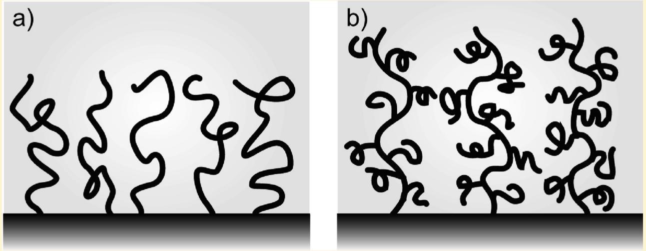
Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

Modeling the Structure and Antifouling Properties of a Polymer Brush of Grafted Comb-Polymers

Wiebe M. de Vos,*[†] Frans A. M. Leermakers,[‡] Saskia Lindhoud,[§] and Stuart W. Prescott[†]

[†]Polymers at Interfaces Group, University of Bristol, Cantock's Close, BS8 1TS Bristol, U.K.
[‡]Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands
[§]Department of Chemistry, University of Bath, Claverton Down, BA2 7AY Bath, U.K.



ABSTRACT: Numerical self-consistent field theory is used to study the structural characteristics of a polymer brush consisting of end-grafted comb-polymers. A comb-polymer brush is shown to retain the parabolic density profile characteristic of the unbranched brush. Increasing either the number of branches or the length of the side-chains leads to an increase in the height (H) of the brush. This is partly because of the branched structure: it is more favorable to stretch the polymer backbone, while leaving the side-chains almost unstretched. The other reason for the increased stretching is simply because of the extra polymer in the brush due to the branches. We find that it does not matter how the side-chains are distributed along the backbone for the predicted density profile; it is only the total amount of polymer in the side-chains that is important. The effect of branching on the brush height can be captured in a simple scaling law: $H \sim N_b(N_T/N_b)^{2/3}$, where N_b is the chain length of the polymer backbone, N_T is the total chain length, thus including the side-chains, and their ratio N_T/N_b is a measure for the amount of branching. The structure of the branched brush is less suitable for keeping away small particles from the grafted interface. It is, however, a good way of increasing the polymer density, and thus its antifouling properties, when the grafting density of the brush is limited.

INTRODUCTION

A polymer brush can be defined as a dense array of polymers, end-attached to an interface that stretches out into the surrounding medium. Over the past 30 years of investigation, the brush has been the subject of many experimental and theoretical investigations.[1−6] This has led to the brush becoming a relatively well understood system. For example, Alexander and de Gennes worked out how the stretching of the polymer chains depends on the brush properties such as the grafting density (σ) and the polymer chain length (N).[7,8] Their most iconic result describes how these parameters determined how far the polymers in the brush stretch away from the grafted interface (the height of the brush, H): $H \sim N\sigma^{1/3}$. Later studies by Milner et al.[9] and Zhulina et al.[10] revealed much of the structure of the polymer brush. Their self-consistent field theory incorporated that the polymers in the brush are not all equally stretched. It predicted that for a monodisperse brush the polymer density (φ) decreases with distance from the grafted interface (z) according to a parabolic density profile.

Another outcome of the many investigations on the polymer brush is that it has led to the identification of many potential applications, for example its use as an antifouling coating.[1,11] The high polymer density in the brush allows its use as a barrier, keeping fouling particles away from the surface. If a fouling particle, for example a protein molecule, comes into the brush, it needs to deform the brush equilibrium structure. The brush responds to this with a restoring force pushing the particle out of the brush, away from the interface. For the same reason the brush can also function to stabilize particle suspensions,[12] the high polymer density around the particles keeping them from aggregating. Furthermore, the brush has been shown to be able to substantially reduce the friction between two interfaces.[13]

Still, for both the brush properties and for its possible applications, research has mostly focused on the most simple brush architectures, a brush made of chemically equal homopolymers. In a sense this is surprising as there is such a wide variety of polymers available such as random copolymers, di- and triblock copolymers, and branched polymer such as star polymers, comb-polymers, and dendrimers. Recently work has intensified on making brushes from diblock copolymers and from two chemically different homopolymers.[14,15] The combination of chemically different polymers allows for surfaces that can be tuned by using selective solvents. Examples are brushes that can be washed with a solvent to specifically swell one of the polymer types.[16,17] After drying it is this polymer that will form the top layer of the interface and determine wettability and friction. Other examples are brushes that can be turned from

Received: December 16, 2010
Revised: February 8, 2011
Published: March 04, 2011

antifouling to protein accommodating by changing the pH of the aqueous phase.[18]

However, we are interested in polymer brushes made from branched polymers. A great many examples of these polymers exists, often showing very different properties in solution than unbranched polymers.[19−22] For example, comb-polymers in a good solvent tend to behave as very stiff polymers, as bending of the backbone leads to an increased overlap between the side-chains. As such, the altered structure of the polymer might have serious implications for the brush structure which in turn might be useful for some of the applications related to polymer brushes. In addition, branching is a good method to combine chemically different polymers in one polymer and thus in one brush. However, first one would simply like to understand the properties of a brush of branched polymers of which the branches are chemically identical to the backbone. Our system of choice is a brush made from comb-polymers as depicted in Figure 1.

