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End-Tethered Chains in Polymeric Matrices

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I. Introduction

At high enough coverage polymer chains tethered by one end to a flat solid surface stretch away from the surface forming a polymer "brush". These brushes—which are of both practical and theoretical interest—have been the subject of intense study since the pioneering work of Alexander and de Gennes,[1,2] and several review articles on the subject are now available.[3-5] Most of the existing studies focus on brushes exposed to a low molecular weight solvent and less is known of the behavior of surface-tethered polymers in polymeric matrices.[6-11] The case where the grafted chains are in contact with a melt of shorter, chemically identical chains was studied theoretically by de Gennes some years ago[2] (see also the work of Leibler[12]) and more recently by Raphaël, Pincus, and Fredrickson[13] (hereafter referred to as RPF). In addition to a Flory-type approach based on a virial expansion for the entropy of mixing, RPF developed a blob analysis of the various existing regimes and introduced the concept of "cylindrical blobs". In this Note we would like to propose a slightly different scaling picture based entirely on spherical subunits. At sufficiently high grafting densities, the subunit diameter Λ is no longer proportional to the average distance between two grafting sites D. In particular, in the regime where the mobile chains are not present in the brush, Λ varies as $\Lambda \cong a(D/a)^2$, where a is the monomer size. Throughout this Note we assume a steplike concentration profile and impose that all the free ends be at the same distance from the surface. In all our formulas the exact prefactors remain undetermined.

II. Flory-Type Argument

Consider a brush made of chains, with degree of polymerization N, terminally grafted onto a flat surface and exposed to a polymeric solvent made of chemically identical chains, with degree of polymerization $P < N$. The number of terminally grafted chains per unit area is σa^{-2}, where a is the monomer size. The average distance between two grafting sites is given by $D = a\sigma^{-1/2}$. At sufficiently low σ, the grafted chains do not overlap (the so-called mushroom regime[2]) and the layer thickness L is given by $L \cong aN^{1/2}$ for $P > N^{1/2}$ and by $L \cong aN^{3/5}P^{-1/5}$ for $P < N^{1/2}$ (see regions 1 and 2 in Figure 1). As σ increases, the different chains begin to overlap for $D \cong L$. This defines an overlap concentration: $\sigma_{ov} \cong N^{-1}$ for $P > N^{1/2}$ and $\sigma_{ov} \cong N^{-6/5}P^{2/5}$ for $P < N^{1/2}$. In a Flory-type approach, the free energy per chain is then given by[2]

$$\frac{F}{kT} \cong \frac{L^2}{a^2N} + \frac{a^3}{P}\frac{N^2}{LD^2} \tag{1}$$

The first term in eq 1 represents the elastic contribution. The second term corresponds to the effect of the (screened) two-body interactions. From eq 1 one can easily construct the (P,σ) diagram represented in Figure 1.[2,11,13] In region 3 (i.e., in regions 3a and 3b), two-body interactions are relevant and the brush thickness is obtained by minimizing eq 1: $L \cong a\,NP^{-1/3}\sigma^{1/3}$. In region 4, repulsive interactions are not sufficient to swell the brush and the conformation of a grafted chain remains Gaussian: $L \cong aN^{1/2}$. At higher σ, we reach region 5 where the P chains are almost completely expelled from the brush: the brush is "dry". In this region the volume fraction of the grafted polymer is of order unity and $L \cong aN\sigma$. The boundaries between regions 3 and 4 and between regions 3 and 5 are given by $\sigma \cong PN^{-3/2}$ and $\sigma \cong P^{-1/2}$, respectively.

III. Scaling Analysis

We now try to build a scaling analysis for the moderate-coverage regime represented by region 3. Let us assume that the fundamental distance of the problem is D, the average distance between two grafting sites. A grafted chain may then be subdivided into spherical blobs of size D, each containing g_D monomers. Within one blob, the chain behaves like a free chain and can therefore be pictured as a self-avoiding walk of subunits called *melt blobs*.[13-14] This leads to the relation $D \cong ag_D^{3/5}P^{-1/5}$. Different blobs repel each other and the brush is essentially a closely packed system of blobs. The volume fraction ϕ of monomers belonging to grafted chains is given by $\phi \cong g_D(a/D)^3 \cong \sigma^{2/3}P^{1/3}$. Since, on the other hand, $\phi \cong Na\sigma/L$, we obtain for the equilibrium brush thickness

$$L \cong aNP^{-1/3}\sigma^{1/3} \tag{2}$$

Note that eq 2 can be rewritten as $L \cong (N/g_D)D$. This last result indicates that the chain can be viewed as a string of blobs almost fully stretched along the normal to the wall. The kT per blob ansatz leads to a free energy per chain $F/kT \cong NP^{-1/3}\sigma^{5/6}$.

