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Adsorption of Comb Polymers

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ABSTRACT: The adsorption of comb polymers is studied using a self-consistent field theory. It is found that adsorbed comb polymers form thin layers as compared to linear polymers due to the absence of long dangling tails. The segments in the backbone of the comb adsorb preferentially over the tooth segments, as the end segments of the teeth can gain entropy protruding into the solution. This leads to a brushlike behavior and a depletion zone adjacent to the adsorbed layer if the teeth are long compared to the backbone spacing. The brushlike behavior is more pronounced in the case of a comb copolymer with an adsorbing backbone, but nonadsorbing teeth.

Introduction

Scheutjens *et al.*[1] have emphasized the role of end segments in polymer adsorption. In the semiplateau of the isotherm, many polymer segments of many molecules compete for adsorption sites. The polymer molecules then prefer to adsorb with their ends protruding in solution to form long tails, and the middle segments form alternating trains (sequences of segments in contact with the surface) and loops. This average conformation is a compromise between gaining as much adsorption energy as possible and at the same time limiting the loss in conformational entropy upon adsorption. The tails are of major importance for colloidal stability, which is one of the main applications of polymer adsorption. Linear polymers can have at most two tails per polymer. For other chain geometries, the number of chain ends is either smaller or larger. For example, ring polymers, which do not have any chain end whatsoever, have been studied by Van Lent *et al.*[2] They found not surprisingly that ring polymers form less extended layers. Chain branching is the other extreme, as it increases the number of chain ends. Often, chain branching can be described by a straightforward extension of existing theories and it can result in interesting new phenomena. Several ways of branching may be distinguished: star polymers, with one central segment and several "arms", star-burst and comb-burst polymers, which are more fractal in nature, randomly branched polymers, and comb polymers.

This paper deals with regular comb polymers, consisting of a long backbone with side chains emanating from it in regularly spaced intervals (Figure 1). If the chemical composition of the side chain segments differ from the backbone segments (Figure 1b), we have a comb copolymer. The official name for these polymers is graft (co)polymers,[3] but in textbooks they are mostly referred to as comb (co)polymers.[4,5] Most of the literature about comb homopolymers deals with the determination of their extension in solution or in a melt; see, *e.g.*, refs 6 and 7. Comb copolymers reveal an interesting phase behavior in the melt.[8] Recently, comb copolymers have attracted attention as possible compatibilizers in polymer blend interfaces[9,10] or in solution as specific solubilizers.[11]

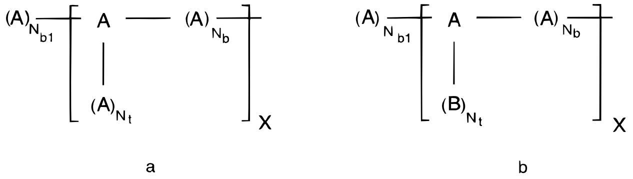

Figure 1. A regular comb homopolymer (a) and a regular comb copolymer (b) with backbone tail length N_{b1}, tooth length N_t, backbone spacing N_b, and polymerization index X.

The difference in adsorption behavior between comb and linear polymers was predicted using Monte Carlo techniques by Balazs and Siemasko.[12] They concluded that comb polymers adsorb in dense but thin layers. This has also been found experimentally by Kawaguchi and Takahashi.[13] Balazs and Siemasko found also that the teeth of comb copolymers adsorb preferentially. This is unexpected, as it will cost more entropy than conformations having the backbone on the surface.

In this paper, we will use the theory for polymer adsorption by Scheutjens and Fleer,[14,15] as extended to the case of chain branching by Leermakers,[16] to explore systematically the parameters governing the adsorption behavior of comb polymers. It may be expected that if the length of the teeth is small as compared to the length of the backbone, the polymer behaves like a linear polymer, whereas typical comb behavior, if present, will show if the teeth are long and the distance betweeen them (the backbone spacing) short. Our method is more suitable to find general trends than Monte Carlo studies, since even long polymer molecules can easily be modeled in a feasible amount of computer time.