Little work has been undertaken on polymer brushes made from branched polymers. Still, early theoretic work on the simplest forms of branching showed clear effects; Carignano and Szleifer[23] used a mean-field approach to show that, for a brush in which each chain has a single (short) side-chain, the side-chain will behave differently than the backbone, for example being less stretched than the backbone. Romiszowski and Sikorski[24] studied a very similar system using a Monte Carlo approach: a star polymer of three similarly long arms grafted to the interface with one arm (the stem). They found that the stem was much more strongly stretched than the two branches. Irvine et al.[25] investigated a brush from grafted star polymers with 5 and 10 arms using self-consistent field theory, predicting a parabolic density profile and suggesting that brushes from star polymers might have better antifouling properties than a brush from linear chains. Specifically of brushes from comb-polymers, only a few experimental examples exist,[26−28] and in none of those cases has the structure of the brush really been examined. Brzozowska made comb-polymer brushes using an adsorption approach and tested their antifouling properties against a number of different protein molecules.[29] While positive effects on the antifouling effects were observed, the brush could not easily be compared to a nonbranched polymer brush. Slightly more work has been done on these brushes theoretically; Zhulina et al.[30] worked out scaling laws for a brush consisting of comb-polymers. They predict a scaling law that depends on the length of the backbone, the side-chains (N_{side}), and the density of side-chains along the main chain (σ_{side}): $H \sim N_{\mathrm{b}}\sigma^{1/3}\sigma_{\mathrm{side}}^{-2/5}N_{\mathrm{side}}^{3/5}$. Work using numerical self-consistent field showed that the parabolic profile associated with the polymer brush is preserved for branched polymer brushes.[31] In recent work, Xu and Cao[32] used density functional theory to investigate the branched brush and its interaction with small colloids. They again show that for the branched brushes the parabolic profile remains and that the branching increases both the brush height and the density in the polymer brush. Because of the higher polymer density in the brush, the brush is able to act as a better barrier to prevent particles from adsorbing to the grafting interface. A problem in their approach however is that by adding branches to the brush two parameters are changed at the same time: the structure of the brush and the amount of polymer in the brush. We will build on their work by separately investigating these parameters and how they affect the brush antifouling properties.

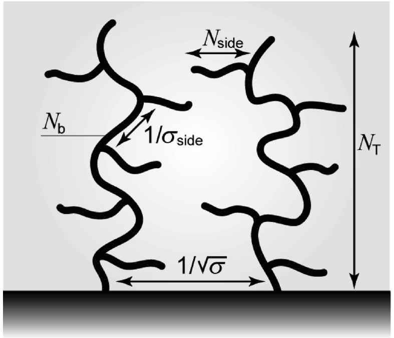


Figure 1. A brush made from comb-polymers. The system is described by a few key parameters: N_{b} = length of the backbone, σ = grafting density (chains per nm^2), N_{side} = length of the side-chains, σ_{side} = graft density of side-chains along the chain (chains per monomer), N_{T} = total number of monomers in entire polymer.

In this investigation we focus on understanding the effect that branching has on the structure and on the antifouling properties of a polymer brush. We use numerical self-consistent field theory to model the brush structure and combine the results with a simple box-model to understand the stretching of the polymers in the brush. In our approach we change the amount of branching while keeping the amount of polymer in the brush fixed. This allows us to separately investigate the effect that the structure of the polymer chains has on the structure and on the stretching of the brush. We compare our results to those of previously predicted scaling laws and build on this to suggest a new simpler scaling law for a brush made of branched comb-polymers. Furthermore, we are able to separately investigate the stretching of the polymer backbone and the stretching of the side-chains. To investigate the antifouling properties, we calculate the energy needed to push a small particle into the brush layer for different degrees of branching. We compare the results to a previous investigation on this topic.

THEORY

Numerical Self-Consistent Field Theory. When modeling the polymers at interfaces, we are not so much interested in specific configurations of the polymers but rather on predicting an average of all possible conformations as this is what we would be able to measure experimentally. For the brush we aim to predict the so-called brush-density profile, thus describing how the polymer density of the brush decreases with distance away from the interface. This also provides us with information such as the height of the brush and the free energy of the system. We do this using self-consistent field theory making use of the discretization scheme of Scheutjens and Fleer.[33] The basis of this approach is to use the analogy between the path followed by a diffusing particle and a single conformation of a polymer chain. To accurately model polymer brushes, it is necessary to solve the Edwards (diffusion) equation for polymer chains in inhomogeneous systems:[34]

$$\frac{\partial G(\mathbf{r}, s|1, 1)}{\partial s} = \left(\frac{1}{6}\nabla^2 - u(\mathbf{r})\right) G(\mathbf{r}, s|1, 1) \qquad (1)$$

Here, the Green's function G represents the statistical weight of all possible conformations of polymer chains with segment $s' = 1$ next to the surface ($\mathbf{r}_z = 1$) and segment $s' = s$ at coordinate $\mathbf{r}$. This quantity is closely related to the chain partition function (that is, when $s = N$) and hence to the free energy of the system. In eq 1 it is necessary to specify the (dimensionless) segment potential $u(\mathbf{r})$. The role of the segment potential is to mimic the excluded-volume interactions from, e.g., molecular crowding effects. This potential also accounts for the solvent quality. Here and below, we assume that the solvent quality is good: the Flory–Huggins parameter $\chi = 0$, and thus the bare second virial coefficient (v) is unity.[9] Assuming for a moment that there is only one relevant coordinate, namely the distance to the wall (for which we use the z-coordinate), the segment potential becomes self-consistent when $u(z) = v\varphi(z)$. A polymer chain should connect its free end, irrespectively of the z-position of this (free) end, to the grafting segment by taking N steps in this potential field. The system can realize this by insisting on a parabolic shape of the segment potential, that is, $u(z) = A - Bz^2$. A parabolic potential directly leads to the well-known parabolic volume fraction profile for a dense brush where the chains are strongly stretched.[9,10]

Numerical solutions for end-grafted polymers can be generated only after choices have been made about the discretization scheme. As discussed we follow the approach of Scheutjens and Fleer wherein we investigate the brush in a cubic lattice, each lattice site representing the size of a polymer segment, but also the size of a single solvent molecule. Polymer conformations are described by freely jointed chains that are attached to the interface at one end. Details of this approach are readily available elsewhere.[33,35,36] Specific to this work is the modeling of the branches along the polymer backbone. side-chains are simply described as separate polymer chains that start from the known positions along the polymer backbone. The side-chains are thus treated in exactly the same way as the backbone; only their graft point is not found at the interface but is determined by the location of the branch point in the brush. As the branch point of a given side-chain will be spread through a portion of the brush, the side-chain conformation will be calculated from all these possible starting points. A detailed description of the treatment of the side-chains is given in recent work by Charlaganov et al.[37] For simplicity, we will always assume monodisperse polymer brushes, although we are well aware that polydispersity can have a large influence on the brush density profile.[38] Most calculations have been done using the distance from the interface (z) as the only relevant coordinate, although we have done calculations in multiple dimensions to allow for the possibility of structures being formed in other directions. No significant differences in the brush density profile were observed between calculations in one and in two gradients. However, the 2-gradient approach was specifically used to model the interaction of our branched polymer brush with a small object such as a protein being inserted into the polymer brush. A schematic depiction of this approach can be found in Figure 2. The approach has been used before to study the effect of grafting density[39] and polydispersity[40] on the antifouling properties of the brush. We now refer to the z-coordinate of the center of mass of the protein as the distance D of the protein to the surface. Systematic variation of D gives insight in the insertion free energy, which is computed by

$$\Delta F(D) = F^{(\mathrm{po})}(D) - F^{(\mathrm{po})}(\infty) \tag{2}$$

where the latter term is calculated for the case that the protein-like inclusion is far from the brush, that is for $D \rightarrow \infty$. The description (po) stands for the use of the partial open free energy. This approach gives insight into the amount of energy that is necessary to move the small particle from outside of the brush into the brush. The larger this energy barrier the better the antifouling properties of the brush are expected to be, at least for small particles.

