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Comb-Branched Polymers: Monte Carlo Simulation and Scaling

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ABSTRACT: The Monte Carlo simulation technique (the bond fluctuation model) has been used for the study of the equilibrium conformations of comb-branched polymers consisting of a long flexible main chain and side chains grafted at a regular separation onto the main chain. The solvent has been supposed to be good (athermal) for the main and side chains. The global conformation and the gyration radius of the polymer, as well as the local conformational structure of the comb, have been analyzed as functions of the length of the side chains and spacers. The effect of induced rigidity of the comb due to the interaction between side chains has been observed. We have found the results of the simulation to be in reasonable agreement with the predictions of the scaling theory of comb-branched polymers.

1. Introduction

Only a few papers have dealt with the simulation of comb-branched polymers to study the dependence of the conformation of the main chain on the density of grafting and on the length of side chains.[1−3] At the same time, interest in the equilibrium and dynamic properties of solutions of polymers with complex architectures has increased noticeably during recent years.

Not only the chemical complexity but also the topological complexity of the macromolecules plays an important role in the processes of intra- and intermolecular aggregation and structure formation and affects the interfacial behavior of macromolecules. Grafted comblike copolymers consisting of a long main chain and many side chains attached at one end onto the main chain present one of the simplest systems in which both chemical and topological complexities are combined, ensuring a wide variety of different regimes of the behavior of these polymers in solution.

The grafting of side chains onto the main chain may lead to a drastic change in the main chain conformation; a very strong dependence of the equilibrium structure and rheological properties of the solution on the length and number of side chains per unit length of the main chain may be observed. The effect is most pronounced under conditions of dense grafting of side chains and in a selective solvent: if the solvent is good for the backbone but sufficiently poor for the side chains, then intra- and intermolecular micellizations occur, while in the opposite case a strong repulsive interaction of the side chains results in the stretching of spacers, thus preventing their collapse and the collapse of the polymer as a whole.

The scaling analysis of the influence of the interaction between side chains on the conformation of comblike grafted copolymers under the conditions of nonselective good or Θ solvent has been reported in ref 4. It was shown that the excluded volume interactions between monomers of sufficiently densely grafted side chains lead to comparatively weak stretching of side chains and spacers with respect to the size of linear chains of the same length under the same solvent strength conditions. The dependencies of different conformational characteristics of the comb (the overall size and the sizes of side chains and spacers) on the branching parameter, i.e., on the ratio between numbers of monomers in a side chain and in a space, have been obtained. Another result of the interaction between side chains is the swelling of the comb on a large scale, even under the conditions of Θ solvent for linear chains.

The interaction between comblike macromolecules in a semidilute solution[5] or in a polymer brush formed by combs attached onto a surface[6] affects both large-scale and local conformational structure. As a result, these systems formed by polymer combs demonstrate a larger variety of different regimes of behavior than similar systems formed by linear polymers.

As has been shown recently by Fredrickson,[7] the repulsive interactions between side chains can induce the rigidity of the comb polymer on a scale much larger than the comb thickness. The corresponding effective persistence length grows rapidly as the length or density of grafting of side chains increases. However, the consideration in ref 7 is based on the assumption of local cylindrical symmetry of the comb on a scale larger than the distance between neighboring grafting points. This condition is not always fulfilled if the backbone is sufficiently flexible.

This paper presents the first part of our study of comb-branched graft-copolymer conformation based on the Monte Carlo simulation method and concerns the case of a nonselective good solvent. We analyze the comb gyration radius as a function of the lengths of side chains and spacers. The local conformation of the comb and the effect of induced rigidity manifested in the correlation of orientation of the end-to-end vectors for large parts of the comb backbone are studied. The results obtained are compared with the prediction of a scaling theory of conformations of comblike graft-copolymers.

2. Theory

Let us consider a comblike polymer consisting of a long main chain (of degree of polymerization N) and side chains (of degree of polymerization n) grafted at one end onto the main chain (the backbone) of the comb (Figure 1). The density of grafting is characterized by the ratio n/m, where m is the length of a spacer (the part of the main chain between two neighboring grafting points). The limit N/m, $N/n \gg 1$ corresponds to a comblike structure, whereas at $N/n \leq 1$ we deal with a star-branched polymer.

