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Effect of Side Chain Rigidity on the Elasticity of Comb Copolymer Cylindrical Brushes: A Monte Carlo Simulation Study

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ABSTRACT: We report the results of a Monte Carlo simulation study of isolated comb copolymer cylindrical brushes. The conformational characteristics of molecules consisting of a flexible backbone densely grafted with side chains strongly depend on the rigidity of the side chains, which is exemplified by using both fully flexible and totally rigid side chains. The short length scale fluctuations of the backbone are not affected by the presence of rigid rod side chains, whereas flexible side chains induce local stretching of the backbone. However, at the large length scale, the persistence length λ of the cylindrical brush is considerably larger for rigid rod side chains than for flexible side chains. Moreover, for rigid side chains the ratio between the persistence length λ and the diameter D of the brush increases approximately linearly as a function of the rod length L, thus supporting the possibility of lyotropic behavior. In contrast to this, in the case of flexible side chains, λ/D is approximately independent of the side chain length M.

Introduction

Comb copolymers are architecturally interesting molecules among others because of the possibility to form extended chain conformations, based exclusively on the intramolecular excluded-volume interactions between side chains densely grafted to the backbone. Such molecules with flexible side chains have been recently considered in experimental,[1−3] theoretical,[4−6] and computational[6−10] papers. However, there are still many unresolved questions. Theoretically, two opposing views about the persistence behavior have been given. According to Fredrickson,[5] in the high coverage limit the persistence length λ of the structure increases as a function of the side chain length M as $\propto M^{15/8}$. In the same limit the diameter D of the comb copolymer brush, defined by the radius of gyration or the end-to-end point distance of the side chains, is predicted to scale as $D \propto M^{3/4}$. This implies that the ratio between the persistence length and the brush diameter D should scale as $\lambda/D \propto M^{9/8}$. The behavior of this ratio is of special interest since it determines whether for large enough values of M lyotropic behavior of the comb copolymer molecules becomes possible.[11,12] However, Birshtein and co-workers[4] came to a different conclusion that “the length of the rigid portion of a comb-like chain is of the order of its thickness, i.e. $\lambda \propto D$”. Therefore, they predict that the ratio λ/D remains constant. Hence, this would mean that lyotropicity cannot be realized by simply using longer side chains. Still, experimental studies[1−3] on cylindrical brushes consisting of a poly(methyl methacrylate) backbone with poly(2-vinylpyridine) or polystyrene side chains demonstrated the presence of strongly extended conformations.

On the computer simulation side, all our results for three-dimensional cylindrical brushes involving flexible side chains[7−9] indicated λ/D to be approximately independent of M, thus supporting the predictions by Birstein and co-workers.[4] However, due to computational difficulties, the size of the structures studied so far was limited to side chains of length $M = 30$ beads only. Therefore, one might argue that the reason for the constant value of λ/D is simply that this is still not in the regime where the upturn of λ/D may be observed. Moreover, our most recent results[9] showed that there is an upturn of λ/D when the molecules are confined inside a two-dimensional slit. This result provides a strong incentive to investigate much longer cylindrical brushes in 3D in order to be able to draw more definite conclusions. Another motivation for the present study is the computationally observed[7−9] interesting property that the correct description of the backbone conformation of a cylindrical brush requires two characteristic length scales. At a short length scale the backbone behaves more flexible, while the persistence (characterized by the persistence length) occurs at a larger length scale.

It the following, we address computationally the problems discussed above first by studying much larger comb copolymer cylindrical brushes with longer flexible side chains than before and, in addition, by considering also in detail molecules with rigid rod side chains. The focus is on the difference in conformational elasticity behavior of cylindrical brushes with flexible and rigid side chains, concentrating on both the short local length scale and larger length scale properties. It will be demonstrated that such an approach reveals many new aspects of the conformational behavior of comb copolymer cylindrical brushes. All the results presented here are in good agreement with recent theoretical predictions forming the subject of a forthcoming paper.[13]

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Model and Details of the Simulation