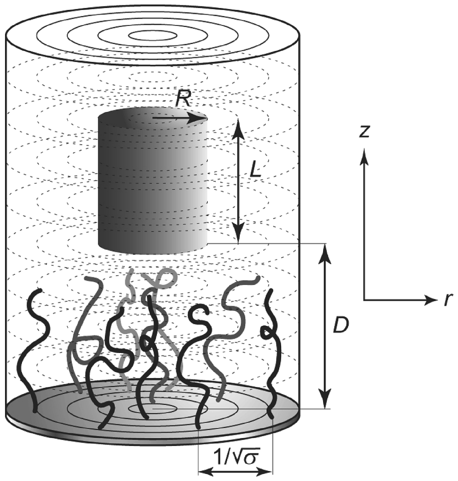


Figure 2. Schematic representation of the coordinate system used in the SF-SCF calculations. Here we show a small particle (top gray cylinder) with radius R and height L positioned at a distance D from the substrate. The two-gradient coordinate system (z,r) is indicated; layers parallel to the surface are numbered z = 1, 2, ..., M_z. In radial directions the lattice shells are numbered r = 1, 2, ..., M_r. At the surface, a polymer brush with grafting density σ is present. In the SCF model we assume that the brush chains are laterally mobile along the surface. To avoid adverse effects of the finite size of the computation box, the boundary condition in the radial direction is mirror-like. Polymers and particle have not been drawn to scale.

Box Model. Scaling laws, such as the famous Alexander and de Gennes scaling law, have always played a very important role in polymer brushes. It allows predictions on polymer brushes without knowing the exact chemical makeup of the brush under investigation. Here we will derive a simple scaling law for a brush made of comb-polymers. For this we use a so-called box model, meaning that we assume that all polymer backbones stretch in exactly the same way up to a certain height H, above the grafting interface. We follow a similar approach as Currie et al.[1,41] for a normal polymer brush but allow for changes because of the branching. We assume the backbone and side-chains to be distributed evenly throughout the brush, and thus there is a certain volume fraction of polymer (φ) and of solvent molecules (φ_s), the sum of which is always 1. The volume fraction of solvent molecules in the bulk (Φ_s) is naturally also equal to 1. The starting point for the box model is the free energy F^{total} *per chain* (in units of k_BT). The equilibrium state of the system follows from the minimum in the free energy. F^{total} is given by

$$F^{\text{total}} = F^{\text{elastic}} + F^{\text{osmotic}} \tag{3}$$

The first term in eq 3 gives the free energy of stretching of the polymer chains in the brush. Here we use the Gaussian chain model:

$$F^{\text{elastic}} = \frac{3}{2}\frac{H^2}{N_b} \tag{4}$$

The Gaussian model treats the polymer chain as a spring. Any deviation from the equilibrium state of the polymer leads to an increase in the free energy and thus to an elastic force counteracting the deviation. Note that we only take the stretching of the backbone into account for the free energy of stretching, thus assuming either that the side-chains are unstretched or that their stretching remains the same when the height of the brush changes. There are a number of good arguments for assuming that the side-chains have a very low stretching. The first is that is only favorable for a chain to be stretched when this reduces the polymer density. As in a comb polymer the side-chains are commonly shorter than the backbone polymer, it is difficult for the polymer to reach the edge of the brush were the lower polymer density is. Stretching of the backbone, however, reduces the polymer density for both the side-chain and the backbone at the same time. We therefore believe that it is much more favorable to stretch the backbone and leave the side-chains relatively unstretched. We will later show that this assumption is valid by testing it with the numerical SCF approach, in which no *a priori* assumption is made on stretching of the side-chains.

The second contribution to the free energy corresponds to the mixing of the solvent with the polymer in the brush. This is calculated by taking the entropy of a solvent molecule in the brush and subtracting the entropy of a solvent molecule in bulk solution:

$$F^{\text{elastic}} = \frac{H}{\sigma}[\varphi_{\text{s}} \ln \varphi_{s} - \varphi_{\text{s}} \ln \Phi_{\text{s}}] = \frac{H}{\sigma}\left[\varphi_{\text{s}} \ln \frac{\varphi_{\text{s}}}{\Phi_{\text{s}}}\right] \qquad (5)$$

Here, the mixing entropies are multiplied by a factor of H/σ, which gives the volume of the brush per chain. Mixing is entropically favorable; hence, the more mixed the solvent and the brush are the lower the free energy will be. The brush height is thus a result of an equilibrium between two opposing contributions to the free energy: one related to the elasticity of only the polymer backbone and the other related to the excluded volume stemming from the high concentration of both the side-chains and the backbone. These opposing contributions to the free energy will lead to a certain equilibrium height and polymer density of the brush. We can find this equilibrium by finding the minimum in the free energy. A simple scaling law is obtained if we assume low polymer densities ($\ln(\varphi\sigma) = \ln(1 - \varphi) \approx \varphi - \varphi^2$)), when we realize that φ is directly related to H ($\varphi = N_T\sigma/H$), and (to find the minimum in the free energy) when we take the derivative of the free energy equation with respect to the height to be zero:

$$\frac{\delta F^{\text{total}}}{\delta H} = \frac{\delta\left(\frac{3}{2}\frac{H}{N_{\text{b}}} + \frac{H}{\sigma}(\varphi - \varphi^2)\right)}{\delta H}$$

$$= \frac{\delta\left(\frac{3}{2}\frac{H}{N_{\text{b}}} + N_T + \frac{\sigma N_T^2}{H}\right)}{\delta H}$$

$$= 0 \rightarrow H \sim N_{\text{b}}\left(\frac{N_T}{N_{\text{b}}}\right)^{2/3}\sigma^{1/3} \qquad (6)$$