The cooperative effects related to the interaction of side chains are expected to be strong if $n/m \geq 1$, i.e., when neighboring side chains are strongly overlapped, and we are interested mostly in this case of sufficiently dense grafting. We assume that the side chains and

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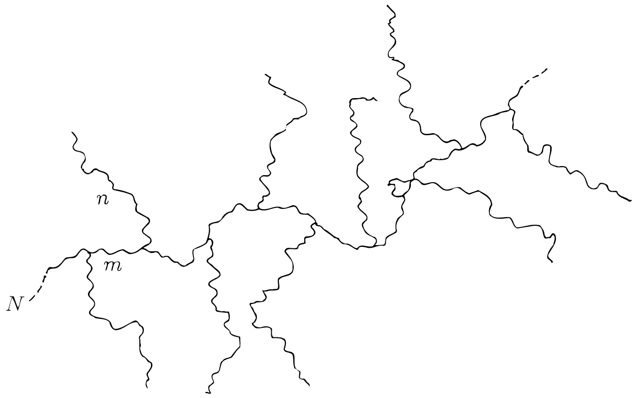

Figure 1. Comblike polymer: N is the number of monomers in the main chain; n is the length of each side chain; N/m is the number of side chains.

the spacers are (i) chemically equivalent, (ii) sufficiently long (n, $m \gg 1$), and (iii) flexible, which means that the elementary length (the monomer size) a coincides with the Kuhn segment length.

The solvent is good (athermal) for monomers of the main and side chains. The dimensionless excluded volume parameter (the second virial coefficient) of monomer–monomer interactions is $v/a^3 \cong 1$.

2.1. Flory Approach. The simplest approach that can be used for the analysis of the equilibrium conformation of a comb polymer in a solution is the mean field Flory-type approach. In this approximation, we neglect (i) the effects of fluctuations and (ii) the spatial variation in the monomer density distribution due to the branched topology of the polymer.

The characteristic equilibrium size, R, of the comb (the gyration radius or the end-to-end distance of the main chain) is determined by the balance between the excluded volume repulsive interaction of all of the monomers belonging to the main and side chains and the elasticity of the comb backbone. This equilibrium size is determined from the condition of minimum free energy:

$$F(R)/T \cong \frac{R^2}{Na^2} + \frac{N^2(1 + n/m)^2 a^3}{R^3} \tag{1}$$

The second term in eq 1 describes the excluded volume interaction in the homogeneous cloud of monomers localized in a volume $\sim R^3$, whereas the first term takes into account the conformational entropy loss due to the stretching of the main chain to size R, thus roughly taking into account the comb topology. The minimization of the free energy (eq 1) with respect to R gives

$$R \cong N^{3/5} a (1 + n/m)^{2/5} \cong N^{3/5} a (n/m)^{2/5} \tag{2}$$

where the last equality refers to the case of densely grafted combs, $n/m \gg 1$, while the first expression is applicable at any value of branching parameter n/m. In spite of the obvious roughness of this approximation, the result (eq 2) is surprisingly close to the results of more sophisticated approaches, which we discuss in the following.

2.2. Local Conformational Structure. As has been shown in ref 4, the local conformational structure of a dense comb is determined by the repulsive interaction between side chains and is characterized by the stretching of side chains and spacers with respect to the characteristic sizes of linear chains of the same length. The equilibrium degree of stretching of side chains and spacers as a function of the branching parameter n/m can be obtained on the basis of the local cylindrical symmetry approximation. This approximation implies that the fluctuations in the main chain around a straight configuration remain much smaller than the side chain size, at least for the parts of the main chain larger than or comparable to a side chain. If this is the case, the comblike polymer can be considered locally as a "bottle brush", i.e., the system of polymer chains grafted at one end onto a thin cylinder.[8]

The equilibrium dimensions of side chains

$$D \cong n^{3/5} a (n/m)^{3/25} \tag{3}$$

and spacers

$$h \cong m^{3/5} a (n/m)^{3/25} \tag{4}$$

are determined by the balance of local contributions to the free energy of the comb: the excluded volume interaction between monomers of side chains and conformational entropy losses in partially stretched side chains and spacers.

As follows from eqs 3 and 4, at $n/m \gg 1$, both side chains and spacers are stretched with respect to the Flory dimension of linear chains of the same degrees of polymerization. The degree of stretching, $(n/m)^{3/25}$, is the same for side chains and for spacers and increases rather weakly with an increase in the degree of overlap of side chains, characterized by the branching parameter n/m.

2.3. Large-Scale Behavior. On a spatial scale much larger than the size of a side chain, the comb polymer can be considered as a wormlike chain with an effective contour length $L \cong Nh(n,m)/m$. This chain is characterized by some specific bending rigidity or by the persistence length. The contribution to the bending rigidity of a comblike polymer arising due to the repulsion of side chains has been calculated in ref 7 under the condition that the bare persistence length of the backbone is much larger than the distance between neighboring grafting points.