Theory

The available space is divided up into lattice layers, parallel to the homogeneous surface. The surface is chosen as the origin of the lattice. The layer number is denoted as z, such that the surface is at $z = 0$, the layer adjacent to the surface at $z = 1$, etc. We consider only inhomogeneities perpendicular to the surface. Upon adsorption, a potential energy profile $u_x(z)$ develops, which depends on the volume fraction profiles $\{\varphi_x(z)\}$ of all the segment types x. For this potential energy, we write

$$u_x(z) = u'(z) + kT\Big(\sum_y \chi_{xy}(\langle\varphi_y(z)\rangle - \varphi_y^{b}) - \chi_{s,x}\delta(z,1)\Big) \quad (1)$$

The first term in eq 1, $u'(z)$, is a "volume-filling potential". It is found iteratively until the lattice is completely filled; *i.e.*, it is calculated from the condition that for all z the following condition holds:

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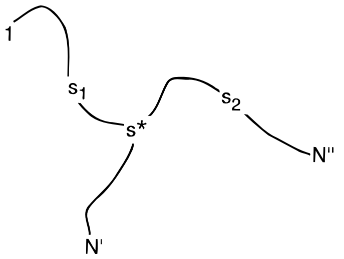

Figure 2. Schematic picture of a polymer with one branch at segment s^*.

$$\sum_x \varphi_x(z) = 1 \tag{2}$$

The second term corresponds to the energetic interactions of polymer segments with each other or with the solvent. As we will take all Flory–Huggins energy parameters χ_{xy} to be zero, this term vanishes. The last term contains the Silberberg adsorption energy parameter $\chi_{s,x}$, which equals the adsorption energy gain in units kT (Boltzmann's constant times the absolute temperature) if a segment of type x replaces a solvent molecule on the surface. The Kronecker delta $\delta(z,1)$ ensures that adsorption energy is counted only in the first layer. By definition, $\chi_{s,x} = 0$ for the solvent, and for the other segment types, it is positive if the adsorption is energetically favorable, *i.e.*, if the adsorption energy is negative.

Next, the free segment weighting factor $G_x(z)$ is defined as the Boltzmann weight connected to the potential energy $u_x(z)$:

$$G_x(z) = \exp(-u_x(z)/kT) \tag{3}$$

Polymer chains are modeled as a series of connected segments, each having the size of one lattice site. In connecting the segments, we have to take into account the molecular architecture around the branches. To illustrate the calculation scheme, we will take a simple molecule with only one branch, at $s = s^*$ (Figure 2). In the SCF formalism of Scheutjens and Fleer, a chain end distribution function (edf) $G(z,s|1)$ is defined. It expresses the combined statistical weight of all possible allowed conformations that the chain fragment from segment 1 to s can assume, under the constraint that s is at a distance z from the surface. This means that the coordinate of segment 1 is left unspecified; the segment can assume all positions provided that it does not violate the connectivity constraints. Thus, for the first segment, we can simply use the free segment weighting factor

$$G(z,1|1) = G_x(z) \tag{4}$$

taking that segment 1 is of type x.

Moving along the chain toward the branch point s^*, we can express the edf of a segment s_1 in the edf of its preceding segment, $s_1 - 1$, by realizing that if s_1 is in layer z, $s_1 - 1$ has to be either in layer $z - 1$, in z, or in $z + 1$, having within a cubic lattice an *a priori* probability of respectively $^1/_6$, $^4/_6$, and $^1/_6$. This leads to

$$G(z,s_1|1) = G(z,s_1)\left\{\frac{1}{6}G(z-1,s_1-1|1) + \frac{4}{6}G(z,s_1-1|1) + \frac{1}{6}G(z+1,s_1-1|1)\right\} \tag{5}$$

where $G(z,s_1)$ equals $G_x(z)$ if segment s_1 is of type x. Equation 5 can be used up to and including the branch point s^*. For the subsequent segments, the branch from N' to s^* has to be incorporated. The edf from the end point N', $G(z,s|N')$, is found analogously to eq 5. The two branches are connected using

$$G(z,s^*|1,N') = \frac{G(z,s^*|1)G(z,s^*|N')}{G(z,s^*)} \tag{6}$$

where $G(z,s^*|1,N')$ is the edf for segment s^* in layer z, given that both segment 1 and segment N' are free to chose their position. For a segment s_2 on the branch from s^* to N'', the recurrence relation becomes

$$G(z,s_2|1,N') = G(z,s_2)\left\{\frac{1}{6}G(z-1,s_2-1|1,N') + \frac{4}{6}G(z,s_2-1|1,N') + \frac{1}{6}G(z+1,s_2-1|1,N')\right\} \tag{7}$$