For a nonbranched polymer brush ($N_{\text{T}} = N_{\text{b}}$) we recover a basic version of the Alexander and de Gennes scaling law. With an increased amount of polymer in the branches ($N_{\text{T}} > N_{\text{b}}$), the height in the brush increases. We discuss this increased stretching effect in the results section. Our results are similar but not identical to the result of Zhulina,[30] who predicted a scaling law of $H \sim N_{\text{b}}\sigma^{1/3}\sigma_{\text{side}}{}^{-2/5}N_{\text{side}}{}^{3/5}$. Still, the result from Zhulina can actually be reasonably easily be rewritten as $H \sim N_{\text{b}}\sigma^{1/3}(N_{\text{T}}/N_{\text{b}})^{3/5}$. The remaining difference is thus a slightly different exponent; this difference can be traced back to the different theories that were used;[1] in Figure 5 both predictions are even shown together to show how small this difference is. Still, the prediction that only one parameter is enough to describe the effect of both the side-chain length and the side-chain density is quite an important result. Our scaling law predicts that it does not matter how the side-chains are distributed along the chain, just the amount of mass in the side-chains matters. This prediction will be tested using the nSCF theory, the results of which will be discussed in the Results and Discussion section. For a system of brushes made from dendrimers a very similar scaling law was recently suggested as a possibility by Polotsky et al.[42] If both scaling laws are confirmed, it could show how similar the behavior is between brushes that are branched in very different ways.

RESULTS AND DISCUSSION

Structure of a Comb-Polymer Brush. We focus our attention on using numerical self-consistent field theory to study the structure of a polymer brush that consists of end-grafted comb-polymers. The polymers in the brush thus consist of a backbone of a certain length (N_{b}), end-attached to the interface with a certain grafting density (σ), with side-chains attached of a certain length (N_{side}) every so many monomers (σ_{side}). A schematic depiction of the brush is shown in Figure 1. In Figure 3, we show the predicted brush density profiles for polymer brushes ($N_{\text{b}} = 100$, $\sigma = 0.1$) for varying the degrees of branching, but changed in two different ways. In Figure 3A we vary the length of the side-chains of the comb-polymers while keeping the number of side-chains ($N_{\text{b}}\sigma_{\text{side}} = 10$) fixed. In Figure 3B it is the number of side-chains that is varied while keeping the side-chain length ($N_{\text{side}} = 5$) fixed. The side-chains are always equally spaced along the backbone. A clear result in both figures is that an increase in branching leads to a higher brush density and the polymer in the brush stretching further away from the grafting interface, something also recently reported by Xu and Cao.[32] This is an expected result as longer branches and/or more branches add to the amount of polymer in the brush. For our brush of backbone $N_{\text{b}} = 100$, 10 side-chains of 10 monomers long doubles the amount of polymer in the brush. Clearly this leads to a higher polymer density in the brush and subsequent stronger stretching of the polymer chains. It is similar to increasing the grafting density of the brush, also something that increasing both the polymer density and the height of the brush.

For lower amounts of branching, the polymer brush retains the parabolic density profile that is characteristic for the unbranched monodisperse polymer brush. At higher amounts of branching the strong stretching of the backbones forces it to adjust to a more blocklike density profile. Additionally, small deviations in the density profile are seen closer to the grafting interface. The polymer density is slightly higher at certain positions. Because the backbone is so strongly stretched, the branch points are quite localized in the brush. At a branch point the polymer density is slightly higher because there is a slightly higher chance of finding the monomers from the side-chains at their grafting point. This effect was also observed by Carignano and Szleifer[23] when studying a brush from polymers with a single side-chain, with a small maximum in the density profile being related to the localization of the graft point. They found this effect to be strongest at high grafting densities when the chains were most

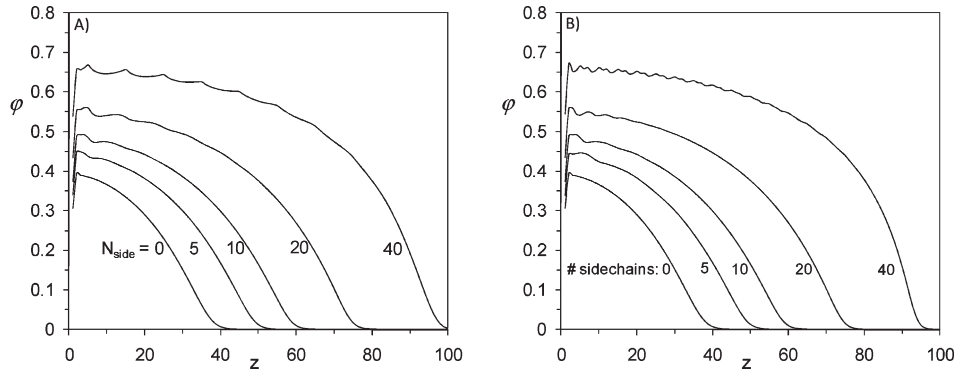


Figure 3. Brush density profile of brushes with different degrees of branching ($N_b = 100$, $\sigma = 0.1$). (A) Varying length of the side-chain as indicated ($N_b\sigma_{side} = 10$). (B) Varying number of side-chains as indicated ($N_{side} = 10$).

