

Scaling Theory of Planar Brushes Formed by Branched Polymers

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ABSTRACT: The equilibrium structure of planar brushes formed by flexible, regularly branched (comblike and starlike macromolecules), and randomly branched polymers is considered. The diagrams of states in τ, σ coordinates ($\tau = (T - \Theta)/T$ is reduced temperature and σ is grafting area per chain) are constructed, and power-law dependencies for the brush thickness H are obtained. It is shown that due to the existence of two different length scales characterizing comblike macromolecules, the scaling behavior of a “combed” brush is more varied than that of conventional brushes formed by linear chains. Weakly overlapping combs exhibit behavior similar to that of a conventional brush in a good solvent ($H \sim \sigma^{-1/3}$) even at the Θ -point. Strongly overlapping combs rearrange their local structure and recover the exponents for linear brushes in a good solvent ($H \sim \sigma^{-1/3}$) and Θ -solvent ($H \sim \sigma^{-1/2}$). For marginal solvents, intermediate between good and Θ -solvents, “combed” brushes exhibit a new exponent ($H \sim \sigma^{-5/13}$). Brushes formed by starlike and randomly branched polymers demonstrate conventional σ -dependencies similar to linear chains. However, the molecular-weight dependencies of the brush thickness H for randomly branched polymers are different.

Introduction

The behavior of polymer brushes and brushlike structures such as micelles, microsegregated block copolymer melts, and mesogels formed by linear polymer chains is well understood at present. Theoretical predictions are in reasonable agreement with experimental observations (see, for example, review 1). Further development of brush theory incorporates more complicated systems: brushes in complex environments,^{2,3} nematic⁴ and polymer solvents, etc.; charged brushes with simultaneous manifestation of the short-range nonelectrostatic and the long-range electrostatic interactions,^{5–9} etc. Another interesting opportunity is the consideration of macromolecules with complicated spatial architecture. Advances in chemical synthesis provide new trends to create polymer molecules with peculiar spatial structure, such as, for example, starburst¹⁰ or comb-burst¹¹ polymers. In certain stages of design of such molecules the concepts of brush theory seem to be applicable. In this paper we consider a planar polymer brush formed by flexible branched polymers. Such systems are of interest with respect to many practical applications—for example, the problems of colloid stabilization—and can serve as well as the starting point for the analysis of the structure of comb-burst and star-burst macromolecules. To our knowledge the analysis of grafted branched polymers is limited to the consideration of stars with three arms.¹² We start our consideration with regularly highly branched macromolecules (stars and combs) and finally consider randomly branched polymers grafted onto the surface. The main goal of our analysis is to outline the difference in the behavior of polymer brushes formed by linear and branched polymers. The paper is organized as follows: after describing the model, we construct scaling-type diagrams of state for the three different cases of

branched polymers (starlike, comblike, and randomly branched macromolecules). The last section summarizes the conclusions and their possible experimental verifications.

The Model

Consider a brush formed by long flexible starlike or comblike homopolymers grafted at one end onto an impermeable planar surface at a grafting density $1/\sigma$. Let $f \gg 1$ and $n \gg 1$ be the number of branches and the number of polymer units per branch in a star, so that $N = fn$ is its total degree of polymerization. For comblike polymers let $n \gg 1$ and $m \gg 1$ be the number of units in a side chain and in a segment of a main chain between two neighboring side chains, respectively (Figure 1). Both side chains and the main chain of a comb as well as the branches of the star are assumed to be flexible, so that the Kuhn segment is of the order of a unit size a . (A symmetrical chain element with its length equal to the chain thickness, a , is chosen as a unit.) We restrict ourselves to the consideration of regularly branched combs and stars with $n \gg m$ and $f \gg 1$, respectively. In the opposite case $n \ll m$ and $f \approx 1$, the behavior of the system is reduced to that of a brush of linear polymers. Let $K \gg 1$ be the number of units in the main chain of the comb. Then the total number N of units in the comblike molecule is given by $N = m(1 + n/m) \approx K(n/m)$. We assume that the brush is immersed in a solvent, the quality of which is determined by the value of the second virial coefficient of unit interaction. $\nu = a^3\tau$, where $\tau = (T - \Theta)/T$ is the reduced temperature (relative deviation from the Θ -temperature). In this paper we consider the conditions of a good or a Θ -solvent, which corresponds to $0 \leq \tau \leq 1$. The third virial coefficient of unit interactions $w \approx a^6$ is assumed to be independent of temperature. The third system which we consider in this paper is the brush formed by randomly branched homopolymers. Such macromolecules can branch at every point with a certain branching probability Λ which is independent of the total molecular weight N of the molecule and grafting

