$. Using the previously fitted value of $\lambda = 21$ segments and the fact that the Kuhn statistical segment size is twice the persistence length this yields for the Kuhn length $l_K \approx 48$ lattice units, corresponding to a value $q \approx 0.075$. This is consistent with what we see from the Holtzer plot since for larger values of $q$ the graph is almost horizontal. It should be noted that only much stiffer chains really reach a perfectly horizontal plateau [34].

For the poor solvent case the situation is quite different. As the radius of gyration for both systems is similar (athermal: $\langle R_g^2 \rangle^{1/2} = 52$, poor solvent: $\langle R_g^2 \rangle^{1/2} = 48$) and the mean bond angle does not differ that much, the contour length per segment is also expected to be similar. However, the persistence length measured in a number of segments is significantly larger for the poor solvent case $\lambda = 36$ and therefore the Holtzer plot is expected to level off for smaller values of $q$ than for the athermal case, which is obviously not the case. Indeed, the Holtzer plot for the poor solvent case does not level off at all, but reaches a minimum first. The data appears to indicate a continuing oscillatory behavior, but for larger values of $q$ the statistical errors become very large. Apparently, the system does not behave like a simple worm-like chain.
Figure 6.3 shows a number of typical snapshots for the system with poor solvent conditions. The core segments are colored black while the segments belonging to the shell are colored grey. The right hand side shows two helical shapes. On the left the bend takes place more in the plane giving more horseshoe-like shapes. If it would be possible to increase the stiffness of the polymer and increase the curvature as well it may be possible to make the ends meet. If, additionally, the ends would be cleared of mutually repulsive segments it may be possible to get ring closure. Further research in this area should provide the answers to matters like whether it is possible to obtain stable rings and whether it is possible to have the polymers alternate between a linear topology and a ring by changing the solvent conditions e.g. by varying the temperature.
Figure 6.1: Bond angle correlation plot for three different cases: Athermal, moderate solvent and poor solvent. The poor solvent case does not show simple persistent chain behavior. The dashed line is a theoretical fit using a model including both stiffness and curvature.
Figure 6.2: Holtzer plot for the athermal case and the poor solution case. Here also the poor solvent case does not show simple worm-like chain behavior.
Figure 6.3: A number of typical snapshots for the poor solvent case.
Concluding remarks

Using the bond fluctuation model we have examined a 3D bottle-brush polymer with dendrite-like side chains. The backbone and the inner parts of the side chains are considered to be chemically indistinguishable and form a cylindrical core. The outer parts of the side chains form a cylindrical shell. Three different cases have been examined. One case is the athermal case in which the conformational behavior of the polymer is governed by architecture and excluded volume only. In both other cases the polymer segments in the outer shell of the cylindrical bottle-brush repel each other whereas the core experiences either moderate solvent conditions or poor solvent conditions. The outer shell serves as a stabilization that prevents a coil to globule collapse.

In the case where the core experiences poor solvent conditions it is found that the conformational behavior of the polymer deviates significantly from that of a simple persistent (worm like) chain. This is illustrated both by a bond angle correlation plot and scattering analysis. In the first case a theoretical fit is included that appears to fit the data surprisingly well considering that the model is the same as introduced in our previous paper on 2D comb copolymers adsorbed at a flat surface [39]. This model includes both stiffness and curvature. The quality of the fit of a 2D theory may be explained by the fact that stiffness and curvature are of the same order of magnitude, in which case the polymer may be considered a 2D object (ring segment) at short length scales.

Our results demonstrate that it is possible to introduce curvature in the present architecture using suitable solvent conditions. Whether it is possible to increase curvature as well as increasing persistence in order to obtain ring closure, depending on solvent conditions, is a matter that should be investigated in future research.
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References