The equilibrium conformations of comb copolymer cylindrical brushes were studied by off-lattice Monte Carlo (MC) simulations. To demonstrate the intramolecular effect of side chain rigidity on the conformational behavior, both molecules with fully flexible and completely rigid (rodlike) side chains were considered. The focus is on the behavior of a single isolated molecule in a good athermal solvent, and therefore, only intramolecular excluded-volume interactions are present in the system. The molecules consisted of a backbone modeled as a freely jointed chain of 300 hard spheres (beads) of which every second, i.e., 150, carry either an equally flexible side chain of a given contour length M or a rigid side chain of length L. All the beads of the system have the same size, which is taken to be the unit of length. Both lengths M and L were considered up to 80 beads, and therefore, the largest structures studied consisted of 12 300 beads. However, to suppress the chain end effects, all the quantities of interest were computed using only the inner part of the molecules by excluding 50 main chain beads from both chain ends and all the beads of the side chains connected to these beads. Therefore, the actual focus is on the molecules consisting of a backbone of 200 beads and 100 side chains of lengths up to 80 beads. All the beads were treated equally during the simulation (no matter if excluded from the real calculations of the average quantities).

Configuration space is sampled according to the Metropolis importance-sampling scheme.[14] Irrespective of the particular side chain structure (flexible or rigid), the trial moves of the main chain beads consist of a set of different local chain motions and global pivot type[15] rotations. For the structures having flexible side chains, the trial moves of the side chain beads consisted of the same type of local and global rotations, and therefore, the simulation procedure is in broad outline the same as introduced in our previous papers.[7-9] However, since in the present study we consider much larger molecules, considerably more effort was used first to improve the simulation code and second to optimize the number and combination of different Monte Carlo trial steps to get efficiently statistically uncorrelated conformations. In the case of rigid side chains, since the rods do not have any intramolecular degrees of freedom, a trial move for a side chain is simply an attempt for a new random direction of the rod starting from the main chain grafting point. All the trial steps were always accepted if the new conformation did not cause an overlap between any beads; otherwise it was rejected.

The initial conformations were formed as 2D structures in the xy-plane. All the simulations were divided into 11 blocks, and the first block was used only to equilibrate the molecules. The number of different types of MC steps needed per simulation block to obtain an acceptable statistical quality depends on the size of the molecule considered. For the largest structure studied with flexible side chains of length $M = 80$, 1.500 MC steps per simulation block were needed. About half of the attempted steps were local rotations while the rest were pivot type “bendings” of the whole end part of the molecule (or the end part of the given flexible side chain). For the above-mentioned structure, a MC step corresponds to 12 300 (total number of beads of the molecule) attempted steps. In the case of rigid side chains, a MC step was taken to correspond to only 600 attempted steps since the equilibration of rigid side chains was assumed to take equivalently only two steps per side chain. For the largest structure studied with rigid side chains of length $L = 80$, 4.000 MC steps per simulation block were used.

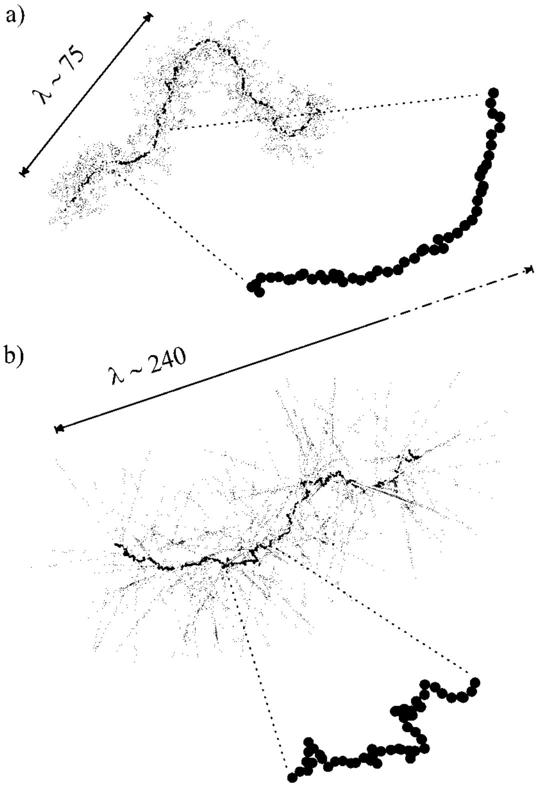

Figure 1. Characteristic conformations of comb copolymer cylindrical brushes consisting of a backbone of 300 beads and 150 side chains. (a) Molecule with flexible side chains of length $M = 40$. (b) Molecule with rigid side chains of length $L = 40$. Magnification shows the local backbone structure.