The volume fraction of segment s_2 in layer z can be found by combining eq 7 with the walk coming from the other free end, N'':

$$\varphi(z,s_2) = \frac{\varphi^{\mathrm{b}}}{N}\frac{G(z,s_2|1,N')G(z,s_2|N'')}{G(z,s_2)} \tag{8}$$

where φ^{b} is the volume fraction in the bulk and φ^{b}/N serves as a normalization constant. For the branch point s^*, we have

$$\varphi(z,s^*) = \frac{\varphi^{\mathrm{b}}}{N}\frac{G(z,s^*|1)G(z,s^*|N')G(z,s^*|N'')}{(G(z,s^*))^2} \tag{9}$$

In this way the volume fraction of all segments in a branched molecule can be found, each time combining all the possible walks from all the end points to the particular segment.

Note that the volume fraction profiles can only be calculated if the potential energy profile is known. However, the potential energy profile depends on the volume fraction profile through eq 1 and the volume-filling constraint (2). The set of coupled equations is solved numerically. Once a solution is found, the adsorption can, for instance, be characterized by the excess amount θ^{exc}, defined as

$$\theta^{\mathrm{exc}} = \sum_z (\varphi(z) - \varphi^{\mathrm{b}}) \tag{10}$$

or using the adsorbed amount θ^{ads}, which is the amount of polymer chains having at least one segment in the first layer.[17] For dilute polymer solutions, the difference between θ^{exc} and θ^{ads} is negligible.

Results and Discussion

The comb polymers that will be used can be characterized by four parameters: the tooth length N_{t}, the backbone spacing N_{b}, the backbone tail N_{b1}, and the number of repeating units X (Figure 1). The total number of segments N equals $N_{\mathrm{b1}} + X(1 + N_{\mathrm{t}} + N_{\mathrm{b}})$. In most cases, the combs are symmetric; *i.e.*, $N_{\mathrm{b1}} = N_{\mathrm{b}}$.

First, we will investigate the difference in adsorption behavior between a comb homopolymer and a linear homopolymer having the same number of segments. Also, the preference of tooth segments for the surface, found by Balazs and Siemasko, is checked. The full advantage of the SCF method is exploited when we systematically vary the parameters mentioned above in

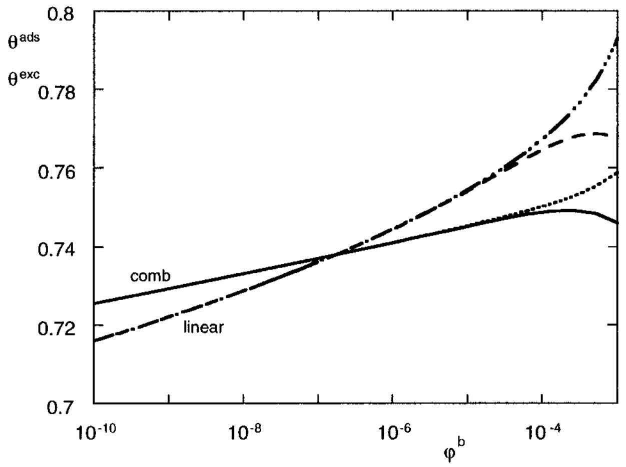

Figure 3. Adsorption isotherm for a comb polymer with $N_{b1} = N_b = 5$, $N_t = 25$, and $X = 50$ (full curve: excess amount; dotted curve: adsorbed amount) and for a homopolymer with $N = 1555$ (dashed curve: excess amount; dashed–dotted: adsorbed amount). Athermal solvent, adsorption energy parameter $\chi_s = 1$.