Although the direct extension of the results obtained in ref 7 to the comb with a flexible backbone requires an additional verification, one can argue that the essential point is the cylindrical symmetry of a comb on a scale much larger than D. This local cylindrical symmetry is provided in turn by the strong repulsive interaction of side chains under the condition of dense grafting, $n/m \gg 1$. The induced persistent length of a comb with a flexible backbone obtained in ref 6 is given by

$$l_p(n,m) \cong D(n,m)(n/m)^{9/10} \cong n^{81/50} m^{-51/50} a \tag{5}$$

Thus, the induced rigidity appears to be a strongly increasing function of n/m.

The equilibrium conformation of the comb polymer on a large scale and the overall size (the gyration radius) depend on the ratio between the induced persistence length $l_p(n,m)$ and the effective contour length of the comb $L(N,n,m) \cong Nh(n,m)/m$. One can obviously distinguish the following regimes: (i) $D(n,m) \ll L(N,n,m) \leq l_p(n,m)$, which is the case at $N \leq n(n/m)^{1/2}$; the comb has a rodlike conformation with a characteristic size

$$R(N,n,m) \cong L(N,n,m) \cong Nan^{3/25} m^{-13/25} \tag{6}$$

(ii) $L(N,n,m) \gg l_p(n,m)$; the comb acquires the conformation of a Gaussian or of a swollen coil with a size given by

$$R \cong L^{1/2}(N,n,m)\, l_p^{1/2}(n,m) \cong N^{1/2} a n^{87/100} m^{-77/100}, \quad L \ll l_p^{3} D^{-2} \tag{7}$$

or

$$R \cong L^{3/5}(N,n,m)\, D^{1/5}(n,m)\, l_p^{1/5}(n,m) \cong N^{3/5} a (n/m)^{27/50}, \quad L \gg l_p^{3} D^{-2} \tag{8}$$

respectively.

Equation 8 is obtained under the assumption that the effective ("thermodynamic") thickness of the comb coincides with the size of the side chains, i.e., the parts of the comb interact like hard cylinders of radius D. This approximation is asymptotically valid under the condition of dense grafting of long side chains, i.e., when neighboring side chains are strongly overlapped (see relevant discussions for the cases of planar or spherical polymer brushes in refs 9 and 10). Actually, an interpenetration on the scale of the last stretching blob leads to a more complicated non-power law dependence of the effective excluded volume parameter on the ratio n/m. However, these delicate effects will be discussed elsewhere.

The crossover between eqs 7 and 8 occurs at $L(N,n,m) \cong l_p^3(n,m)D^{-2}(n,m)$, which corresponds to the condition $\zeta \cong 1$. Here $\zeta \cong L^{1/2} D l_p^{-3/2}$ is the conventional parameter characterizing the strength of excluded volume interactions in a coil formed by a persistent chain of length L, thickness D, and persistence length l_p.[11] By using eqs 3 and 5, we obtain

$$\zeta \cong \left\{ \frac{N/m}{(n/m)^{21/10}} \right\}^{1/2} \tag{9}$$

Thus, the comblike polymer with a comparatively short main chain $N \ll m(n/m)^{21/10}$ behaves as a Gaussian coil, whereas if the main chain is sufficiently long, $N \gg m(n/m)^{21/10}$, the comb polymer swells on a large scale.

Let us briefly discuss the dependence of comb size on the branching parameters n, m, and n/m described by eqs 6–8. If the main chain is short and the comb is in a rodlike conformation, then an increase in the comb size with an increase in the length of the side chains n or a decrease in the spacer length m occurs due to additional stretching of the comb backbone (see eq 4). Consequently, the dependencies of R on n and m are comparatively weak.

The strongest dependence of the comb size on the length of side chains (almost linear growth) takes place in the Gaussian regime described by eq 7. This is due to a sufficiently strong dependence of the coil size on the persistence length ($R \sim l_p^{1/2}$) and due to the strong dependence of the induced persistence length on the ratio n/m (eq 5).

Finally, if the comb is sufficiently long for the manifestation of the excluded volume effects in large-scale behavior, then an increase in the comb size with an increase in n and a decrease in m is determined by all three reasons: (i) an increase in the spacer stretching, (ii) an increase in the induced rigidity l_p, and (iii) an increase in the effective comb thickness D. However, as the dependence of the swollen coil dimension on the persistence length (eq 8) is comparatively weak, the comb size grows with an increase in n or a decrease in m weaker than in the Gaussian regime. Note that according to eq 8 the comb size in this case depends only on the ratio n/m and is approximately proportional to the square root from n/m.

