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Published in:
Macromolecular Rapid Communications

DOI:
[10.1002/\(SICI\)1521-3927\(20000201\)21:2<110::AID-MARC110>3.0.CO;2-P](https://doi.org/10.1002/(SICI)1521-3927(20000201)21:2<110::AID-MARC110>3.0.CO;2-P)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2000

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Saariaho, M., Subbotin, A., Ikkala, O., & Brinke, G. T. (2000). Comb copolymer cylindrical brushes containing semiflexible side chains: a Monte Carlo study. *Macromolecular Rapid Communications*, 21(2). [https://doi.org/10.1002/\(SICI\)1521-3927\(20000201\)21:2<110::AID-MARC110>3.0.CO;2-P](https://doi.org/10.1002/(SICI)1521-3927(20000201)21:2<110::AID-MARC110>3.0.CO;2-P)

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The off-lattice Monte Carlo method is applied to investigate the equilibrium conformations of isolated comb copolymer cylindrical brushes in an athermal solution. The molecules considered consist of a flexible backbone, which is densely grafted with semiflexible side chains. The study focuses on the influence of the degree of intrinsic stiffness, λ_{side} , of the side chains on the conformational behavior of the molecules. It is demonstrated that with a fixed side chain length, M , the local length scale conformational fluctuations of the backbone increase as a function of λ_{side} . However, the persistence length, λ , of the cylindrical brush increases considerably with the side chain stiffness, indicating that the backbone becomes more extended at the large length scale. Moreover, as a function of λ_{side} , there is an increase in the ratio λ/D of the persistence length and the diameter, D , of the brush. This behavior is in good agreement with recent theoretical predictions and provides important new insight in the latest experimental observations.

Characteristic conformation of a comb copolymer cylindrical brush consisting of a flexible backbone of 300 beads (black) and 150 semiflexible side chains (white) of length $M = 60$. Intrinsic stiffness of the side chains is given by λ_{side} ($\tau = 165^\circ$)/ $M \approx 0.48$. Magnification shows the strongly fluctuating local backbone structure and illustrates the definition of the angle, $\theta(s)$, between two chain segments separated by a distance s along the backbone

Communication

Comb copolymer cylindrical brushes containing semiflexible side chains: a Monte Carlo study

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(Received: August 16, 1999; revised: October 1, 1999)

Introduction

Due to entropy, linear flexible polymer chains typically assume coillike conformations. However, when such a simple molecule is densely grafted with side chains to form a comb copolymer structure, it may adopt a highly extended cylindrical wormlike conformation in a dilute good solvent, as shown by recent experimental studies^{1–5}. It is also well established that the extension of the backbone may be based exclusively on the excluded volume

interactions between side chains, i.e. no additional driving forces – e.g. charges or amphiphilicity – are required.

Among the most interesting questions related to cylindrical brushes with high grafting density of side chains is the dependence of the backbone stiffness, described by the persistence length, λ , on the length, M , of the side chains. Moreover, the aspect ratio λ/D , where D is the brush diameter, has a particular importance since it deter-

mines the possibility of lyotropic behavior^{6,7}. From a theoretical and computational point of view, however, the complex molecular architecture of comb copolymer cylindrical brushes has made it challenging to draw definite conclusions about the conformational behavior^{8–21}. In the case of molecules with fully flexible side chains of length M in a good solvent, Birshtein and co-workers predicted⁸ more than a decade ago that the persistence length is proportional to the brush diameter, $\lambda/D \propto 1$, and, therefore, no lyotropic behavior should result from simply increasing M . In contrast, Fredrickson⁹ later derived that the asymptotic scaling for long side chains should be $\lambda/D \propto M^{9/8}$. This is in qualitative agreement with the most recent prediction, $\lambda \propto M^2$, by Subbotin and co-workers¹¹, based on the self-consistent field approach.

Off-lattice Monte Carlo simulations^{12–15} have not yet confirmed the theoretically predicted increase of λ/D as a function of M , but rather showed λ/D to be approximately constant in the regime reached computationally ($M \leq 80$). An explanation is given by the theoretical observation¹¹ that the prefactor for the $\lambda \propto M^2$ scaling is very small, thus suggesting that still longer side chains are required to see the upturn of λ/D . On the other hand, in the case of molecules with rigid rodlike side chains of length L , a similar scaling behavior, $\lambda \propto L^2$, is predicted¹⁰, but this time with a considerably larger prefactor compared to the case of flexible side chains. This provides a possible explanation why we do observe in our recent simulations¹⁵ the increase of λ/D as a function of the length, L , of the rodlike side chains, already for relatively short side chains ($L \geq 20$). Also, when the molecules are confined inside a two-dimensional slit, the increase of λ/D as a function of M is observed in the simulations¹⁴ even in the case of flexible side chains, apparently due to a more pronounced excluded volume effect.