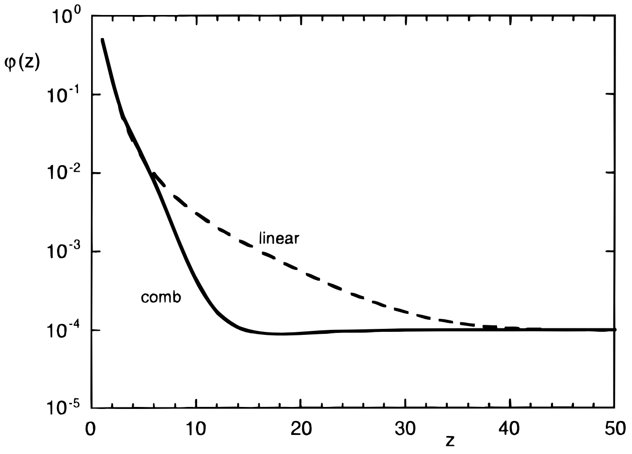

Figure 4. Volume fraction profile from the polymers in Figure 3 at $\phi^b = 10^{-4}$.

order to analyze any "typical comb" behavior if present. As we expect entropic factors to play a role in the adsorption of combs, we will look at the situation near the desorption point, where the energetic contributions are of the same order as the entropic ones. Lastly, comb copolymers are considered.

Homopolymers. In Figure 3 adsorption isotherms are shown, where the full curve corresponds to a comb polymer with $N_{b1} = N_b = 5$, $N_t = 25$, and $X = 50$. The dashed curve is for a linear homopolymer with the same number of segments, $N = 1555$.

At low bulk volume fractions the comb polymer adsorbs to a greater extent than the linear polymer. This is due to the fact that a comb polymer loses less entropy upon adsorption than a linear chain: a comb polymer has more free ends that can stick out into the solution. At higher bulk concentration, the curves cross. If the driving force for adsorption is high enough, more linear polymer adsorbs because it can form longer tails. This can be seen more clearly if we compare the volume fraction profiles in Figure 4, which are taken at $\varphi^b = 10^{-4}$. The occupation in the first few layers is almost equal, but the linear polymer protrudes much further into the solution. This result agrees with the predictions of Balazs and Siemasko[12] and with the measurements of Kawaguchi and Takahashi:[13] comb polymers form thin layers. The excess amount in Figure 3 has a maximum for all polymers: as the bulk volume fraction increases, the second term in eq 10 starts to dominate. In the limiting case of a polymer melt ($\varphi^b = 1$), the excess amount is necessarily zero. The adsorbed amount, on the other hand, is a continuously increasing function of the bulk volume fraction.

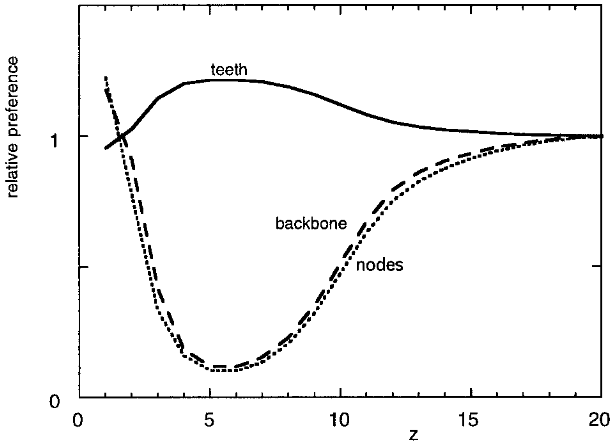

Figure 5. Relative preference profiles for the segments of the comb polymer used in Figure 3 at $\phi^b = 10^{-4}$. Full curve: tooth segments; dashed curve: backbone segments (including nodes); dotted curve: node segments.

The distribution of segments within the adsorbed layer of a comb polymer can be illustrated by making a relative preference profile for the constituting segments of the comb (Figure 5). The relative preference of a segment of type σ in layer z is defined as $\sum_{s=\sigma} N\varphi(z,s)/N_\sigma\varphi(z)$, where N_σ is the number of segments of type σ and σ can be either a backbone segment, a tooth segment, or a branch point (node). Note that the curve for the backbone in Figure 5 includes the nodes, as they are part of the backbone. If the relative preference for a particular group of segments in a certain layer exceeds unity, those segments are present more than average in that layer.