We remark that if the effect of induced rigidity is not taken into account, one obtains $R(N,n,m) \cong L(N,n,m)^{3/5} D(n,m)^{2/5} \cong N^{3/5} a (n/m)^{9/25}$, which is practically indistinguishable from eq 2 obtained without detailed analysis of the conformations of the side chains and spacers.

Note that the extension of the results obtained in ref 7 to the combs with a flexible backbone is not straightforward, because the fluctuations in the main chain configuration may result in a significant decrease in the induced rigidity, as is the case for flexible polyelectrolytes.[12]

3. Simulation Method

As for star polymers,[13] the earlier simulations of comblike polymers were carried out by using the enrichment method or the Rosenbluth–Rosenbluth algorithm.[14,15] According to these sampling methods, one allows the comb polymer to grow, and for each successful attempt the value of interest (like the gyration radius) is stored. Then the mean value is calculated after several samples. In ref 16, the cooperative motion algorithm was used. This algorithm, previously developed for a highly dense system, seems to be very efficient for a comb polymer in a dense medium. We use a modified bond fluctuation model (BFM) algorithm for the study of a polymer with long side chains and a long backbone to check the scaling predictions for this system. The bond fluctuation model is especially well designed for branched objects.[14,15,17] It is possible to apply BFM in our case because the estimated local monomer density in our system is equal to 0.3, which is far below the maximum value for BFM (see refs 14, 15, and 17 for discussions).

The bond fluctuation model is a coarse-grained model of polymer chains in which an "effective monomer" consists of an elementary cube whose eight sites on the hypothetical cubic lattice are blocked for further occupation. A polymer chain is made of effective monomers joined by bonds. Each bond corresponds to the end-to-end vector of a group of 3–5 successive chemical bonds and can fluctuate in some range. It is represented by vectors $\mathbf{l}$ of the set P(2,0,0), P(2,1,0), P(2,1,1), P(3,0,0), and P(3,1,0), which guaranteed that intersection of the polymer chain with other chains or with itself is virtually impossible. All of the lengths here are measured in units of the lattice spacing and the symbol P denotes all the permutations and sign combinations of the Cartesian coordinates (l_x, l_y, l_z). The algorithm displays Rouse behavior for all spatial dimensions and combines typical advantages of the lattice MC methods with those of the continuous Brownian dynamics algorithm. The adequacy of the BFM algorithm for the description of static and dynamic behavior of polymers has been proven in sensitive investigations.[17]

The main chain and each of the side chains are stored as independent linear chains with the constraint for each side chain that one end has the same monomer as the main chain at each branching point. However, this monomer is only moved during the move sequence of the monomers of the main chain. In order to avoid self-interaction of the comb polymer due to the finite size of the box, the simulation is carried out in a 120 × 120 ×

120 cubic box, which corresponds to the limit of the computer capacity with the BFM on a work station. The gyration radii of all observed comb polymers are always smaller than the size of the box. The comb polymers with two main chain lengths, 800 and 200 monomers, are studied. Those values are very great for this simulation model but we were looking for the scaling behavior which can be seen only in the limit of long chains. If the backbone is too small, we have a polymer with a structure between comb and star polymers, which has to be avoided.

The start configuration corresponds to the compact main chain conformation in the *x*,*y* plane while all the side chains are extended parallel to the *z* axis. The choice of this kind of a start configuration has two origins. First of all, it is impossible to generate (at least in a reasonable amount of computer time) a fully relaxed start configuration of the comb polymer using a growth process. We remark that our polymers are densely branched and that a monomer needs eight empty sites in this model. Second, the gyration radius of the main chain in the start configuration is then much smaller than the value corresponding to a self-avoiding walk. The relaxation toward equilibrium is then clearly seen by an increase in the gyration radius. It seems that this is a reasonable choice, because the value of the gyration radius at equilibrium appears to be greater than it has been expected. If a more extended start configuration giving a greater value of the gyration radius for the start configuration than at the equilibrium were chosen, we would have some doubts about the results at the beginning of our study. We have tried to use a relaxed configuration of a more densely grafted comb polymer in order to obtain faster relaxation by eliminating side chains or monomers. Surprisingly, the comb polymer configuration has not relaxed faster than in the case where we have used our usual start configuration. This cannot be explained by topological difficulties such as local entanglements. It is more likely to be related to the long-range correlation in the system, as will be shown in the following. The relaxation of the configuration with only local moves is a very slow process and more than 1 month at CPU time, i.e., several millions of MC steps, is needed for the relaxation of a comb polymer with the main chain containing 800 monomers. To speed up the relaxation of the main chain, we were looking for any other additional algorithm. We tried a slithering snake algorithm for the main chain. In this algorithm the side chains were not moving with the main chain. If a monomer disappearing at the end of the main chain and growing at the other end also belonged to a side chain, the side chain was effaced and grew at the other end. The probability that the chain would grow in the same way as in the enrichment method was so small that we allowed them to grow choosing empty lattice sites and then to relax with several local moves of the whole comb polymer before attempting a new slithering snake-like step. Typically, 32 000 MCS were needed for the relaxation of side chains of a length of 30 monomers if only local moves were used. Unfortunately, the mixing of this algorithm and local moves in various proportions has only led to a trapping of the main chain in a collapsed state, i.e., the side chains played the role of obstacles for the main chain. An efficient algorithm for the relaxation of a long comb polymer is still lacking. This fact has limited our ability to simulate long comb polymers in a reasonable amount of time. That is also why some results are given for the comb with the backbone containing only 200 monomers.