The persistence length, λ , is used to describe the large length scale persistence of the molecules. However, there is also another characteristic length for cylindrical polymer brushes, this time describing the local length scale behavior. It was recently shown, both by theory and simulations^{10,15}, that for cylindrical polymer brushes the local length scale conformational fluctuations depend on the flexibility of the side chains: flexible side chains induce local stretching, whereas rigid side chains do not influence the local backbone conformations. In fact, the existence of these two characteristic lengths is also supported by the most recent experimental studies^{4,5} where the main chain of a cylindrical brush was observed to be “locally coiled” and persistent at the large length scale.

The size of the computationally considered cylindrical polymer brushes¹⁵ (backbone of 300 beads and 150 side chains of lengths up to 80 beads each) is clearly comparable with the experimentally studied molecules^{1–5} having e.g. polystyrene side chains of length about 50 monomer

units. Therefore, based on the simulation data, we may assume that also real cylindrical polymer brushes with rigid and flexible side chains should display a pronouncedly different elastic behavior at the two length scales. Moreover, the ratio λ/D is expected to be practically constant for molecules with fully flexible side chains in the regime of polymer brushes studied experimentally^{1–5}, although it should finally increase for molecules with sufficiently long side chains. Therefore, the experimentally observed large persistence length (of the order of 100 nm)¹ is probably due to the semiflexible nature of the side chains.

In conclusion, the use of rigid rodlike side chains is an efficient way to obtain an extended conformation of a cylindrical brush at the large length scale, whereas a locally smooth backbone conformation may be achieved by using flexible side chains. However, side chains of real cylindrical brushes are neither fully flexible nor totally rigid, as assumed in the previous computational studies^{12–15}, but rather semiflexible. Therefore, we decided to study the crossover behavior by considering molecules with semiflexible side chains and a fixed side chain length ($M = 60$). We focus on the effect of the intrinsic side chain stiffness on the conformational behavior at the two length scales introduced above.

Model and details of the simulation

Off-lattice Monte Carlo (MC) simulations were used to study the equilibrium conformations of comb copolymer cylindrical brushes containing semiflexible side chains. The focus is on the behavior of a single isolated molecule in a good athermal solvent, and, therefore, only intramolecular excluded volume interactions between beads are present in the system. The backbone of the molecules was modeled as a fully flexible freely jointed chain of 300 beads, every other of which was grafted with a side chain of length $M = 60$ beads. A simple way was used to account for the intrinsic stiffness of the side chains by modeling them as freely rotating chains of beads with a fixed valence angle, τ , between two successive side chain segments. This model may be viewed as a discrete representation of the continuous wormlike chain model (also known as the Kratky-Porod model)^{22,23}, which is, however, additionally modified to include excluded volume. All the beads of the system have the same size, which is taken to be equal to the segment length and is used as the unit of length. Based on the relation valid for ideal freely rotating chains, the persistence length of the side chains, λ_{side} , describing the intrinsic local stiffness, may be estimated by $\lambda_{\text{side}} = 0.5 \cdot (1 - \cos(\tau))/(1 + \cos(\tau))$, where the prefactor 0.5 follows from the definition that the Kuhn segment length is equal to twice the persistence length.

In the present model, the case of totally rigid rodlike side chains is obtained by setting $\tau = 180^\circ$ ($\lambda_{\text{side}} = \infty$). To

study the other extreme of fully flexible side chains, we applied the freely jointed chain model, i.e. with non-fixed τ , for the side chains. Our simulations show that this model leads to side chain conformations with the average bond angle, $\langle\tau\rangle$, between side chain segments equal to approximately 111° . In good agreement with this, it was found that a molecule with freely rotating side chains and a fixed bond angle $\tau = 110^\circ$ behaves almost identically as a freely jointed chains with respect to the numerical values of all the quantities of interest. Therefore, we may conclude that for the cylindrical brushes considered the case of fully flexible side chains is effectively obtained by using freely rotating side chains with $\tau = 110^\circ$. Consequently, the studied range of fixed bond angles of the side chains was chosen to be $110^\circ \leq \tau \leq 180^\circ$ to cover the whole range of intrinsic stiffnesses.