For all the remaining 10 actual simulation blocks the average values of the quantities of interest were computed using at least 100 conformations taken from the simulation block at equally spaced intervals. Finally, the average of the block averages was calculated, and the errors were estimated with 95% confidence intervals using the standard deviation of the block averages.

Results and Discussion

In this section, we present the results of the off-lattice MC simulations concerning equilibrium conformations of isolated comb copolymer cylindrical brushes in athermal solvent. Our main interest is the effect of side chain rigidity on the elasticity at two length scales of the originally flexible backbone, which is demonstrated by using both fully flexible and totally rigid rodlike side chains. Figure 1 shows typical conformations of molecules consisting of a backbone of 300 beads and 150 either flexible (a) or rigid (b) side chains of lengths $M = 40$ and $L = 40$, respectively. Already the presentation in Figure 1 illustrates some striking differences in the conformational behavior of the structures depending on the side chain rigidity. First, as shown by the magnification of the backbone, for flexible side chains the backbone seems at short length scale quite stretched and the contour appears smooth, whereas for rigid side chains the local fluctuations are much stronger. Second, at larger length scale, the structure with rigid side chains seems to have a much stronger preferred direction of propagation; i.e., the persistence length λ is

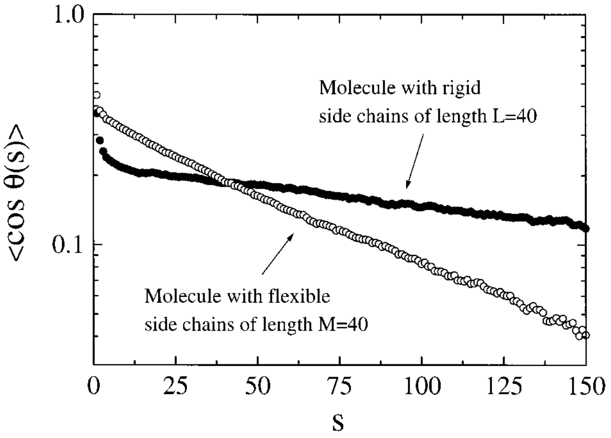

Figure 2. Bond angle correlation $\langle\cos(\theta(s))\rangle$ of the backbone as a function of the separation, s, along the backbone for molecules with flexible side chains of length $M = 40$ and rigid side chains of length $L = 40$.

larger. In fact, all these conclusions are in excellent agreement with recent theoretical predictions.[13] In the following we show the very same facts in more detail by considering the numerical data of the simulations.

To progress in estimating the persistence lengths, let us first look at Figure 2 which shows in a semilogarithmic presentation the average of the cosine of the angle $\theta(s)$, $\langle\cos\,\theta(s)\rangle$, between two backbone chain segments separated by a distance s along the backbone. The data are for the structures with the same size as the characteristic examples shown in Figure 1, thus corresponding to $M = 40$ for the flexible side chain case and $L = 40$ for the rigid side chain case. Figure 2 clearly confirms the previously mentioned conclusions of the two length scales of the system. At short lengths (small s values), the decline of the directional correlation is particularly rapid which demonstrates the local flexibility of the molecules. At larger lengths (larger s values) the decrease of $\langle\cos\,\theta(s)\rangle$ becomes much weaker (and linear in a semilogarithmic presentation), which implies an increase in the persistence length λ. Figure 2 also shows that the persistence length is much larger in the case of rigid side chains than in the case of flexible side chains. However, according to the same figure, it is evident that the local fluctuations of the backbone are stronger for molecules with rigid side chains than for molecules with flexible side chains, in good agreement with the impression from Figure 1.