It can be seen that the tooth segments avoid the surface and stick out into the solution, whereas the reverse holds for the backbone segments. Balazs and Siemasko[12] have found the opposite: in their Monte Carlo simulations, the tooth segments are closer to the surface than the backbone. This may be due to an underestimation of the time scale for rearrangement of the comb polymer. It can be expected that in the kinetics of the adsorption process the tooth segments will adsorb first and during the subsequent exchange between tooth and backbone segments the surface coverage will hardly change. The constancy of the surface coverage was the stop criterion in the simulations, so that it is very well possible that equilibrium was not reached yet.

The branch points or node segments are even closer to the surface than the rest of the backbone. This is because the nodes have three adjacent adsorbing segments pulling them toward the surface. Note that we permit backfolding of the chain onto itself. If more than one side chain emanates from the node segments and direct backfolding is excluded, for instance using the rotational isomeric state scheme method of ref 16, the branch points cannot reach the surface anymore because of the excluded volume.[18]

We now systematically vary the three parameters controlling the molecular architecture of the combs, starting from the molecule used in Figure 3. The results

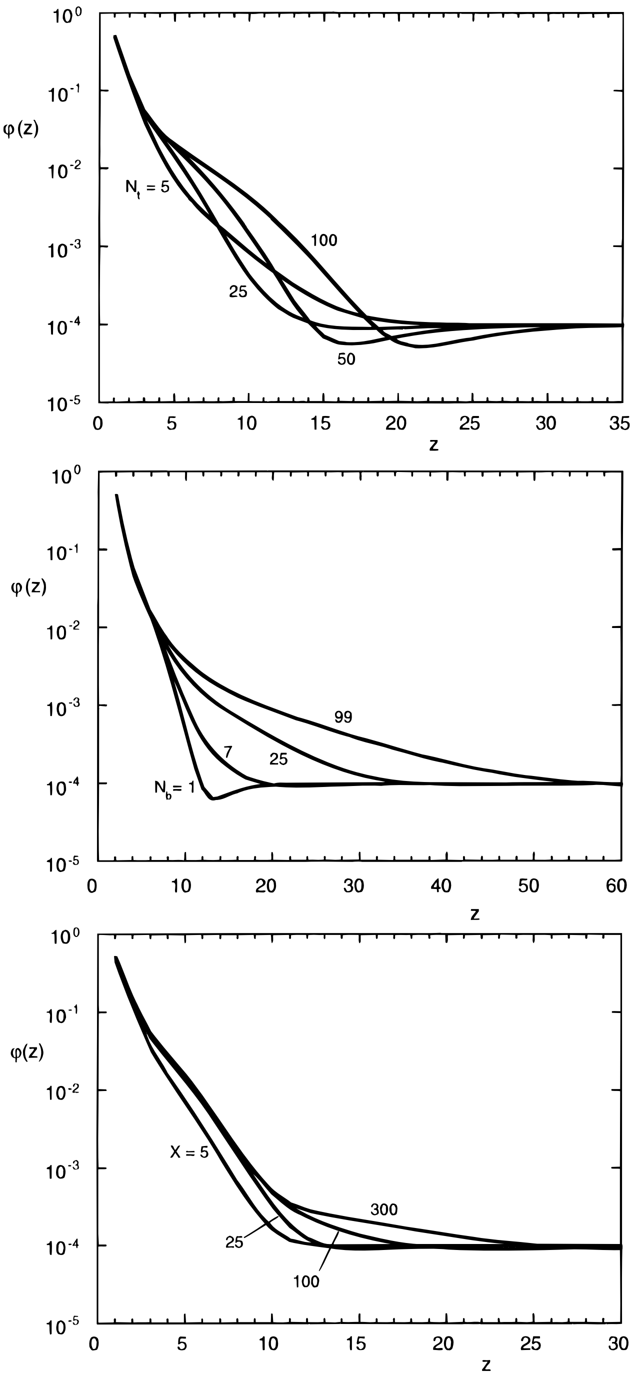

Figure 6. Volume fraction profiles for several comb polymers. Athermal solvent, bulk volume fraction 10^{-4}, adsorption energy = 1 kT. Top diagram: $N_{b1} = N_b = 5$, $X = 50$, N_t as indicated. Middle diagram: $N_t = 25$, $X = 50$, $N_{b1} = N_b$ as indicated. Bottom diagram: $N_{b1} = N_b = 50$, $N_t = 25$, X as indicated.