Configuration space is sampled according to the Metropolis importance-sampling scheme²⁴. The initial conformations were formed as 2D structures in the xy -plane. Trial moves of the main chain beads consist of a set of different local and global chain motions described in detail in our previous papers^{12–15}. About half of the attempted main chain steps were local motions while the rest were more global “bendings” of the whole end part of the molecule. For the semiflexible freely rotating side chains, trial moves consist of pivot type rotations around the side chain segments. This type of procedure preserves all the values of the valence angles, τ , of the side chains.

Results and discussion

A typical simulated structure of a comb copolymer cylindrical brush containing semiflexible side chains is shown in Fig. 1. The molecule consists of a backbone of 300 beads and 150 side chains of length $M = 60$ beads each with a fixed valence angle $\tau = 165^\circ$. The intrinsic stiffness of the semiflexible side chains of this particular structure is given by $\lambda_{\text{side}} \approx 28.8$. However, it is clearly more instructive to use λ_{side} scaled by the side chain length $M = 60$, i.e. to use λ_{side}/M . When λ_{side}/M approaches 1.0, we may expect nearly rodlike behavior. The magnification in Fig. 1 clearly illustrates how the backbone exhibits strong local conformational fluctuations, whereas at the large length scale the backbone has a strong preferred direction of propagation, i.e. the persistence length, λ , is large. Fig. 1 also exemplifies the definition of the angle, $\theta(s)$, between two chain segments separated by a distance s along the backbone. The average cosine of this angle, $\langle\cos\theta(s)\rangle$, is the correlation function of the backbone and will be used to analyze the behavior of the molecules at the two length scales.

Fig. 2 shows the semilogarithmic presentation of the correlation function $\langle\cos\theta(s)\rangle$ of the molecule shown in Fig. 1, and also of the molecules with fully flexible and totally rigid side chains of the same length of beads. The

Fig. 1. Characteristic conformation of a comb copolymer cylindrical brush consisting of a flexible backbone of 300 beads (black) and 150 semiflexible side chains (white) of length $M = 60$. Intrinsic stiffness of the side chains is given by λ_{side} ($\tau = 165^\circ$)/ $M \approx 0.48$. Magnification shows the strongly fluctuating local backbone structure and illustrates the definition of the angle, $\theta(s)$, between two chain segments separated by a distance s along the backbone

correlation data clearly demonstrate the existence of two characteristic lengths for all the molecules considered. At the local range (small s values) there is a fast decline of the correlations, whereas at the large range the correlations decrease much slower. Moreover, as a function of the side chain stiffness, the local correlations decrease but the large length scale correlations increase.

A more detailed understanding of the local length scale behavior of the molecules is obtained from Fig. 3, which shows the nearest neighbor bond angle correlation $\langle\cos\theta(s=1)\rangle$ as a function of the parameter λ_{side}/M (where $M = 60$) describing the effect of the intrinsic stiffness of the side chains. Fig. 3 also includes the limiting values of $\langle\cos\theta(s=1)\rangle$ obtained for the molecules with rigid side chains ($\tau = 180^\circ$, $\lambda_{\text{side}}(180^\circ)/M = \infty$) and freely jointed flexible side chains. The first observation is that the local backbone correlations decrease monotonously as a function of λ_{side}/M , thus indicating that the backbone becomes locally more coiled for stiffer side chains. Moreover, the correlation $\langle\cos\theta(s=1)\rangle$ practically declines only in the region $\lambda_{\text{side}}/M < 1.0$, after which the limiting value of totally rigid side chains is nearly reached. Apparently, the reason for this behavior is that at the point $\lambda_{\text{side}}/M = 1.0$ the side chains are already so stiff that they do not fold back towards the backbone to induce any local stretching.

The persistence length, λ , of the molecules is defined by the correlation function as $\langle\cos\theta(s)\rangle \propto \exp(-s/\lambda)$, which holds for large values of s . Therefore, in practice, the estimate of λ is obtained from the slope of

Fig. 2. Bond-angle correlation function $\langle \cos \theta(s) \rangle$ of the cylindrical brushes with flexible, semiflexible, and rigid side chains of length 60 beads each. The semiflexible case corresponds to the molecule shown in Fig. 1

Fig. 3. Nearest neighbor correlation function value, $\langle \cos \theta(s=1) \rangle$, describing the local length scale conformational fluctuations, of the cylindrical brushes with a fixed side chain length $M = 60$ as a function of the parameter λ_{side}/M describing the intrinsic stiffness of the side chains. The limiting values for the molecules with flexible and rigid side chains are also shown. Statistical errors are 1% at maximum

Fig. 4. Persistence length, λ , describing the large length scale behavior, of the cylindrical brushes with a fixed side chain length $M = 60$ as a function of the parameter λ_{side}/M describing the intrinsic stiffness of the side chains. The limiting values for the molecules with flexible and rigid side chains are also shown. Statistical errors are 15% at maximum