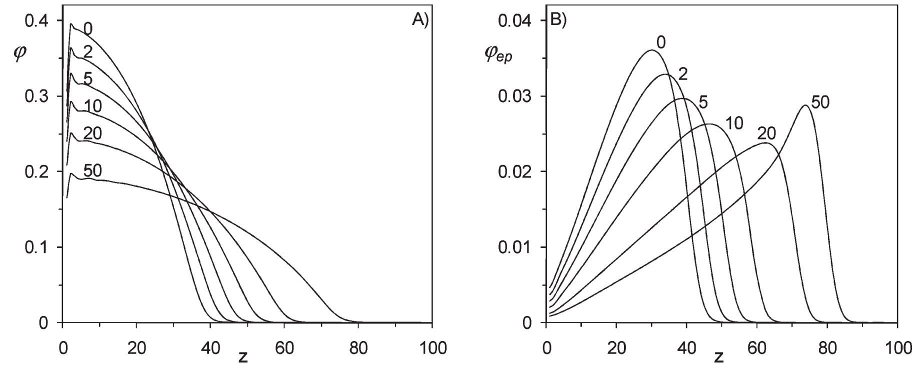


Figure 4. Density profile of brushes with different degrees of branching using conserved mass ($N_b = 100$, $N_T\sigma = 10$, $N_b\sigma_{side} = 10$). (A) Polymer density as shown for varying length of the side-chains as indicated. (B) Density profile of end-points of the polymer backbones. Varying length of the side-chain as indicated. End-point density was normalized to the grafting density of the unbranched brush for easier comparison.

strongly stretched. The effect is most pronounced in Figure 3A where there are 10 side-chains, as opposed to Figure 3B where there are up to 40 side-chains. When there are more graft points, the effect is naturally more spread out along the chain.

When we further compare the brush profiles depicted in Figure 3A,B, we find that they are nearly identical. The depicted graphs were specifically chosen so that equal numbers represent the same amount of mass in the side-chains. Our results indicate that the density profile only depends on the amount of monomers that are in the side-chains, not how the side-chains are distributed along the backbone. Only at the highest number of side-chains/side-chain length (40) do we see small differences when we compare both density profiles. For very long side-chains there is the possibility that the side-chains extend further away from the interface than the backbone; this leads to a small difference with many small side-chains that do not have this possibility. Additionally, there is the small effect of the polymer density being slightly higher exactly at the branch points, as was discussed before. We have tested the similarity for much more density profiles than shown here, also for more extreme cases such as many very short chains compared to just a few long ones. As long as the amount of mass in the side-chains is the same, the density profile will be almost identical.

A very useful outcome of this is that when discussing branched polymer brushes we can reduce the number of parameters that we need to take into account. Instead of discussing the comb polymer with a certain side-chain length and side-chain densities, we can simply reduce this to a ratio between the total polymer weight and the weight of the backbone: $N^* = N_T/N_b$. If $N^* = 1$, then the polymer is unbranched, while if N^* becomes larger an increasing part of the polymer will consist of side-chains. We will first investigate the structure of the branched brush in more detail before we discuss this observation further.

As discussed, we believe that is important to investigate the effect that branching has on the structure of the brush without the amount of polymer in the brush changing. We use the following approach to fix the amount of polymer in the brush. Whenever branching is changed by increasing the branch length or by adding more branches, the amount of grafted chains at the interface is reduced to conserve the total amount of monomers that form the brush. In this way every change in the brush density profiles will stem only from the change in polymer structure and not from the change in amount of polymer. Results for the density profile are shown in Figure 4A, where the amount of branching was changed by increasing the length of the side-chains. We have also done the same calculations, but changing the amount of side-chains while keeping the side-chain length fixed. The density profiles were found to be nearly identical, just as is shown in Figure 3A,B. For this reason we are not showing the results of those calculations.

From Figure 4A we get a very clear picture of the effect that the branched structure has on the polymer brush: the polymer density decreases as the branched polymers stretch further away from the interface. It is also important to note that the parabolic profile is retained in all cases. The increased stretching is a direct effect of the branching. In the branched brush it is more favorable

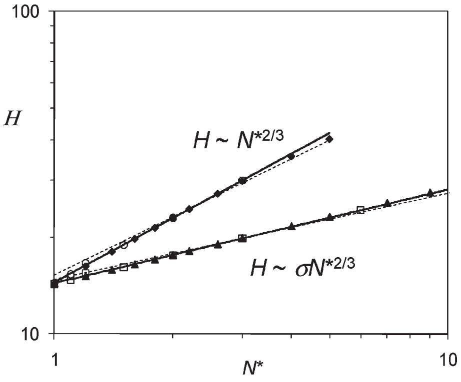


Figure 5. Average monomer height (H) of polymer brushes as depicted in Figures 3 and 4 as a function of the total amount of branching N^*. Top line for fixed grafting density (Figure 3) and bottom line for fixed mass (Figure 4). Closed points are calculated data for systems in which the side-chain length was changed; open symbols are data for the systems in which the number of side-chains was varied. Continuous lines are a fit to the scaling law $H \sim N_b \sigma^{1/3} N^{*2/3}$; dotted lines are a fit to the scaling law by Zhulina and Vilgis[30] (see text).

to stretch the backbone as this reduces the density not only for itself but also for the side-chains connected to it. In a sense the backbone stretches extra to reduce the stretching of the side-chains. As it is the backbone that determines the height of the brush, its increased stretching also leads the observed increase in height. That the side-chains have relatively little stretching would also provide an explanation for the observation that the density profiles only depend on the amount of polymer in the side-chains and not on how the side-chains are distributed along the backbone. If the side-chains are unstretched, then it indeed does not matter if it is many small chains or few long chains. The stretching of the side-chains will be investigated in more detail further on in this paper.

To get some more information on the structure of the branched brush, we plot the distribution of end-points of the backbone throughout the brush as a function of distance away from the interface (Figure 4B). These end-point distributions indicate quite clearly that the stretching is distributed throughout the brush. At a given time some polymers end-points will be close to the interface and the polymer will only be lightly stretched while other polymers have the end-points right at the end of the brush and will hence be stretched much stronger. The effect that branching has on the distribution of end-points is that with increased branching the end-point are distributed over a larger volume, as the height of the brush increases, but also the end-point localization becomes sharper at the end of the brush. The stronger stretching forces the polymers in the brush to behave more uniformly. These effects are very similar to the effects observed in the end-point distributions of polyelectrolyte brushes that are strongly stretched due to the Coulombic repulsion between the chains.[43]

In the Theory section, a box model was used to predict a scaling law for a brush made of comb-polymers. It predicts that the height of the brush depends on the properties of the comb-polymers in the brush: $N_b \sigma^{1/3} N^{*2/3}$. Our results were similar to those of Zhulina et al.[30] but simpler as only one parameter is used to describe the amount of branching of the comb-polymers. In Figure 5, the height of the brush is presented as a function of the amount of branching (on a log–log scale). As a definition of height we use the average height of the monomers that form the brush; this is a more useful definition than simply determining at which height the polymer density goes to zero and as polymer fluctuation taken into account in nSCF theory make that a quite arbitrary number.[36]

In Figure 5 it is clearly shown that our nSCF calculations come to the same scaling law as was discussed in the Theory section using the concept of the box model. In addition, it is again shown that only one parameter, N^*, is enough to describe the effect of branching in the polymer brush. It also strengthens our hypothesis that the side chains in the brush are not or only very little stretched as this was the main assumption made in the box model to come to this scaling law. The clear effect of branching on the brush height also provides a property that could be experimentally investigated. If one could make well-defined brushes of different levels of branching, one could use techniques such as neutron reflection, ellipsometry, or atomic force microscopy to investigate the height of the polymer brush.