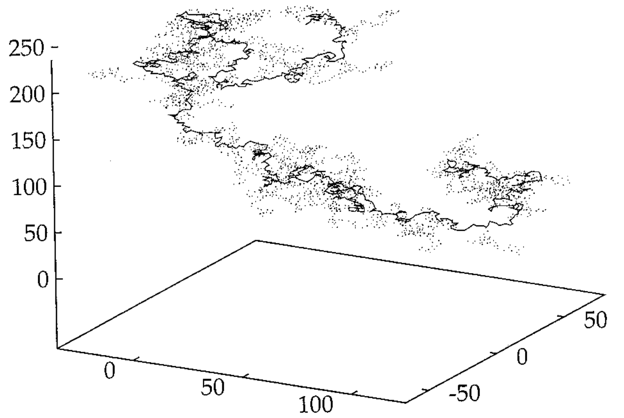

Figure 2. Snapshot of a typical conformation of the comb polymer with the main chain consisting of $N = 800$ monomers and side chains of length $n = 35$; the main chain and side chains are shown by solid and dotted lines, respectively.

4. Simulation Results

We have simulated two series of comblike polymers with the main chain consisting of $N = 800$ or 200 monomers, respectively. The snapshot of a typical conformation of a comb polymer with the main chain consisting of $N = 800$ monomers and with 80 side chains, each consisting of $n = 35$ monomers, is presented in Figure 2.

In the first case ($N = 800$) we varied the length of the side chains (from 20 to 41 monomers) while the length of the spacers was kept constant and equal to 10 monomers, and, consequently, the number of side chains remained equal to 80. Thus the branching parameter n/m varied in the range from 2 to 4.

In the second case we kept the length of the side chains constant and equal to 16 monomers and changed the length of the spacers from 16 to 3 monomers. Of course the scaling relations derived in section 2 for combs with long, flexible spacers are hardly applicable if each spacer consists of only a few monomers. However, we have studied the limiting case of the very dense grafting of side chains to observe the main tendencies in the behavior of dense combs.

4.1. Global Comb Conformation. Let us start with the case $N = 800$ and consider the dependence of the mean-square gyration radius of the comb on the number of monomers in the side chains presented in Figure 3 (curve 1). We see that even in the log−log coordinates this dependence is described by a monotonically increasing function with a growing slope. At comparatively small side chain lengths $n = 20-30$, corresponding to the beginning of their overlap, $n/m = 2-3$, the slope is close to 0.75, while at stronger overlap, $n = 30-40$ or $n/m = 3-4$, the slope is equal to approximately 1.95. Taking into account the accuracy of our numerical experiment, we find these results to be in a good agreement with the scaling picture of the comb polymer conformation described earlier. In the beginning of the overlapping of side chains (at $n/m = 2-3$), the interaction between neighboring chains is rather weak and does not lead to significant changes in their conformation or to the stiffening of the comb on large scales. Consequently, we can expect that eq 2 gives a valuable estimation $R \sim n^{0.4}$ in this range of n/m.