In $\langle \cos \theta(s) \rangle$ in the linear region shown in Fig. 2. We decided to use the region $25 \leq s \leq 140$ for the fitting, which leads to the values of the persistence length as a function of λ_{side}/M ($M = 60$) shown in Fig. 4, together with the limiting values obtained for the flexible and rigid side chain cases. The backbone becomes more extended at the large length scale as a function of the intrinsic stiffness of the side chain, as confirmed by the monotonous increase of λ in Fig. 4. However, in contrast to the behavior at the local length scale, this time the limiting value of rigid side chains is not yet achieved at $\lambda_{\text{side}}/M = 1.0$, but λ still increases in the region $\lambda_{\text{side}}/M > 1.0$. In fact, at λ_{side}/M

$= 1.0$ the persistence length is only around 350, whereas the limiting value to be reached is almost 500. The observations can be explained by the fact that although the side chains are essentially rigid in the region $\lambda_{\text{side}}/M > 1.0$, the length of these “rigid rods” still increases as a function of λ_{side}/M . As a consequence, in this regime the persistence length λ increases as a function λ_{side}/M , just as it does in the case of real rigid rodlike side chains as a function of the side chain length $L^{10,15}$.

As discussed in the introduction, one of the most important quantities of comb copolymer cylindrical brushes is the ratio, λ/D , between the persistence length

Fig. 5. Ratio between the persistence length and the brush diameter, λ/D , of the cylindrical brushes having a fixed side chain length $M = 60$ as a function of the parameter λ_{side}/M describing the intrinsic stiffness of the side chains. The limiting values for the molecules with flexible and rigid side chains are also shown. Statistical errors are 15% at maximum. The inset shows the behavior of λ/D as a function of the side chain length M (flexible side chains) or L (rigid side chains) (for details see ref.¹⁵⁾)

and the brush diameter, since for large values of this ratio lyotropic behavior may become possible. Twice the root-mean-square end-to-end distance of the side chains may be used as a reasonable approximation of the diameter D . This leads to the behavior of λ/D as a function of λ_{side}/M , as shown in Fig. 5. Again, the limiting values for the flexible and rigid side chain cases are also shown. The most striking observation is that λ/D increases steadily as a function of λ_{side}/M , due to the fact that the flexible and rigid side chain case correspond to different values of λ/D . In accordance with the behavior of λ , the ratio λ/D also increases considerably in the region $\lambda_{\text{side}}/M > 1.0$, due to the increase of the length of the effectively rigid side chains as a function of λ_{side}/M .

Finally, for the studied structures ($M = 60$), the ratio λ/D is about 2.7 for the molecules with flexible side chains, whereas a clearly larger value of about 4.0 is observed in the case of rigid side chains. However, in the regime reached computationally ($M \leq 80$)¹⁵⁾, λ/D already increases as a function of the length, L , of the rigid side chains, whereas not even a beginning of an upturn is observed as a function of the length, M , of the flexible side chains. This is shown by the inset in Fig. 5, which represents the behavior of λ/D as a function of the lengths M and L ¹⁵⁾. Therefore, the difference in λ/D between the two extreme cases becomes even larger for longer side chains, at least as long as the scaling regime for the case of flexible side chains is not reached^{9, 11)}.

Concluding remarks

The results presented in the current paper concern the equilibrium conformational behavior of comb copolymer cylindrical brushes containing semiflexible side chains. Off-lattice Monte Carlo simulations were performed in order to compute the average values of the quantities of interest. It was shown that the intrinsic stiffness, λ_{side} , of the side chains drastically influences the conformational behavior of the cylindrical brushes at two length scales. First, at the local length scale, the backbone structure becomes coiled for stiff side chains, as shown by the decrease in the short-range bond angle correlations. Moreover, at the large length scale, determined by the persistence length, λ , the extension of the backbone increases monotonously as a function of λ_{side} . Finally, the ratio, λ/D , between the persistence length and the brush diameter, also increases as a function of the side chains stiffness. In conclusion, the semiflexible nature of the side chains of real cylindrical brushes is of particular importance with respect to conformational elasticity and the possibility of lyotropic behavior.

Acknowledgement: The work has been supported by Finnish Academy (Graduate School of Materials Physics) and Technology Development Centre (Finland), and the Organization of Scientific Research of The Netherlands (NWO). M.S. acknowl-

edges grants from the *Jenny and Antti Wihuri Foundation*. *CSC Finland* is acknowledged for providing supercomputing time.

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