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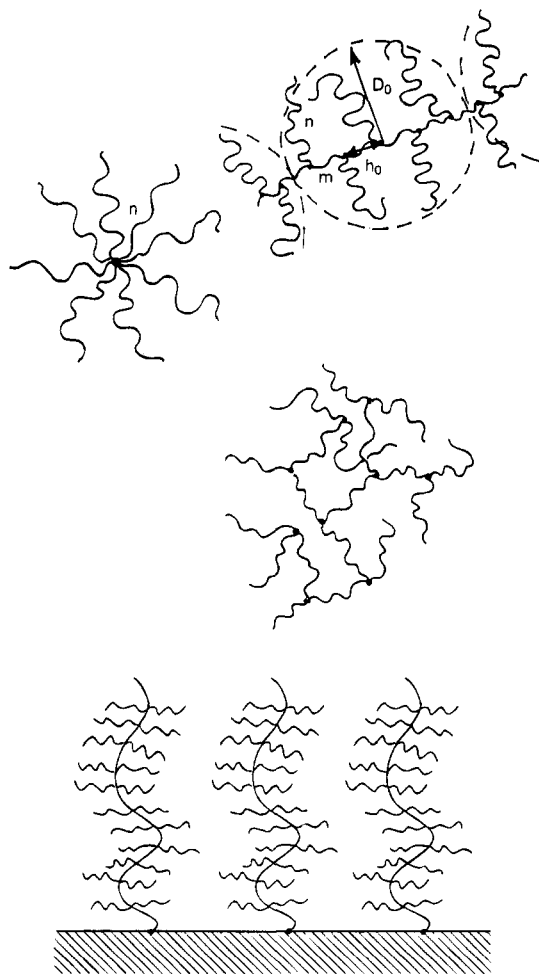


Figure 1. Schematic sketch of the systems under investigation.

density $1/\sigma$. The branching probability Λ determines the average number of units n between two neighboring branching points, $n \sim \Lambda^{-1}$. For $\Lambda \approx N^{-1}$ we come to the limit of linear chains, $n \approx N$, whereas $\Lambda \approx 1$ corresponds to the high-branching limit, i.e., $n \approx 1$.

Planar Brush of a Starlike Polymer

The scaling behavior of an isolated starlike macromolecule with a high number of branches $f \gg 1$ was considered by Daoud and Cotton¹³ and Birshtein and Zhulina.¹⁴ Based on the blob model, according to which a starlike macromolecule can be envisioned as a system for closely packed increasing blobs (spherical brush of flexible chains), the total size R_0 of the star was shown¹³ to scale as

$$R_0 \approx \begin{cases} a\tau^{1/5}f^{-2/5}N^{3/5} & \text{good solvent, } I_+ \\ aN^{1/2}f^{-1/4} & \Theta\text{-solvent, } I_\Theta \end{cases} \quad (1)$$

The same asymptotic can be obtained by the minimization of the free energy ΔF within the mean-field approximation,¹⁴

$$\Delta F = f \frac{R_0^2}{a^2 N} + \begin{cases} \tau \frac{N^2 a^3}{R_0^3} & \text{good solvent, } I_+ \\ a^6 \frac{N^3}{R_0^6} & \Theta\text{-solvent, } I_\Theta \end{cases} \quad (2)$$

where the first term in (2) accounts for the elastic stretching of all f branches of the star from their

Gaussian value $R_G^2 \approx a^2 n$ to the equilibrium size R_0 , whereas the second term incorporates pair or ternary contacts between units. Minimization of eq 2 with respect to R_0 gives the asymptotical dependencies.¹

I. Sparse Grafting, $\sigma \gg R_0^2$. Grafting of an individual star by its center onto the surface does not change the scaling asymptotics (1) and affects only the prefactor omitted in eq 1.

$$H \approx R_0 \quad (3)$$

Each grafted star retains its spherical symmetry in space above the surface and can be envisioned as one-half of the star with doubled number of branches $2f$.

II. Overlapping Stars, $\sigma \ll R_0^2$. Far below the overlapping threshold $\sigma \ll R_0^2$ the system loses its local spherical symmetry and grafted stars recover the behavior of a planar brush formed by linear chains of $n = N/f$ units grafted with the grafting density f/σ . Brush thickness H in this regime can be, thus, obtained from the minimization of the free energy (per molecule)

$$\Delta F \approx f \frac{H^2}{a^2 n} + fn \begin{cases} \tau \frac{fn a^2}{\sigma H} & \text{good solvent, } II_+ \\ a^6 \frac{(fn)^2}{(\sigma H)^2} & \Theta\text{-solvent, } II_\Theta \end{cases} \quad (4)$$

where the first term accounts for the elastic stretching of all f branches normal to the surface from their Gaussian size $R_G \approx a^2 n$ up to the brush thickness H , whereas the second term incorporates pair or ternary contacts between units. Minimization of (4) with respect to H provides the equilibrium brush thickness

$$H \approx \begin{cases} a\tau(\sigma/a^2)^{-1/3}Nf^{-2/3} & \text{good solvent, } II_+ \\ aN(\sigma/a^2)^{-1/2}f^{-1/2} & \Theta\text{-solvent, } II_\Theta \end{cases} \quad (5)$$

Smooth crossover of the dependencies (1) and (5) at $\sigma \approx R_0^2$ indicates that there is no other regime in the vicinity of the overlapping threshold. Thus the dependencies (5) determine the thickness of the grafted stars' layer in a wide range of grafting densities, $fa^2 \ll \sigma \ll R_0^2$. The upper limit of the grafting densities $\sigma \approx fa^2$ is determined from the condition of full stretching of the star branches,

$$H \approx an = a \frac{N}{f} \quad (6)$$

The range of $\sigma < fa^2$ thus cannot be realized.

The above results are summarized in the scaling-type diagram in Figure 2b. (For the sake of comparison, the similar diagram for the case of linear chains, $f = 1$, is presented in Figure 2a.) The boundaries between various regions can be obtained by equating the corresponding asymptotical dependencies for brush thickness H . As is seen from Figures 2a and 2b, the only difference between the behavior of linear and star polymers is the appearance of the new dependence of H on f (for linear chains $f = 1$); all other exponents which determine the dependence of H on N , σ , and τ are the same. This is not surprising since there is actually one length scale in both systems—the size R_0 of an individual molecule, and R_0 scales similarly for both linear and starlike molecules (except for the f -dependence).