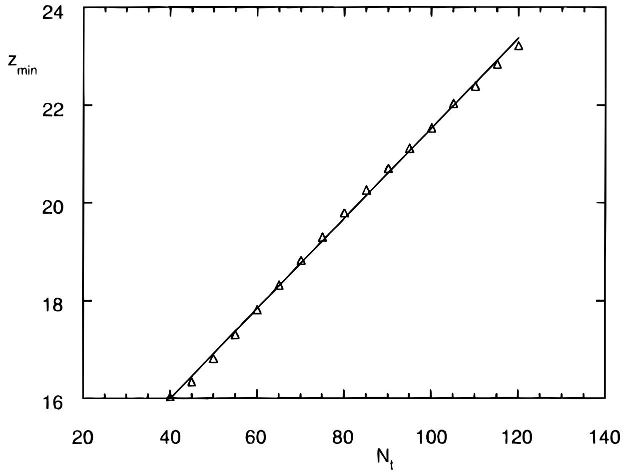

Figure 7. Position of the minimum in the volume fraction profile of Figure 6a as a function of the tooth length N_t.

are shown in Figure 6. If the length of the teeth is increased (top diagram), the adsorbed amount increases, but only because the longer tails protrude further into the solution; the occupation in the first few layers (determining most of the adsorbed amount) is almost constant. If the tails get longer than about 40 segments, a depletion zone develops just before the polymer concentration reaches the bulk value. The profile then falls off so steeply that the free polymers in the bulk feel the adsorbed polymer layer as a nonadsorbing wall. The position of the depletion "dip" turns out to be linear in the tail length (Figure 7). This indicates a brushlike behavior, with the backbone adsorbed on the surface and the teeth forming the brush. The lower concentration of polymer in the dip leads to a local decrease in viscosity. Hence, this system could be interesting for lubrication purposes: the adsorbed layer prevents aggregation, whereas the depletion dip facilitates the sliding of particles.

If we increase the spacing between branches in the backbone (middle diagram of Figure 6), we see that the polymer behaves more and more like a linear homopolymer: the characteristic steep decay and the depletion dip disappear. Indeed, the difference between the volume fraction profile of the polymer with $N_b = 99$ and the corresponding linear polymer with $N = 6255$ is negligible.

The effect of increasing the polymerization index X is shown in the bottom diagram of Figure 6. For high values of X, an extra shoulder appears in the volume fraction profiles at high z. Here, the outer parts of the backbone behave as tails and are lifted from the surface.

Critical Adsorption Energy. A linear, flexible polymer adsorbing from solution onto a solid surface loses conformational entropy as it cannot use the half-space occupied by the adsorbent. Therefore, a polymer will avoid the surface if the adsorption energy is not large enough to compensate this entropy loss. The minimum adsorption energy needed to give net adsorption is called the critical adsorption energy. In a cubic lattice, a polymer loses one out of six possibilities to place a segment, so that the critical adsorption energy equals $kT \ln(6/5)$, or 0.182 kT. This value is independent of the polymer chain length, as long as the polymer is not too short (say, a few hundred segments). The critical adsorption energy for a particular polymer is defined here as the adsorption energy where the excess amount vanishes. The critical adsorption energy of a large variety of linear and comb molecules can be determined from Figure 8. The open circles, pluses, and crosses correspond to homopolymers: all segments have the same adsorption energy. The open circles represent the linear case, and the crosses and pluses are for two different comb polymers. The molecular architecture turns out not to change the critical adsorption energy in the homopolymer case: for all molecules the critical value is 0.182 kT. This conclusion was also reached for the adsorption of ring polymers: the entropy difference per segment between rings and linear chains converges to zero in the limit of ininite chain length.[2]