Stretching of the Side-Chains. Above, we discussed the possibility that the side-chains are unstretched as a possible explanation why branched brushes are so much more stretched and why only one parameter is enough to describe the amount of branching in a polymer brush. In Figure 6A, we show a calculation to test our hypothesis. A density profile is presented specifically for the end points of the side-chains and for the graft points of the side-chains. For side-chains stretched in the z-direction, the density profile would have to be shifted to further away from the interface than the density profile of the grafting points. As can be clearly seen, the density profiles are almost overlapping, indicating that the grafting point and end-point of the side-chain are, on average, at the same height and thus that the side-chain is unstretched in the z-direction. In Figure 6B we investigate the stretching in the x–y-directions. Again we show the density profile for both the grafting point and the end point of the side-chain. We look at a single polymer in the brush, which has been grafted to the interface at position $x = 25$. As in Figure 6A, the two density profiles are nearly identical, indicating that the side-chains are unstretched. Thus, the side-chains are unstretched in both directions and thus behave as polymer coils. This explains the main observations made so-far: the increased stretching of the backbone and the dependence on the amount of materials in the side-chains and not on how it is distributed along the backbone. It also validates the assumptions made for the scaling law as discussed in the Theory section.

It is important here to do an additional check to validate the self-consistent field theory for comb-polymer brushes. In Figure 6 we show very clearly that the side-chains are not stretched due to the average excluded volume stemming from all the possible polymer conformations. However, for comb-polymers in solution it has been found that if the chains are grafted densely enough along a polymer backbone, the chains will stretch slightly away from the backbone to reduce polymer density directly surrounding the backbone.[19−22] This in turn makes the comb-polymer behave as a stiffer polymer since bending of the comb-polymer will increase the side-chain overlap. This stretching specifically due to the interaction between neighboring side-chains at high side-chain grafting densities is something that is not taken into account correctly in this nSCF theory. However, what we will show here is that this is only a problem if one would want to investigate a single comb-polymer. The stretching of side-chains due to overlap of neighboring side-chains is something that almost completely disappears inside of a dense polymer brush. A big difference between the side-chains in the

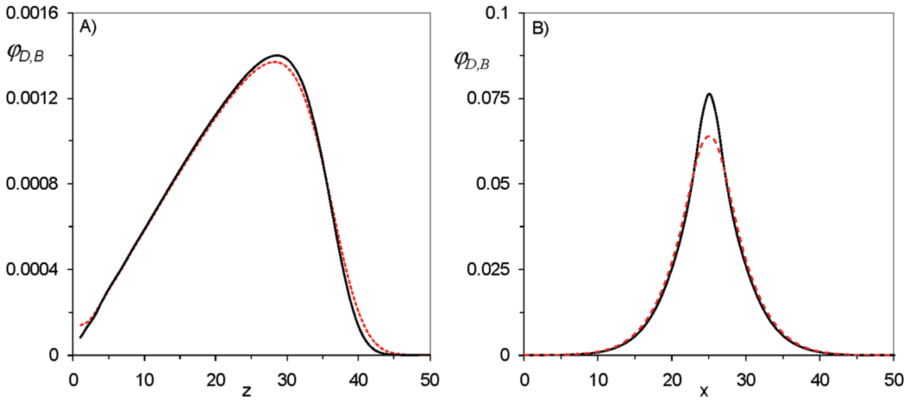


Figure 6. Density profile of the branch points (φ_B, continuous line) and the side-chain end-points (φ_D, dotted line) in a polymer brush (N_b = 100, σ =0.1, N_{side} = 10, σ_{side} = 10). (A) Profile in the z-direction. (B) Profile in the x/y-direction for a single polymer in the brush grafted at x = 25 (see text).

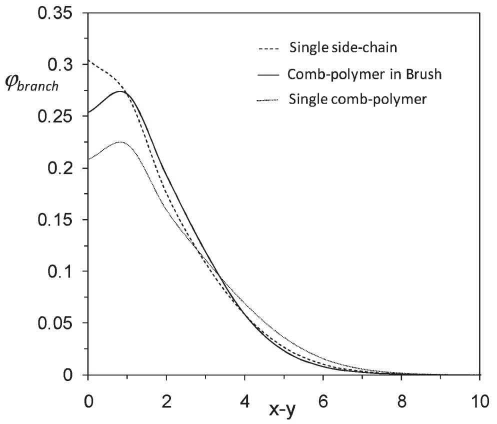


Figure 7. Polymer density of side-chains (N_{side} = 20, σ_{side} = 10, N_b = 100) as a function of distance from their branch points in the $x-y$ plane. Modeled with and without a polymer brush of identical chains (σ = 0.1) as indicated and compared to the behavior of a single side-chain. For the investigated comb-polymer only a single conformation is taken into account: the polymer is 50% stretched, and all branch-points are located exactly in the middle of a cylindrical coordinate system (see Figure 2).

polymer brush and in solution is that in solution the side-chains stretch to escape the high polymer density. In the brush they are immersed in a high polymer density layer and stretching to escape is far more difficult. This is also related to the observation that when a polymer brush is immersed in a solution containing other polymers that this will reduce the stretching of the brush with increasing polymer concentration.[44] If the stretching does not allow the polymer chains to reach a lower polymer density, then the polymer chains will not stretch. We can show this effect by not using our nSCF model to calculate all possible conformations of a branch-copolymer, but to limit ourselves to a single conformation. Results are shown in Figure 7.