The persistence length λ may be estimated by using the relation of the correlation function $\langle\cos\,\theta(s)\rangle = \exp(-s/\lambda)$. However, as mentioned above, this persistence behavior is found for sufficiently large values of s only. Using the region $25 < s < 140$ for the fitting, the values presented in Figure 3 are obtained for the persistence length as a function of M (flexible side chain case) and L (rigid side chain case). Figure 3 shows that the persistence length becomes much larger with rigid side chains than with flexible side chains. The most interesting observation is that the dependency of the persistence length on L is clearly more than linear, whereas a much weaker dependency of λ as a function of M is found. An important implication is that the ratio between the persistence length and the diameter, λ/D, which determines the possibility of lyotropic behavior of the molecules, may increase as a function of L whereas the same ratio could be approximately constant as a function of M. This will be discussed next.

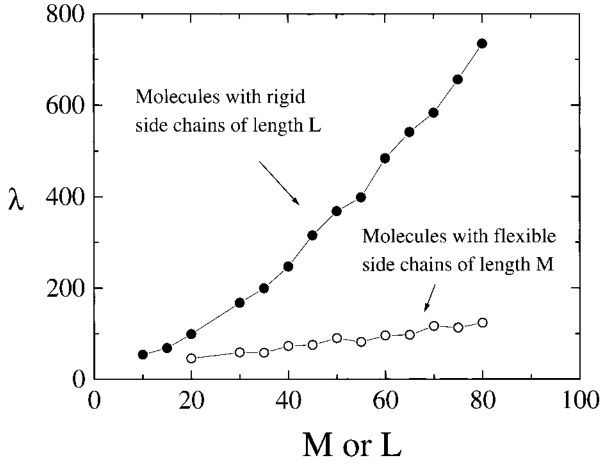

Figure 3. Persistence length λ of the comb copolymer cylindrical brushes for flexible and rigid side chains as a function of their lengths M and L, respectively.

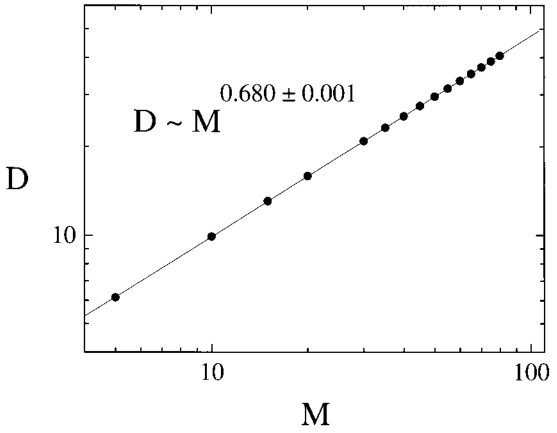

Figure 4. Diameter D, defined as twice the average end-to-end point distance of the side chains, of the comb copolymer cylindrical brushes in the case of flexible side chains as a function of the side chain length M.

In this paper we approximate the diameter of the comb copolymer cylindrical brush, D, by the root-mean-square end-to-end distance of the side chains. Of course, other definitions such as the average height perpendicular to the backbone would work equally well. Hence, in the case of rigid side chains, the relation $D = 2L$ holds. For the flexible side chains, Figure 4 shows in a log–log plot the values of the diameter as a function of M calculated in this manner. The scaling prediction obtained by fitting these data is $D \propto M^{0.680\pm0.001}$. Obviously, due to the intramolecular excluded-volume interactions, the increase of the end-to-end distance of the side chains as a function of M is stronger than the corresponding increase of simple free self-avoiding walks (SAW) of the same length. However, in the regime studied, the scaling exponent is still clearly smaller than the theoretically predicted value of 072.[4]

Figure 5 presents λ/D as a function of the side chain lengths M and L. The first important observation is that for flexible side chains λ/D is approximately independent of M, as already suggested in our previous papers[7–9] which were, however, restricted to much shorter side chains. Even more interestingly, for the rigid side chains we obtain approximately $\lambda/D \propto L$, in excellent agreement with our theoretical analysis to be presented in a forthcoming paper. Therefore, a pronounced different elastic behavior at the larger length scale is observed