This situation changes drastically if copolymers are considered. Van Lent and Scheutjens[19] have shown that a random AB copolymer differing in adsorption energy

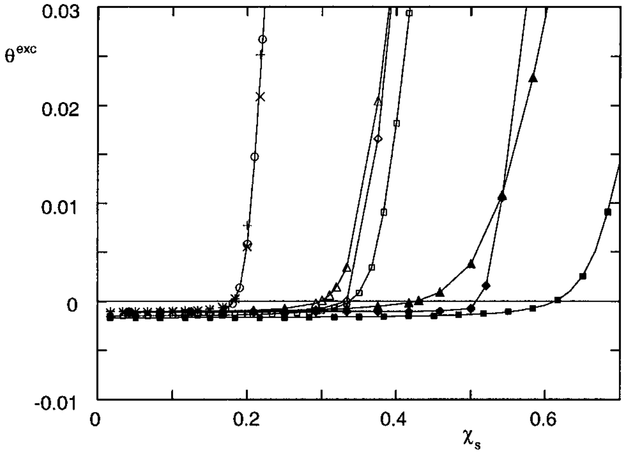

Figure 8. Critical adsorption energy for polymers varying in molecular architecture and adsorption energy. Open circles: linear polymer, $N = 1555$; pluses: $N_{b1} = N_b = 5$, $N_t = 25$, $X = 50$; crosses: $N_{b1} = 0$, $N_b = 5$, $N_t = 6$, $X = 100$. All segments have the same adsorption energy parameter χ_s. Open triangles: $N_{b1} = 0$, $N_b = 5$, $N_t = 6$, $X = 100$, tooth segments have the adsorption energy as indicated on the abscissa, backbone segments $\chi_s = 0$. Open diamonds: same as open triangles, but backbone segments have an adsorption energy, for all tooth segments $\chi_s = 0$. Open squares: multiblock copolymer $(A_6B_6)_{100}$, A block: $\chi_s = 1$, B block: $\chi_s = 0$. Filled triangles: $N_{b1} = N_b = 5$, $N_t = 25$, $X = 50$, outer 6 segments of teeth have an adsorption energy, for all other segments $\chi_s = 0$. Filled diamonds: $N_{b1} = N_b = 5$, $N_t = 25$, $X = 50$, backbone segments except b1 segments have an adsorption energy, for the tooth segments and b1 segments $\chi_s = 0$. Filled squares: multiblock copolymer $(A_6B_{25})_{50}$, A block: $\chi_s = 1$, B block: $\chi_s = 0$. In all cases: athermal solvent, bulk volume fraction $\phi^b = 10^{-4}$.

adsorbing from an athermal solvent can be described as a homopolymer with effective adsorption energy

$$\chi_s = \chi_{s,B} + \ln(\nu_B + \nu_A \exp(\chi_{s,A} - \chi_{s,B})) \qquad (11)$$

with $\chi_{s,A}$ and $\chi_{s,B}$ the adsorption energy parameters of the A and B blocks, and ν_A or ν_B the fraction of A and B blocks, respectively. Using $\chi_{s,B} = 0$, $\nu_B = 1 - \nu_A$, and for χ_s the homopolymer critical adsorption energy ln(6/5), we find for the critical adsorption energy for the A blocks in a fully random copolymer

$$\chi_{sc,A} = \ln\left(\frac{1 + 5\nu_A}{5\nu_A}\right) \qquad (12)$$

For a (long) diblock copolymer, the critical adsorption energy is almost equal to that of a homopolymer: at the point of desorption ($\theta^{exc} \approx 0$) the nonadsorbing block simply forms a long dangling tail that does not hinder the few adsorbed chains connected to the surface. If we divide up the adsorbing blocks so that we get a multiblock copolymer, the nonadsorbing blocks are always close to the adsorbing blocks. Hence, for the multiblock copolymer $(A_6B_6)_{100}$, shown in Figure 8 in open squares, we find the value for the random copolymer with $\nu_A = 0.5$, namely, 0.336. If we now imagine the nonadsorbing blocks of the multiblock as side chains on the adsorbing main chain, we get the comb copolymer indicated with open diamonds, which turns out to have exactly the same threshold value. However, if the nonadsorbing blocks form the main chain and the tooth segments are adsorbing (open triangles), the critical adsorption energy is shifted toward a smaller value: a conformation with only a few (outer) tooth segments adsorbed leaves more entropy for the rest of the chain. Such a conformation is thus more favorable, and less energy is needed to get adsorption.