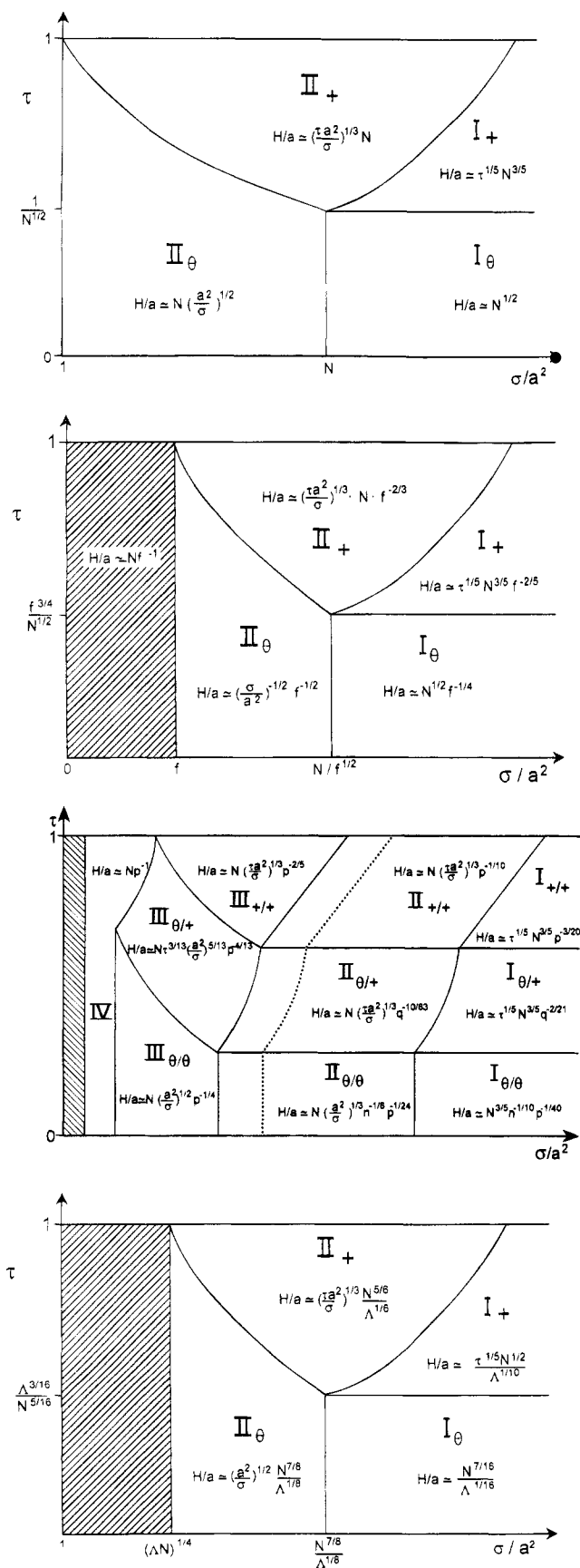


Figure 2. Phase diagrams of the different systems (see text).

For comblike polymers the situation is expected to be more complicated due to the existence of more than one (two) length scales: the total size R_0 and the characteristic scale D_0 of the local main chain structure.

Planar Brush of Comblike Polymers

The scaling behavior of an isolated comblike molecule in solution was considered by Birshtein et al.¹⁵ Here we summarize briefly the results of ref 15, which are relevant for our further analysis. As was shown in ref 15, the structure of an individual comblike macromolecule is characterized by two different length scales. On a local level a comblike molecule can be envisioned as a cylindrical brush, formed by side chains grafted onto the cylinder axis—the main chain. Both the side chains and the main chain are strongly stretched with respect to their Gaussian dimensions, and the thickness D_0 of this “bottle brush” is the characteristic length scale of the local structure. At length scales $\sim D_0$, the main chain can be considered as a rigid axis of the comb whereas at length scales much larger than D_0 , the comb molecule can be envisioned as a chain of symmetric impermeable elements of the size D_0 . Such a chain element (the so-called superblob) comprises D_0/h_0 side chains, where h_0 is the distance between neighboring side chains along the axis of the comb. Equilibrium parameters of the local comb structure, D_0 and h_0 , are determined by the balance of the elastic free energy of the main chain ΔF_m and the conformational free energy of the side chains ΔF_n . The latter accounts for both stretching and volume interactions in the cylindrical brush of side chains. Depending on the solvent quality (the value of τ), the main chain can be locally swollen by pair interactions (and, thus, exhibit Pincus elasticity,¹⁶ or be Gaussian). If h is the distance between two side chains, ΔF_m is given by

$$\Delta F_m \approx \begin{cases} \frac{h^{5/2}}{(a\tau^{1/5}m^{3/5})^{5/2}} & \tau \gg \frac{h}{m} \\ \frac{h^2}{a^2m} & \tau \ll \frac{h}{m} \end{cases} \quad (7a)$$

where the upper and the lower expressions correspond to a swollen or a Gaussian chain, respectively. Here and below, all numerical coefficients are omitted and all energy values are expressed in kT units.