In Figure 7, the single side-chain acts as our starting point as this polymer is unstretched and behaves as a simple Gaussian chain corrected for excluded volume. For the side-chains of the comb-polymer, however, the polymer density is lower close to the graft points and higher further away in solution; the side-chains are indeed more stretched. Still, for the comb-polymer inside the polymer brush this effect is only very small and is only observed directly at the graft site. Clearly, in a brush the side-chains of the comb-polymer behave much more like the unstretched free chain than like the more stretched side-chains of the single comb-polymer, and thus our previous conclusion that the side-chains have almost no stretching is completely valid. However, we have investigated this effect further for higher side-chain densities and longer side-chain lengths. Indeed, for very high chain densities (>1 side-chain per two monomers), in combination with longer chain lengths (N_{side} > 20), the differences become larger, and for that reason we have not included such high side-chain densities, in combination with longer side-chains, in our investigation.

When we now compare the results of our investigation into grafted comb-polymers and the results of investigations of comb-polymers in solution,[19−22] there are clear similarities. In both cases the backbone will be more strongly stretched than it would have been without the side-chains, as its stretching reduces the polymer density for the side-chains. A difference is that is in solution this effect stem from the side-chains along the backbone interacting with each other, while in a dense polymer brush this effect stems almost completely from the interaction of the side-chains with the other grafted polymers.

Antifouling Properties. The most important current application for polymer brushes is its use as an antifouling coating.[1,11] To test the effect that branching might have on the antifouling properties of the brush, we have calculated the energy necessary to push a small particle into a polymer brush for different degrees of branching. We do this by comparing the (partial open) free energy (see eq 4) for the particle outside the brush and the particle being inside the brush at a distance D from the grafting interface. The difference between the two free energies is the energy caused by the interaction between brush and particle. The higher this free energy of interaction, the better we expect the antifouling properties of the brush to be, since it will be harder for the particle to reach the interface. In Figure 8A, we show the energy of interaction as a function of distance away from the interface. As we can see, for the more branched brushes the energy increase further away from the interface but stays lower. This is in complete agreement with the density profiles as shown in Figure 3B; a more branched brush stretches further away from the interface and has a lower polymer density. It is the density of polymer that provides the brush with its antifouling properties; the denser the brush, the better it acts as a barrier. This indicates that the structure of the branched brush is less suitable than that of an unbranched brush when it comes to antifouling properties. Still, there are many systems where the grafting density of the

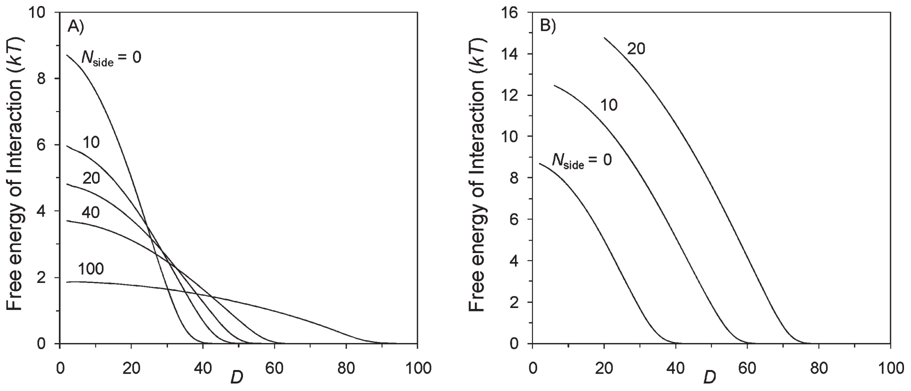


Figure 8. Free energy of interaction between a small particle (2 × 3) and a brush of various degrees of branching as a function of distance between particle and grafted interface. (A) Branching changed using conserved mass approach, $N_b = 100$, $N_T\sigma = 10$, number of side-chains = 10, various side-chain lengths as indicated. (B) Branching changed using conserved grafting density approach, $N_b = 100$, $\sigma = 0.1$, number of side-chains = 10 various side-chain lengths as indicated.

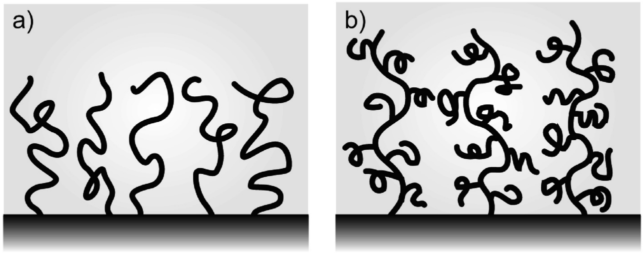


Figure 9. Schematic depiction of the main conclusions on the structure of the branched polymer compared to that of an unbranched polymer brush. A branched structure leads to increased stretching and thus a lower polymer density compared to an unbranched brush of equal mass. Side-chains are unstretched while the backbone is strongly stretched.

brush is limited, for example, because there are only limited grafting sites on an interface. In that case it might be a good idea to make a brush branched, not because of its structure but simply as a method to add more mass to the polymer brush. In Figure 8B, we show the energy of interaction between a small particle and the polymer brush for different degrees of branching while keeping the brush grafting density fixed. Indeed, we now see that the energy of interaction is always higher, indicating a better barrier for incoming fouling particles, for more branching. This is completely in line with the brush density profiles in Figure 2 showing that for all cases of increased branching at fixed grafting density leads to increases in the polymer density in the brush. So even though the branched structure does not help the brush act as a barrier for fouling particles, there can be systems in which the brush grafting density is limited and in which using a branched brush will improve its antifouling properties.