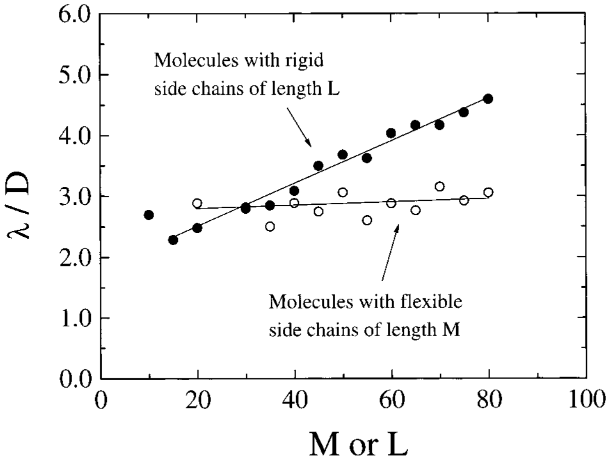

Figure 5. Ratio between the persistence length λ and the bottle-brush diameter D, λ/D, as a function of the side chain length. The fitted solid straight lines are to guide the eye.

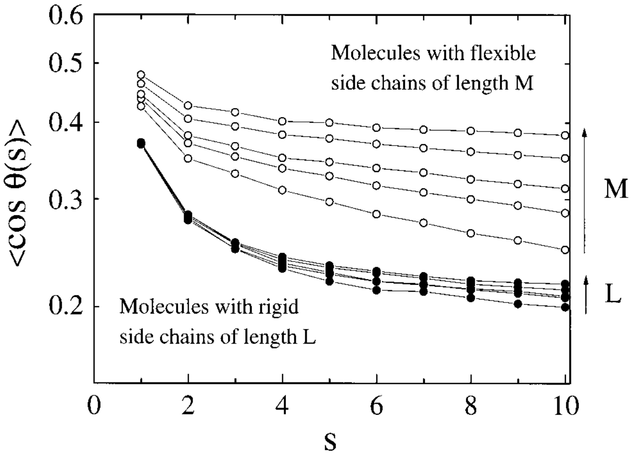

Figure 6. Small s value behavior of bond angle correlation $\langle\cos(\theta(s))\rangle$ for the molecules with flexible side chains of length M and rigid side chains of length L. The values of M and L increase from the bottom upward as $M, L = 20, 30, 40, 60, 80$.

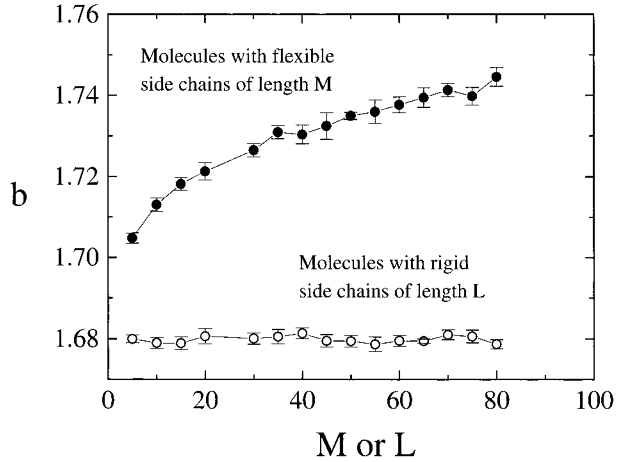

Figure 7. Distance b between main chain grafting points of the comb copolymer cylindrical brushes in the case of both flexible side chains and rigid side chains as a function of the lengths M and L, respectively. Note that for the densely grafted structures studied $1 \leq b \leq 2$.