As the ratio n/m increases, the effect of cooperative interactions described in section 2.3 is expected to come

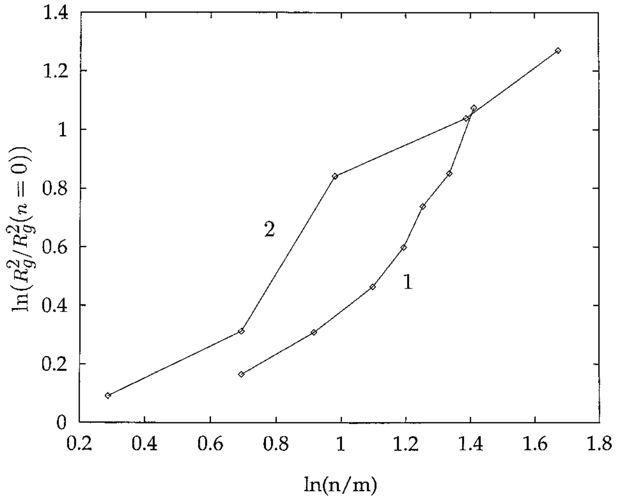

Figure 3. log–log plot of the reduced mean-square gyration radius of the main chain as a function of the overlap parameter n/m. Curve 1 corresponds to main chain length $N = 800$ spacer length $m = 10$, and the length of side chains varied as $n = 20$, 25, 30, 35, 38, and 41. Curve 2 corresponds to main chain length $N = 200$, side chain length $n = 16$, and the spacer length varied as $m = 3$, 4, 6, 8, and 16.

into play. Thus, we can expect that the comb behavior in this range corresponds to the semiflexible wormlike chain with a strong excluded volume interaction. In the limit of large N, the size of the comb is described by eq 8, so that $R \sim n^{0.54}$. Consequently, the slope of the dependence ln R(ln n) increases slightly.

Further increases in n at a fixed number of monomers in the main chain lead to a decrease in the number of effective segments in the comb and, consequently, a decrease in the parameter ζ (see eq 9). Thus, the comb passes to the Gaussian regime described by eq 7. In this regime, the dependence of the comb size on n becomes even stronger, $R \sim n^{0.87}$, which is indicated by an increasing slope of the right part of the curve 1 in Figure 3.

Equation 8 gives, at fixed N, some kind of intermediate asymptotic behavior of the dependence of R on n. Simple estimations show that the range of n where we can expect excluded volume large-scale behavior increases with the length of the main chain approximately as $\Delta \ln n \cong 0.5 \ln(N/m)$, so that sufficiently large N is required for the manifestation of this regime. Thus, the results of simulation for the comb with $N = 800$, $m = 10$ are in qualitative agreement with the prediction concerning the strong dependence of the induced rigidity of the comb on the degree of overlap of side chains.

Let us turn now to curve 2 in Figure 3, describing the dependence of the mean-square gyration radius of the comb with a main chain consisting of $N = 200$ monomers on the inverse spacer length $1/m$ at a fixed number ($n = 16$) of monomers in each of the side chains. We see that in the range of weak overlap of side chains, i.e., when the spacers are comparatively long, $m = 8-16$, the slope of the dependence ln R^2(ln(1/m)) is again close to 0.75, which coincides with the prediction of the simple Flory-type theory (eq 2). It is surprising that in the range of strong overlap, $m = 3-4$, the slope is almost the same; only in the intermediate range, $m = 6-8$, is the slope noticeably larger that can be related to a decrease in the degree of interpenetration of distant parts of a comb. Thus, curve 2 gives us no evidence of significant stiffening of a comb polymer with short side chains and spacers under the condition of strong overlap of side chains.

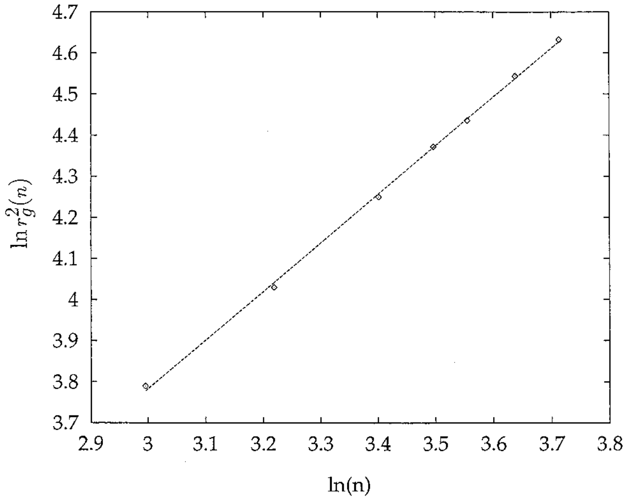

Figure 4. log–log plot of the mean-square gyration radius of a side chain as a function of the number of monomers per side chain; the main chain length is $N = 800$, and the spacer length is $m = 10$.