■ CONCLUSIONS

We have investigated the structure, properties, and antifouling effects of a polymer brush made from end-grafted comb-polymers using nSCF. Adding branches to the polymers in a brush makes the brush more stretched and increases the polymer density in the brush. Part of this effect is because of the addition of extra polymer to the brush; the other part stems from the branched structure. This can be shown by increasing the amount of branching and fixing the amount of polymer in the brush. In that case, branching still increases the amount of stretching but lowers the polymer density. For a branched polymer the stretched state is more favorable as stretching not only lowers the polymer density for the stretching polymer backbone but also for all connected side-chains. This effect is so strong that side-chains can be considered completely unstretched. A result of this is that it does not matter for the structure of the brush how the polymer is attached. For example, a brush of comb-polymers with a few long side-chains will give an almost identical brush density profile as a brush from comb-polymers with many small side-chains as long as the amount of mass in the side-chains is the same. A simple scaling law can be derived for a brush consisting of end-grafted comb-polymers using a simple box-model and was shown to be identical to one predicted with the nSCF theory. The height of the brush scales as follows: $H \sim \sigma^{1/3}N^{*2/3}N_b$. In Figure 9 we give a graphical conclusion on the effect that branching has on a polymer brush. The structure of the branched brush is less suitable for keeping away small particles for the grafted interface, but as the branching does increase the amount of polymer in the brush, it is a good way of increasing the polymer density when the grafting density of the brush is limited.

■ ACKNOWLEDGMENT

EPSRC, UK, is acknowledged for the funding of WdV through Grant EP/H014861.

■ REFERENCES

(1) Currie, E. P. K.; Norde, W.; Cohen Stuart, M. A. *Adv. Colloid Interface Sci.* **2003**, *100*−*102*, 205.
(2) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25*, 677.
(3) Birschtein, T. M.; Amoskov, V. M. *Polym. Sci., Ser. C* **2000**, *42*, 172.
(4) Milner, S. T. *Science* **1991**, *251*, 905.
(5) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühe, J. *Polymer Brushes*; Wiley-VCH: Weinheim, 2004.
(6) Tsujii, Y.; Ohno, K.; Yamamoto, S.; Goto, A.; Fukuda, T. *Adv. Polym. Sci.* **2006**, *197*, 1.
(7) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.
(8) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(9) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(10) Zhulina, E. B.; Priamitsyn, V. A.; Borisov, O. V. *Polym. Sci. USSR* **1989**, *31*, 205.

(11) Halperin, A.; Leckband, D. E. *C. R. Acad. Sci. Paris* **2000**, *Serie IV*, 1171.

(12) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1983.

(13) Klein, J.; Kumacheva, E.; Mahalu, D.; Perahla, D.; Fetters, L. J. *Nature* **1994**, *370*, 634.

(14) Cohen Stuart, M. A.; Huck, W. T. S.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. *Nature Mater.* **2010**, *9*, 101–113.

(15) Chen, T.; Ferris, R.; Zhang, J.; Ducker, R.; Zauscher, S. *Prog. Polym. Sci.* **2010**, *35*, 94–112.

(16) Draper, J.; Luzinov, I.; Minko, S.; Tokarev, I.; Stamm, M. *Langmuir* **2004**, *20*, 4064–4075.

(17) Motornov, M.; Minko, S.; Eichhorn, K.-J.; Nitschke, M.; Simon, F.; Stamm, M. *Langmuir* **2003**, *19*, 8077–8085.

(18) Houbenov, N.; Minko, S.; Stamm, M. *Macromolecules* **2003**, *36*, 5897–5901.

(19) Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2007**, *129*, 6633–6639.

(20) Zhang, M.; Müller, A. H. E. *J. Polym. Sci., Part A* **2005**, *43*, 3461–3481.

(21) Rathgeber, S.; Pakula, T.; Wilk, A.; Matyjaszewski, K.; Hyung-il, L.; Beers, K. L. *Polymer* **2006**, *47*, 7318–7327.

(22) Hsu, H.; Paul, W.; Rathgeber, S.; Binder, K. *Macromolecules* **2010**, *43*, 1592–1601.

(23) Carignano, M. A.; Szleifer, I. *Macromolecules* **1994**, *27*, 702–710.

(24) Romiszowski, P.; Sikorski, A. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 393–398.

(25) Irvine, D. J.; Mayes, A. M.; Griffith-Cima, L. *Macromolecules* **1996**, *29*, 6037–6042.

(26) Lee, H. J.; Nakayama, Y.; Matsuda, T. *Macromolecules* **1999**, *32*, 6989.

(27) Nakayama, Y.; Sudo, M.; Uchida, K.; Matsuda, T. *Langmuir* **2002**, *18*, 2601.

(28) Yu, W. H.; Kang, E. T.; Neoh, K. G. *Langmuir* **2005**, *21*, 450.

(29) Brzozowska, A. M.; de Keizer, A.; Detrembleur, C.; Cohen Stuart, M. A.; Norde, W. *Colloid Polym. Sci.* **2010**, *288*, 1621.

(30) Zhulina, E. B.; Vilgis, T. A. *Macromolecules* **1995**, *28*, 1008.

(31) Cui, S.-M.; Chen, Z. Y. *Phys. Rev. E* **1997**, *55*, 1660.

(32) Xu, X.; Cao, D. *J. Chem. Phys.* **2009**, *130*, 164901.

(33) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.

(34) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613.

(35) Roefs, S. P. F. M.; Scheutjens, J. M. H. M.; Leermakers, F. A. M. *Macromolecules* **1994**, *27*, 4810.

(36) Wijmans, C. M.; Scheutjens, J. M. H. M.; Zhulina, E. B. *Macromolecules* **1992**, *25*, 2657.

(37) Charlaganov, M.; Kosovan, P.; Leermakers, F. A. M. *Soft Matter* **2009**, *5*, 1448.

(38) De Vos, W. M.; Leermakers, F. A. M. *Polymer* **2009**, *50*, 305.

(39) Steels, B. M.; Koska, J.; Haynes, C. A. *J. Chromatogr., B* **2000**, *743*, 41.

(40) De Vos, W. M.; Leermakers, F. A. M.; de Keizer, A.; Kleijn, J. M.; Cohen Stuart, M. A. *Macromolecules* **2009**, *42*, 5881.

(41) Currie, E. P. K.; Leermakers, F. A. M.; Cohen Stuart, M. A.; Fleer, G. J. *Macromolecules* **1999**, *32*, 487.

(42) Polotsky, A. A.; Gillich, T.; Borisov, O. V.; Leermakers, F. A. M.; Textor, M.; Birshtein, T. M. *Macromolecules* **2010**, *43*, 9555–9566.

(43) Biesheuvel, P. M.; de Vos, W. M.; Amoskov, V. M. *Macromolecules* **2008**, *41*, 6254–6259.

(44) Wijmans, C. M.; Zhulina, E. B.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3238–3248.