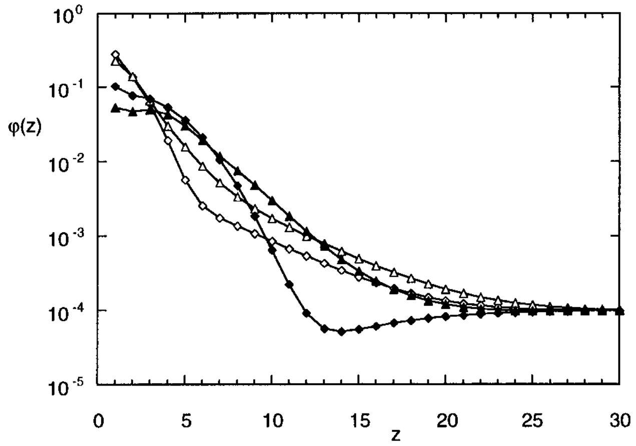

Figure 9. Volume fraction profiles for four of the polymers used in Figure 8 at $\chi_s = 1$. Symbols as in Figure 8.

We can increase the length of the nonadsorbing block even further to 25 out of 31 segments in a repeating unit ($\nu_A = 0.19$), leading to the multiblock copolymer $(A_6B_{26})_{50}$, the filled squares in Figure 8. The nonadsorbing spacers are so large here that they can more easily move away from the surface as compared to a random copolymer, which leads to a lower value of the critical adsorption energy: about 0.61 instead of the random value 0.71. More interestingly, if we use the adsorbing blocks as the backbone for a comb copolymer and the long nonadsorbing block as the side chain (filled diamonds), the teeth can protrude into the solution, leading to an increase in entropy, and thus a lower critical adsorption energy. Lastly, it is even more favorable to have only the last 6 segments of the long teeth able to adsorb (filled triangles).

Comb Copolymers. We have already discussed some aspects of comb copolymers in the last paragraph, around the desorption point. We concluded that it is more favorable to have adsorbing teeth, as this can lead to an extended conformation with only a few end segments on the surface and the rest of the molecule stretched out into the solution. In Figure 9, we compare the volume fraction profiles of the same comb copolymers as in Figure 8 at a higher adsorption energy of 1 kT for the adsorbing segments. The triangles correspond to adsorbing teeth, the diamonds to an adsorbing backbone, the open symbols to long polymers ($X = 100$) with short teeth ($N_t = 6$) and 600 adsorbing segments, and the filled symbols to shorter chains ($X = 50$) with longer teeth ($N_t = 25$) and 300 adsorbing segments. It can be seen that more of the longer polymers is adsorbed: the ratio of adsorbing to nonadsorbing segments is more favorable. Also, longer teeth lead to thicker adsorbed layers. More interesting is the difference between an adsorbing backbone and adsorbing teeth: an adsorbing backbone (diamonds) leads to higher adsorbed amounts but thinner layers than adsorbing teeth. Basically, the nonadsorbing teeth only increase the typical "comb behavior" of backbone segments near the surface and the entropically favorable effect of having the teeth sticking out.

Conclusions

Upon increasing the number of end segments in polymer molecules by considering the series formed by ring polymers, linear polymers, and comb polymers, we find that linear polymers are the most efficient in forming thick adsorbed layers. Ring polymers do not have any tails that can protrude into the solution, and comb polymers adsorb with the branch points preferentially on the surface. Comb polymers with long teeth and a small backbone spacing show a brushlike behavior, with a depletion dip in the volume fraction profile immediately adjacent to the adsorbed layer. If the chemical species of the teeth and the backbone species differ, thicker layers are formed if the tooth segments have a higher adsorption energy than the backbone segments. However, the adsorbed amount is less in this case.

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