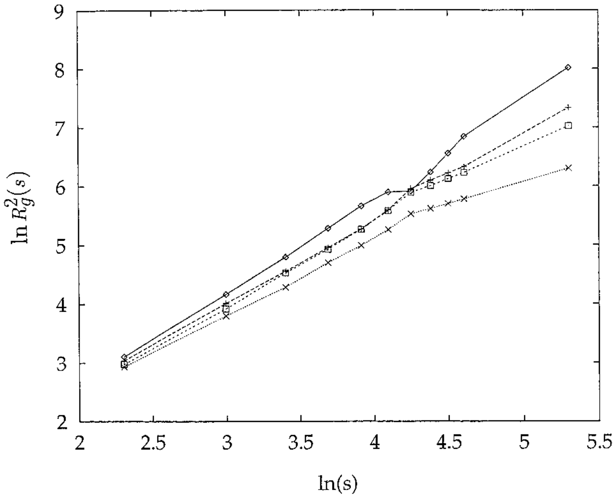

Figure 5. log–log plot of the mean-square gyration radius, $R^2(s)$, of the part of the main chain consisting of $s \geq m$ monomers versus s: $N = 200$, $n = 16$, and the spacer length m is equal to 3 (◇), 4 (+), 6 (□), and 8 (×).

4.2. Local Conformational Structure. Let us consider the conformation of a comb on the scale of a spacer length and start with the case $N = 800$, $m = 10$. As follows from our calculation, an increase in the length of side chains in the range $n = 20-41$ almost does not affect the size (the square gyration radius) of individual spacers, which remains equal to the size of a linear chain of 10 monomers with excluded volume interaction. As for the size of the side chains, it increases with an increase in n as $\sim n^{3/5}$ (Figure 4). This is not surprising because the degree of overlap $n/m = 2-4$ is still rather weak and corresponds to the margin of a densely grafted comb regime. Indeed, the degree of stretching of side chains, $\sim(n/m)^{3/25}$, as well as the free energy (the number of blobs) per side chain $\sim(n/m)^{3/10}$, remains on the order of unity.

However, it is interesting to consider the dependence of the size $R(s)$ of a part of the main chain consisting of s monomers on s. This dependence presented in Figure 5 for $N = 200$, $n = 16$, and $m = 3-8$ is almost linear in log–log coordinates at least for $s \leq 70$. The slope of the curve ln R^2(ln s) indicates that the conformation of a part of the main chain consisting of several spacers is perturbed by the interaction of side chains. The slope

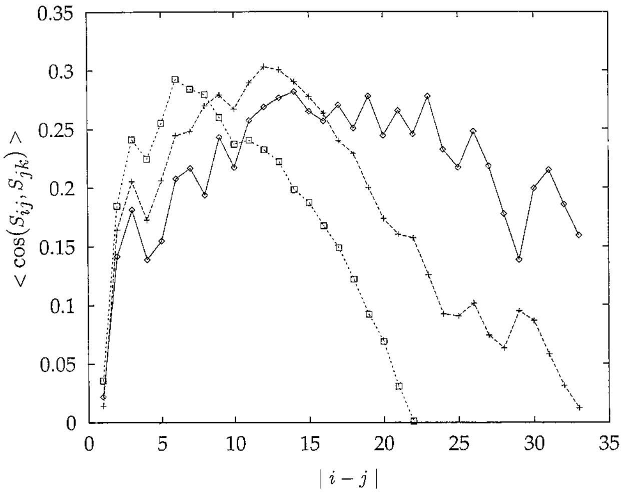

Figure 6. Correlation function $\langle \mathbf{S}_{ij}\mathbf{S}_{jk}\rangle$ between vector $\mathbf{S}_{ij}$ connecting the ith and the jth monomers of the backbone and vector $\mathbf{S}_{jk}$ connecting the jth and the kth monomers as a function of $l = j - i = k - j$ for the main chain consisting of $N = 200$ monomers. The side chain length is equal to $n = 16$ monomers, and the spacer length is equal to 3 (◇), 6 (□), and 8 (+).

gradually increases from 1.32 to 1.70, remaining less than 2 as the degree of overlap of side chains increases from 2 to 5.3 due to a decrease in the length of spacers. Thus, even at a grafting density close to the limiting value ($m = 3$), the main chain is not stretched on the scale of several spacers. However, the tendency of an increase in the slope of ln R(ln s) curves with an increase in n/m indicates that this stretching occurs at sufficiently large n/m.

All of the curves presented in Figure 5 demonstrate that the transition from small-scale behavior corresponding to a partially stretched backbone to large-scale behavior corresponding to a swollen or Gaussian coil conformation occurs at $s \cong 70$; the slope of the ln R(ln s) curves becomes noticeably smaller at $s \geq 70$, which indicates the flexibility of the comb on a large scale. We see that the scale on which the comb backbone is partially stretched, as well as the size of the side chains, is almost independent of the degree of overlap at fixed n.