For side chains, forming the cylindrical brush, we have^{17,18}

$$\Delta F_n \approx \begin{cases} n^{3/8} \tau^{1/8} (h/a)^{-5/8} & \tau \gg \left(\frac{h}{a}\right)^{-1/3} \\ n^{1/3} (h/a)^{-2/3} & \tau \ll \left(\frac{h}{a}\right)^{-1/3} \end{cases} \quad (7b)$$

where the upper and the lower expressions again correspond to a brush swollen in a good solvent or a Θ -solvent, respectively. At a given value of h , the thickness D of a cylindrical brush is given by¹⁷

$$D/a \approx \begin{cases} \tau^{1/4} n^{3/4} (h/a)^{-1/4} & \tau > \left(\frac{h}{a}\right)^{-1/3} \\ n^{2/3} (h/a)^{-1/3} & \tau < \left(\frac{h}{a}\right)^{-1/3} \end{cases} \quad (8)$$

Balancing ΔF_n and ΔF_m , one obtains the equilibrium parameters of the local comb structure, h_0 and D_0 , and $\Delta F_0 \approx \Delta F_n \approx \Delta F_m$ as summarized in Table 1. As is seen from Table 1, three different regimes (marked $+/+$, $+\Theta$, and Θ/Θ) are distinguishable. At high τ values, $\tau_1 < \tau$, where $\tau_1 \approx (1/m^{1/2})(n/m)^{3/20}$, both the main chain and the side chains are under the conditions of a good solvent (regime $+/+$). With decreasing $\tau_2 < \tau < \tau_1$, where $\tau_2 \approx (1/m^{1/2})(n/m)^{-3/8}$, the main chain loses its local swelling and starts to exhibit Gaussian elasticity, whereas the side chains are still locally swollen (regime $+\Theta$).

Table 1

τ	h_0/a	D_0/a	ΔF_0	L_0/D_0	
$\frac{1}{\sqrt{m}}\left(\frac{n}{m}\right)^{3/20} < \tau < 1$	$m^{3/5}\left(\frac{n}{m}\right)^{3/5} \tau^{5/5}$	$n^{3/5} \tau^{1/5} \left(\frac{n}{m}\right)^{3/25}$	$\left(\frac{n}{m}\right)^{3/10}$	$\left(\frac{n}{m}\right)^{9/10}$	+/+
$\frac{1}{m^{1/2}}\left(\frac{n}{m}\right)^{-3/8} < \tau < \frac{1}{m^{1/2}}\left(\frac{n}{m}\right)^{3/10}$	$m^{1/2}\left(\frac{n^{3/5} \tau^{1/2}}{m^{1/2}}\right)^{5/2}$	$n^{3/5} \tau^{1/5} \left(\frac{\tau^{1/5} n^{3/5}}{m^{1/2}}\right)^{4/21}$	$\left(\frac{\tau^{1/5} n^{3/5}}{m^{1/2}}\right)^{10/21}$	$\left(\frac{\tau^{1/5} n^{3/5}}{m^{1/2}}\right)^{10/7}$	+/Θ
$0 < \tau < \frac{1}{m^{1/2}}\left(\frac{n}{m}\right)^{-3/28}$	$m^{1/2}\left(\frac{n}{m}\right)^{1/8}$	$n^{1/2}\left(\frac{n}{m}\right)^{1/8}$	$\left(\frac{n}{m}\right)^{1/4}$	$\left(\frac{n}{m}\right)^{3/4}$	Θ/Θ

Finally, at low τ values, $\tau < \tau_2$, both the main chain and the side chains are under the conditions of a Θ -regime (Θ/Θ).

A recent analysis by Fredrickson¹⁹ demonstrated that a comblike chain has a certain rigidity induced by the interactions between the side chains: bending of the "bottle brush" leads to an increase in the free energy δF with respect to a purely straight conformation. The corresponding "persistence length" L of a comb molecule viewed as a wormlike chain is determined by the free energy change on bending per unit contour length as

$$\delta F \approx L/\rho^2$$

where ρ is the radius of curvature. On the other hand, at small relative curvatures $D_0/\rho \ll 1$, an increase in the free energy per unit length due to uniform bending of the "bottle brush" should scale as

$$\delta F \approx \frac{\Delta F_0 (D_0)^2}{h_0 \rho}$$

Thus, one obtains the following scaling law for the comb persistence length L_0

$$L_0 \approx \frac{\Delta F_0 D_0^2}{h_0} \quad (9)$$

The scaling expression for (L_0/D_0) in various ranges of τ are collected in Table 1. Under the conditions of a good solvent (regime +/+), eq 9 gives the same dependence for L_0 as obtained by Fredrickson.¹⁹

The scaling dependence for the overall size of an individual comb molecule R_0 coincides with that for a semiflexible chain of $N_D = (N/n)(h_0/D_0)$ impermeable superblobs of size D_0 with the persistence length L_0

$$R_0 \approx D_0 N_D^{3/5} \left(\frac{L_0}{D_0}\right)^{1/5} \quad (10)$$

and can be calculated using the results of Table 1.