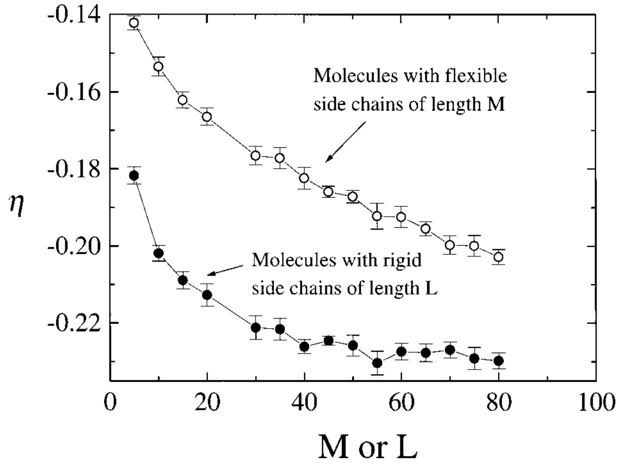

Figure 8. Order parameter η of side chains of comb copolymer cylindrical brushes in the case of both flexible side chains and rigid side chains as a function of the lengths M and L, respectively.

between molecules with rigid rod and flexible side chains.

Let us next consider in more detail the local short length scale behavior of comb copolymer cylindrical brushes by zooming in on the small s behavior of $\langle\cos\theta(s)\rangle$. Figure 6 demonstrates that in the case of rigid rod side chains the length L has no influence on the local flexibility (see especially that $\langle\cos\theta(s=1)\rangle$ is a constant) whereas in the case of flexible side chains $\langle\cos\theta(s)\rangle$ increases as a function of M. The same phenomenon is also illustrated in Figure 7, which presents the average distance between main chain grafting points b as a function of the lengths M and L. The results show again a striking difference in the elasticity behavior of structures with rigid and flexible side chains, however, this time at the shorter local length scale. Of course, this difference is directly related to the fact that the flexible side chains interact with the backbone locally and with their nearest neighbors. The rods do not interact with the backbone (except for the grafting points) and with other rods only via one monomer. This result fully agrees with the more elaborated theoretical model.[13]

Finally, let us consider the orientation of the side chains with respect to the cylinder axis (direction of the backbone). Figure 8 shows the order parameter $\eta = {}^{1}/_{2}\langle 3\cos^2\alpha - 1\rangle$ of the side chains as a function of the side chain lengths M and L, where α is the angle between side chain direction (end-to-end vector) and the local backbone direction. (We used a local direction defined by main chain beads separated by 10 beads.) As expected, the data imply that the side chains orient more and more perpendicular to the backbone as the side chains length is increased.

Concluding Remarks

In this paper, we presented the results of a computational study on the differences between the equilibrium conformations of isolated comb copolymer cylindrical brushes containing either flexible or rigid side chains in an athermal solvent. All the interactions in the system were of the intramolecular excluded-volume type. We reported a strikingly different elastic behavior at two length scales depending on the side chain rigidity.

The main observations of this study are the following. First of all, comb copolymer cylindrical brushes need to be characterized at two length scales. At the shorter (local) length scale, rigid rod side chains do not cause any change in the conformational behavior of the backbone; i.e., the main chain remains locally coiled. In contrast to that, the local tension in the backbone does depend on the length M of the flexible side chains. However, at the larger length scale, the persistence length λ of the backbone is considerably larger for the rigid side chains structures than for the structures with flexible side chains. Moreover, for rigid rod side chains, the ratio between the persistence length and the diameter, λ/D, increases linearly as a function of the length of the rods L, whereas for flexible side chains this ratio is approximately constant as a function of M. So, we may conclude that the use of rigid rod side chains is a much more effective way to obtain a stiff cylindrical brush than flexible side chains.

Finally, let us consider the recent experimental investigations on cylindrical brushes[1−3] where backbones of poly(methyl methacrylate) were grafted with several different side chains including polystyrene and poly(2-vinylpyridine). It is obvious that these side chains are much stiffer than those employed in the computer simulations devoted to flexible side chains. Therefore, our results on rigid rod side chains suggest that the experimentally observed large persistence length (of the order of 100 nm) may be due to the semiflexible nature of the side chains. This is also corroborated by their most recent experimental results[16,17] on cylindrical brushes, where they concluded that the main chain is “locally coiled” but persistent on larger length scales—just as our results for the rigid side chains.

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