To observe the effective stiffening of a comb due to the interaction of side chains, we have studied the correlation in orientation of end-to-end vectors of the parts of the main chain consisting of $l \gg m$ monomer units as a function of l. In Figures 6 and 7, we present the dependencies of the average cosine of the angle between end-to-end vectors of the neighboring parts of the main chain containing l monomers on l for different values of the spacer length (Figure 6) or for different lengths of side chains (Figure 7).

We expect that the correlation function, $\langle S_{ij}S_{jk}\rangle$, must differ from zero if $l = j - i = k - j$ is smaller than the number of main chain monomers in the effective rigid segment of the comb. If we consider the parts of the main chain consisting of several effective segments, the orientation of the end-to-end vectors of these parts becomes uncorrelated.

As follows from Figure 6, an increase in the degree of overlap of side chains (a decrease in the length of spacers) results in a noticeable increase in the number of monomers in correlated parts of the main chain. However, it is easy to see that the size of the effective segment estimated from the condition of vanishing of the correlation function defined earlier grows with $1/m$ much more slowly than could be expected from eq 5. The same tendency can be observed in Figure 7, where we present the same correlation function for different values of the side chain length at constant spacer length. The length of correlated parts of the main chain increases with an increase in the side chain length. However, the large statistical error in this case does not allow us to reliably determine the value of l at which the correlation function tends to zero.

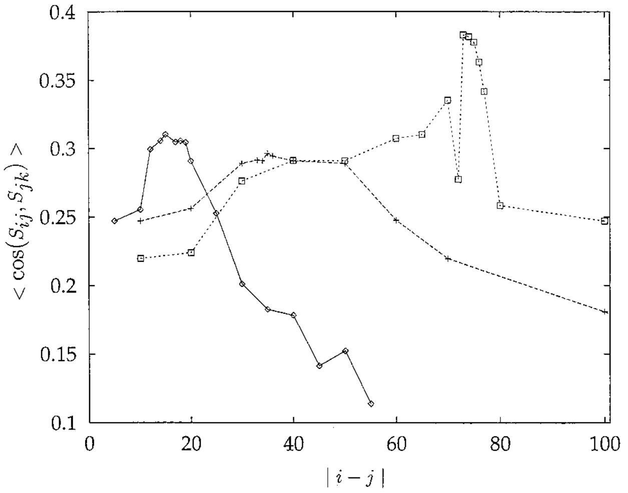

Figure 7. Same as Figure 6, except that the main chain contains $N = 800$ monomers, the spacer length is $m = 10$ monomers, the side chains contain 25 (◇), 30 (+), and 35 (□) monomers.

The origin of this statistical error, which results in a noticeable scattering of data presented in Figures 6 and 7, is of course the limited number of uncorrelated data points available. As only one polymer consisting of a large number [$N(1 + n/m)$] of monomers has been simulated, the computational time required to obtain enough uncorrelated configurations has appeared to be too long. The relaxation has also been slowed down by large values of local monomer density: the probability that a monomer near the grafting point finds an available site is strongly reduced. On the other hand, the lengths of the main and side chains, as well as the number of side chains, have been chosen to be sufficiently large to observe the large-scale effects predicted by the theory. Thus, the large value of the statistical error is a penalty for the possibility to observe the large-scale behavior of a long, strongly branched polymer.

5. Conclusions

The equilibrium conformation of comblike polymers in a dilute solution has been studied by the Monte Carlo simulation technique on the basis of the bond fluctuation model. The main chain and the side chains were long and flexible, and the number of side chains was sufficiently large. The main point of interest for us was to make a comparison of our simulation results with the scaling theory of conformations of comblike polymers in solution. The prediction of the theory concerning the strong dependence of the induced rigidity on the degree of overlap of side chains was of particular interest for us. Although we varied the degree of overlap n/m, of side chains in the range 2−4, we observed only weak perturbation of the conformations of side chains and spacers. However, the interaction of side chains has affected the conformation of the comb on the intermediate and large scales: we observed partial stretching of the backbone on the scale of several spacer lengths and correlations in the orientation of end-to-end vectors of the corresponding parts of the backbone. In the case of longer side chains, $n = 20-40$, an increase in the degree of overlap, n/m, results in the rapid increase in the overall comb dimension in accordance with the prediction of the scaling theory. We have not obtained the same results in the case of shorter side chains and spacers, although the conformation of the comb on the intermediate scale is strongly affected by the interaction of the side chains.

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