I. Sparse Grafting, $\sigma \gg R_0^2$. Grafting of an individual comb at one end onto a surface does not change the scaling dependence (10) for the end-to-end distance of a comb molecule. Thus, for sparse brushes, when neighboring combs do not overlap, the brush thickness H scales as

$$H \approx R_0 \quad (11)$$

II. Weakly Overlapping Combs, $D_0^2 \ll \sigma \ll R_0^2$. With decreasing σ , neighboring macromolecules start to overlap and interact with each other. At $R_0^2 \gg \sigma \gg D_0^2$, this intermolecular interaction does not disturb the local comb structure, $D_0 = \text{const}(\sigma)$, and the brush thickness H can be obtained by the same scaling arguments as for ordinary linear chains.

Representing the brush thickness H in this regime as

$$H = R_0 \left(\frac{R_0^2}{\sigma}\right)^x \quad \sigma \ll R_0^2$$

one obtains the value of the exponent x from the evident consideration that intermolecular interactions should stretch the chains proportionally to their molecular weight, $H \sim N$. This gives the familiar exponent $x = 1/3$ and the expression for the brush thickness

$$H \approx R_0^{5/3} \sigma^{-1/3} \approx D_0 N_D \left(\frac{D_0^2}{\sigma}\right)^{1/3} \left(\frac{L_0}{D_0}\right)^{1/3} \quad (12)$$

where R_0 is given by eq 10 and Table 1. The interesting prediction following from eq 12 is that even under the conditions of a Θ -solvent (regime Θ/Θ), the brush thickness H scales as $H \sim \sigma^{-1/3}$, contrary to the situation in linear brushes, where $H \sim \sigma^{-1/2}$.²⁰ This is the direct consequence of a swelling behavior of an individual comblike molecule, which exhibits self-avoidance even under the conditions of a Θ -solvent, eq 10.

$$R_0 \sim a N^{3/5}$$

The origin of this effect is the local structure of a comb molecule: strongly stretched side chains provide the repulsion of superblobs and their impermeability even in Θ -solvents.

In both regime I (isolated comb) and regime II (weakly overlapping comb) the brush structure is similar to that of a brush formed by linear chains consisting of $N_D = (N h_0)/(n D_0)$ units of size D_0 with the effective virial coefficient of unit interactions $v_D \approx D_0^3$ and the persistence length L_0 . Variation of solvent quality (diminishing of τ) affects the brush structure only through the values of D_0 , L_0 , and $N_D = (N h_0)/(n D_0)$ (as follows from Table 1) and does not change the scaling dependence, eq 12.

As is known, the elasticity of a semiflexible chain ($L/a > 1$) is lower than that for a flexible chain ($L/a \approx 1$). Grafted onto the surface, semiflexible chains thus reach their maximal extension at the grafting densities $a^2/\sigma \approx a/L < 1$.²⁰ This effect is present for grafted combs as well. As follows from eq 12, the chain of superblobs approaches its maximal extension, $H \approx D_0 N_D$, at $D_0^2/\sigma \approx D_0/L_0 < 1$. Within scaling approximation, further increase in $1/\sigma$ does not lead to additional stretching of the grafted combs, since at $\sigma > D_0^2$ the repulsive interactions between superblobs are still weaker than the intralob interactions. Both contributions become of the same order of magnitude only at $\sigma \approx D_0^2$. Thus, in the range of $D_0^2 < \sigma < L_0 D$ one expects a plateau in the dependence $H = H(\sigma)$ and the brush thickness H scales here as

$$H \approx D_0 N_D \approx \frac{N}{n} h_0 \quad (13)$$

III. Strongly Overlapping Coils, $\sigma < D_0^2$. Further decrease in σ leads to the rearrangement of local chain structure. At $\sigma = D_0^2$ the brush can be envisioned as a melt of superblobs of size D_0 in which each chain forms totally stretched strings of superblobs normal to the surface. In lateral directions, however, each chain of superblobs exhibits Gaussian statistics. Decreasing $\sigma < D_0^2$ causes the diminishing of the superblob size $D < D_0$. A similar situation takes place in concentrated solutions of comblike macromolecules²¹ when the volume fraction of polymer in solution c exceeds that in an unperturbed superblob $c > c_0 = (na^3)/(D_0^2 h_0)$. At $c > c_0$ an increase in polymer concentration c in solution diminishes the stretching of both the main and side chains and leads to the decrease of the overall size of the comb molecule.²¹ In a polymer brush the situation is different. Under the conditions $\sigma < D_0^2$ the size of the superblob is determined by the grafting density

$$D \approx \sigma^{1/2} \quad (14)$$

The average concentration of units in a superblob coincides now with that in a brush and is given by

$$C \approx \frac{na^3}{hD^2} \approx \frac{na^3}{\sigma h} \approx \frac{Na^3}{\sigma H}$$

The latter expression provides the scaling dependence for the brush thickness H as

$$H \approx \frac{N}{n} h \quad (15)$$

where $h = h(\sigma)$ is now the unknown equilibrium distance between neighboring side chains. One can use the following arguments to determine h in regime III.

When a superblob is compressed by other chains so that its size $D < D_0$, the conformational free energy at a side chain ΔF_n increases. This increase in ΔF_n is due to the increase in the concentration part of ΔF_n . The second, stretching part of ΔF_n decreases, since superblob compression leads to the diminishing of side chain stretching. Thus at $D < D_0$, ΔF_n is determined mainly by volume interactions of a given side chain with the surrounding chains, providing the average concentration c of polymer units in the system. Using scaling expressions for the interaction free energy of a chain in a semidilute solution,²² one has

$$\Delta F_n \approx \begin{cases} n\tau^{3/4} c^{5/4} & c < \tau \\ nc^2 & c > \tau \end{cases} \quad (16)$$

where the upper and lower expressions correspond to the conditions of a good solvent or a Θ -solvent, respectively. Taking into account the interconnection between c and h in the brush, $c = (na^3)/(\sigma h)$, and balancing ΔF_n (eq 16) with the stretching free energy ΔF_m of the main chain, eq 7, one obtains the set of equilibrium values of h , corresponding to various τ ranges:

$$h/a \approx \begin{cases} \tau^{1/3} n^{3/5} m^{2/5} \left(\frac{\sigma}{a^2}\right)^{-1/3} & +/+ \\ \tau^{3/13} n^{9/13} m^{4/13} \left(\frac{\sigma}{a^2}\right)^{-5/13} & +/\theta \\ n^{3/4} m^{1/4} \left(\frac{\sigma}{a^2}\right)^{-1/2} & \theta/\theta \end{cases} \quad (17)$$

Substituting eqs 17 into eq 15, one obtains the brush

thickness H . The equations of boundaries between these three different regimes can be obtained by equating the corresponding expression for h (or H). Comparison of relationship 17 with those collected in Table 1 shows that for strongly overlapping combs ($\sigma < D_0^2$), stretching of the main chain increases with decreasing σ . This additional stretching permits a decrease of the average concentration c of units in the brush and a diminishing of the repulsive volume interactions. Whereas for weakly overlapping combs ($\sigma > D_0^2$, regime II), this diminishing of polymer concentration in the brush is attained by spatial rearrangement of superblobs at a fixed degree of stretching of the main chain, $h_0 = \text{const}(\sigma)$, for strongly overlapping combs ($\sigma < D_0^2$, regime III) additional stretching of the main chain is the only opportunity to increase H (eq 15) and diminish strong repulsion between side chains.

Finally, at small values of σ the main chain reaches its maximal stretching, $h/a = m$, and further decrease in σ leads to lateral compression of the side chains, without an increase in H (regime IV). Here, the brush thickness H coincides with the contour length of the totally stretched main chain,

$$H \approx aK \approx aN \frac{m}{n} \quad (18)$$

Diagram of States of the "Combed" Brush. Figure 2c presents the scaling-type diagram of the brush in τ, σ coordinates, summarizing the above results. It contains various regions indicated as described in the text: The first number (I, II, III, or IV) determines the range of σ -values, whereas the indices $+/+$, $+/ \theta$, and θ/ θ indicate the state of the main and side chains. For example, regime $\text{II}_{+/ \theta}$ corresponds to the conditions $D_0^2 < \sigma < R_0^2$ and the τ -range when the main chain is under Θ -conditions whereas side chains are under the conditions of a good solvent. We indicated also the scaling dependencies for the brush thickness H in all regimes of the diagram of Figure 2c. (The dimensionless parameters p and q are equal to $p = n/m$ and $q = \tau^{1/5} n^{3/5} / m^{1/2}$.) Equating the scaling expressions in two neighboring regimes, one obtains the equation of the corresponding boundary.

As is seen from Figure 2c, the diagram of states of a brush formed by comblike polymers demonstrates a variety of regimes with different values of exponents in the dependencies of brush thickness H on τ , N , σ , n , and m . Under the conditions of sparse grafting (regimes I in Figure 2c), the combed brush splits into separate coiled macromolecules similarly to the sparse brush of linear chains or starlike chains (regimes I in Figure 2). For such sparse brushes immersed in a good solvent, the exponents α_τ and α_N in the dependencies $H \sim \tau^{\alpha_\tau} N^{\alpha_N}$ are the same for both comblike and linear molecules: $\alpha_\tau = 1/5$; $\alpha_N = 3/5$. Under Θ -conditions, however, the difference is noticeable. Whereas linear chains and starlike polymers lose their swelling and become Gaussian, $\alpha_N = 1/2$, comblike molecules retain their swelling and conserve the value of exponent $\alpha_N = 3/5$. As was already mentioned, this is the result of the "bottle brush" local structure of a comb molecule. Volume interactions in the "bottle brush", formed by the side chains, are strong in the whole range of τ values $0 \leq \tau \leq 1$, due to the high local concentration of polymer units $c_0 = N/(D_0^2 h_0)$. Thus, the conformational free energy of a "bottle brush" element (superblob) is $\Delta F_D \approx \Delta F_0 - (D_0/h_0) \gg 1$ even in Θ -solvents. This provides impermeability of superblobs and the effective second virial

coefficient of their interaction $v_D \approx D_0^3$. A similar situation takes place in solutions of starlike macromolecules in Θ -solvents:²³ Swollen by ternary interactions, stars retain their impermeability both in dilute solutions and in the so-called quasi-globular regimes of semidilute solutions.

The impermeability of superblobs of comblike molecules in regimes I and II ($\sigma \gg D_0^2$) reduces actual comblike molecules consisting of N units into the equivalent chain of $N_D = (N/n)(h_0/D_0)$ symmetrical units with their own volume D_0^3 , where the values of D_0 and h_0 in various τ -ranges are collected in Table 1. Correspondingly, it is not surprising that in all brush regimes II ($0 \leq \tau \leq 1$) comblike macromolecules exhibit self-avoiding behavior, and brush thickness H scales here as $H \sim \sigma^{-1/3}$. Note that for a brush of linear chains or starlike polymers in a Θ -solvent, H scales as $H \sim \sigma^{-1/2}$ (regime II $_{\Theta}$ in Figure 2a,b).

Whereas overlapping of linear chains and starlike polymers ($\sigma < R_0^2$) leads to a single brush regime II, which lasts until maximal possible values of grafting density $1/\sigma \approx a^{-2}$ or $\sigma \approx f^2 a^2$ (see Figure 2a,b) comblike molecules exhibit two different brush regimes II and III, reflecting the existence of two different length scales of comb structure, R_0 and D_0 . At $\sigma > D_0^2$ (regimes II), the "bottle brush" local structure of a comb is insensitive to the value of σ (Table 1), whereas at $\sigma < D_0^2$ (regimes III), rearrangement of this local structure provides new features in brush behavior.

Within regimes II one can distinguish also subregimes in which the chains of the superblobs are totally stretched and the brush thickness H scales according to eq 13. Thus, here both D_0 and H are independent of σ . The right-side boundaries of these subregimes are shown by dotted lines in the diagram of Figure 2c.

Under the conditions of regimes III, one can envision the "combed" brush as a brush of main chains immersed in a semidilute solution of side chains with concentration $c = (Na^3)/(\sigma H)$. One can use additional simple arguments to obtain the scaling dependencies for H in these regimes. Due to the lateral homogeneity of the solution of side chains, each comb experiences now the repulsive potential from neighboring chains, which can be described as

$$\Delta F_{\text{conc}} \approx \begin{cases} N\tau^{3/4}c^{5/4} \approx \tau^{3/4}N^{9/4}(\sigma H/a^3)^{-5/4} & \tau > c \\ Nc^2 \approx N^3(\sigma H/a^3)^{-2} & \tau < c \end{cases} \quad (19)$$

where the upper and lower expressions correspond to the conditions of a good and a Θ -solvent, respectively. These repulsive volume interactions can be reduced by additional stretching of the main chains, whose elastic free energy is given by

$$\Delta F_{\text{el}} \approx \begin{cases} \frac{H^{5/2}}{(a\tau^{1/5}K^{3/5})^{5/2}} & \tau > \frac{H}{K} \\ \frac{H^2}{a^2K} & \tau < \frac{H}{K} \end{cases} \quad (20)$$

Balancing ΔF_{conc} and ΔF_{el} , one obtains scaling dependencies for H as indicated in regions III in the diagram of Figure 2c. One can check using these results that the main chains are so strongly stretched that their stretching blob ξ_s (which is the part of a chain that is not actually perturbed by stretching and retains the properties of an unstretched individual coil¹⁶) is always smaller than the concentration blob ξ_c ²² of the sur-

rounding solution. Thus, the elasticity of the main chains is not affected by the presence of the surrounding solution and eq 20 for the elasticity of an isolated coil is indeed applicable.

It is interesting to note that in regime III $_{++}$ and regime III $_{\Theta\Theta}$ the combed brush recovers the familiar exponents in the dependence $H \sim \sigma^{\alpha_\sigma}$: $\alpha_\sigma = -1/3$ and $\alpha_\sigma = -1/2$ in a good and Θ -solvent, respectively. In the intermediate range of solvent qualities (regime III $_{+\Theta}$), a new value of the exponent, $\alpha_\sigma = -5/13$, is predicted, which lies in between $-1/3$ and $-1/2$.

Regime IV of brush saturation is reached at very high grafting densities $1/\sigma$. Here the main chains are totally stretched, $H = aK$, and the concentration of polymer units in a saturated brush is given by

$$c = \frac{Na^2}{\sigma K} = \left(\frac{a^2}{\sigma}\right)\frac{n}{m} \quad (21)$$

At $\sigma/a^2 \approx n/m$ one obtains a melted brush: a densely packed system of rodlike main chains in a disordered melt of interpenetrating side chains. (The forbidden range of $\sigma/a^2 < n/m$ is shaded.)

Planar Brush of Randomly Branched Polymers

Following the above scheme for regularly branched polymers, we continue by considering an individual randomly branched macromolecule. It was shown by Zimm and Stockmayer²⁶ that the Gaussian dimensions R_G of a phantom randomly branched polymer consisting of N units scale as

$$R_G \approx a \left(\frac{N}{\Lambda}\right)^{1/4} \quad (22)$$

where Λ is the branching activity. In a weak-branching limit $\Lambda \approx 1/N$, eq 22 recovers the familiar result for a linear Gaussian chain ($R_G \approx aN^{1/2}$), whereas in a strong-branching limit $\Lambda \approx 1$, one has $R_G \approx aN^{1/4}$.

The self-similarity of randomly branched polymers provides certain restrictions on the deformation (stretching) of such macromolecules. Whereas for linear chains ($\Lambda \approx 1/N$) the maximal extension corresponds to the total contour length of the chain, $H^* \approx aN$, for strongly branched polymers ($\Lambda \approx 1$) the maximal possible extension H^* scales as $H^* \approx aN^{3/4}$.^{27,28} (Topological constraints do not allow further stretching of strongly branched polymers.) One can determine the limiting extension H^* at an arbitrary value of branching activity Λ using the following arguments. We assume that $H^*(\Lambda)$ can be represented in the scaling form as

$$H^*(\Lambda) = H^*(\Lambda = 1)\Lambda^x \approx aN^{3/4}\Lambda^x$$

Utilizing the evident condition $H^*(\Lambda = 1/N) = aN$, we obtain $x = -1/4$ and

$$H^*(\Lambda) \approx a \frac{N^{3/4}}{\Lambda^{1/4}} \quad (23)$$

The dimensions R_0 of the individual randomly branched macromolecules immersed in a good solvent or a Θ -solvent can be obtained along the usual lines of the Flory approach developed for linear chains, i.e., by the minimization of the free energy²⁹⁻³¹

$$\Delta F \approx \frac{R_0^2}{R_G^2} + \begin{cases} \tau \frac{N^2 a^3}{R_0^3} & \text{good solvent} \\ a^6 \frac{N^3}{R_0^6} & \theta\text{-solvent} \end{cases} \quad (24)$$

Note that the expression for the stretching entropy of randomly branched chains $\Delta F_{el} \approx R_0^2/R_G^2$ is, indeed, applicable due to the self-similarity of such molecules. (It breaks down for regularly branched star- and comblike polymers, as discussed in ref 14.)

Minimization of eqs 24 with respect to R_0 gives

$$R_0 \approx \begin{cases} a\tau^{1/5} N^{1/2} \Lambda^{-1/10} & \text{good solvent, } I_+ \\ aN^{7/16} \Lambda^{-1/16} & \Theta\text{-solvent, } I_\Theta \end{cases} \quad (25)$$

I. Sparse Grafting, $\sigma \gg R_0^2$. As before, grafting of an isolated randomly branched polymer onto an impermeable surface does not lead to the change of scaling asymptotics (25), and the brush thickness H scales in this regime as

$$H \approx R_0 \quad (26)$$

II. Overlapping Regime, $\sigma \ll R_0^2$. As for the starlike and comblike polymers considered above, one expects a change of the brush behavior below the overlapping threshold $\sigma \approx R_0^2$. Here the modification of eq 24 is necessary due to the fixation of the area σ per chain at $\sigma \ll R_0^2$

$$\Delta F \approx \frac{H^2}{R_G^2} + \begin{cases} \tau \frac{N^2 a^3}{\sigma H} & \text{good solvent, } II_+ \\ a^6 \frac{N^3}{(\sigma H)^2} & \Theta\text{-solvent, } II_\Theta \end{cases} \quad (27)$$

Minimization of ΔF with respect to H gives

$$H/a \approx \begin{cases} \tau^{1/3} (\sigma/a^2)^{-1/3} N^{5/6} \Lambda^{-1/6} & \text{good solvent, } II_+ \\ (\sigma/a^2)^{-1/2} N^{7/8} \Lambda^{-1/8} & \Theta\text{-solvent, } II_\Theta \end{cases} \quad (28)$$

Figure 2d presents the scaling-type diagram of such a brush, summarizing the above results. As is seen from Figure 2d, qualitatively the behavior of the brush formed by randomly branched polymers resembles that of a brush formed by starlike and linear polymers: in regimes II_+ and II_Θ the familiar values for the exponents are recovered, and the number of various regimes is actually the same, as for starlike polymers. The shaded region in the diagram of Figure 2d has the same origin as in Figure 2b and 2c: at the right boundary of this region, $\sigma/a^2 \approx (\Lambda N)^{1/4}$, the branched chains reach their maximal extension, $H \approx H^*$. This maximal extension is caused by strong volume interactions since at this boundary the average concentration of units in the brush tends to unity, $\varphi = (Na^3)/(\sigma H) \approx 1$. A similar situation takes place at the right boundaries of the shaded regions in the diagrams of Figures 2b and 2c.

Conclusions

In this paper we considered planar brushes formed by regularly branched (comblike and starlike) polymers as well as randomly branched polymers. We found that, within the primitive scaling approach used in this work, the most interesting predictions concern the behavior of the brush formed by regularly branched comblike polymers. One can try to create such brushes experimentally with the techniques used for the design of

linear brushes: i.e., grafting of end-functionalized combs to the surface, selective adsorption of block copolymers with nonadsorbing combed block, etc. Most probably, such designed brushes will be under the conditions of regimes II in the diagram of Figure 2c (sparse brushes, $\sigma \gg D_0^2$). As follows from the results of this work, contrary to all other brushes, "combed" brushes are expected to exhibit the dependence $H \sim \sigma^{-1/3}$ in a wide range of solvent strengths, including Θ -solvent. In an experimental situation, the value of σ can be varied by changing the energy of attraction of the anchoring block to the surface (by increasing its length). Thus it is, probably, possible to distinguish experimentally between the dependencies $H \sim \sigma^{-1/3}$ for combed brushes via $H \sim \sigma^{-1/2}$ for linear brushes expected in Θ -solvents.

Another possibility is to check the shape of the density profile. Though the details of the density distribution in a combed brush are beyond the scope of the scaling methods used in this paper, certain predictions about the density profile can be made. As is known, in planar brushes of linear chains immersed in a good solvent, the density profile is of parabolic shape.^{24,25} As was mentioned above, in sparse combed brushes (regimes II of the diagram of states, $0 \leq \tau \leq 1$) combed molecules can be regarded as linear chains of N_D units with the effective second virial coefficient $v_D \approx D_0^3$, i.e., as linear chains in a good solvent. Thus, a parabolic density profile in a combed brush is expected in a wide range of solvent strengths including the Θ -point. Variation of solvent quality (diminishing of τ) is expected to affect (increase) the average concentration of units in the brush but leave the parabolic shape of the profile unchanged.

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