When the grafting density increases, the blob size D progressively decreases up to a point where it is of the order of the melt blob size $l_c \cong aP$. The crossover occurs for $D \cong aP$, that is for a grafting density $\sigma^* \cong P^{-2}$ (this grafting density corresponds to the broken line of Figure

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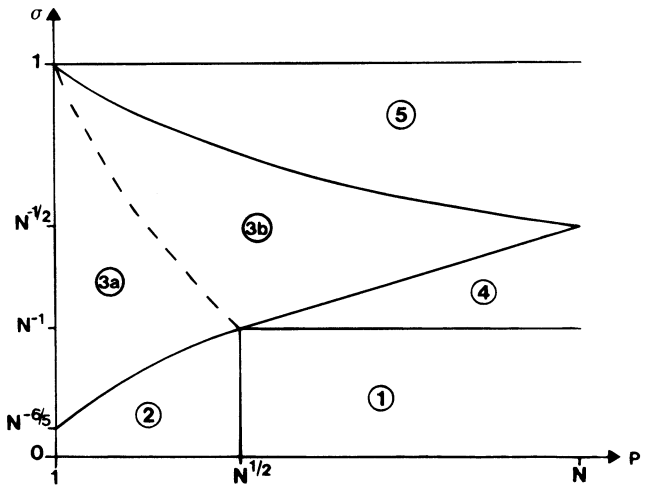

Figure 1. Schematic (P,σ) diagram for a brush exposed to a chemically identical high molecular weight solvent. The thickness of the layer in the different regions is given as follows: region 1, $L \cong aN^{1/2}$; region 2, $L \cong aN^{3/5}P^{-1/5}$; region 3, $L \cong aNP^{-1/3}\sigma^{1/3}$; region 4, $L \cong aN^{1/2}$; region 5, $L \cong aN\sigma$. According to the scaling analysis, region 3 is subdivided into regions 3a and 3b (see text).

1). Therefore, the blob picture developed above is only valid in region 3a of the (P,σ) diagram.

What happens in region 3b? By analogy with the blob picture developed for region 3a, one might consider describing the chain as a linear string of subunits of size D. Since D is now smaller than the melt blob size l_c, the chain behavior at a scale smaller than D is ideal ($g_D \cong (D/a)^2$ monomers per subunit). This picture leads to a brush thickness

$$L \cong (N/g_D)D \cong aN\sigma^{1/2} \tag{3}$$

This result is however in disagreement with the Flory prediction $L \cong aNP^{-1/3}\sigma^{1/3}$. In order to solve that problem, RPF introduced the concept of "cylindrical blobs".[15] We here propose another approach where one has to give up the idea that the subunit size is proportional to the average distance between two grafting sites D. Our picture is as follows (see Figure 2): (i) Each chain can be viewed as a string of nonoverlapping spherical subunits, of size Λ larger than D, almost fully stretched along the normal to the wall. (ii) At a scale smaller than Λ, the chain behaves like an ideal chain of $g_\Lambda \cong (\Lambda/a)^2$ monomers. It is important to notice that in a plane parallel to the wall, subunits of different chains do overlap and therefore the brush as a whole cannot be described as a closely packed system of subunits (see Figure 2). In order to calculate the subunit size Λ, we have to consider the perturbation parameter $\zeta \cong a^3P^{-1}g_\Lambda C$, where C is the average concentration of monomers belonging to grafted chains. Within a given subunit the total number of monomers (belonging to grafted chains) is given by $G_\Lambda \cong g_\Lambda(\Lambda/D)^2$, leading to $C \cong G_\Lambda/\Lambda^3 \cong \Lambda/(aD)^2$. At a scale larger than Λ, the chain ceases to be ideal. The subunit size Λ is therefore determined by the condition $\zeta \cong 1$. Thus

$$\Lambda \cong aP^{1/3}\sigma^{-1/3} \tag{4}$$

and

$$g_\Lambda \cong (\Lambda/a)^2 \cong P^{2/3}\sigma^{-2/3} \tag{5}$$

Since the different subunits of a grafted chain repel each other, the brush thickness is given by

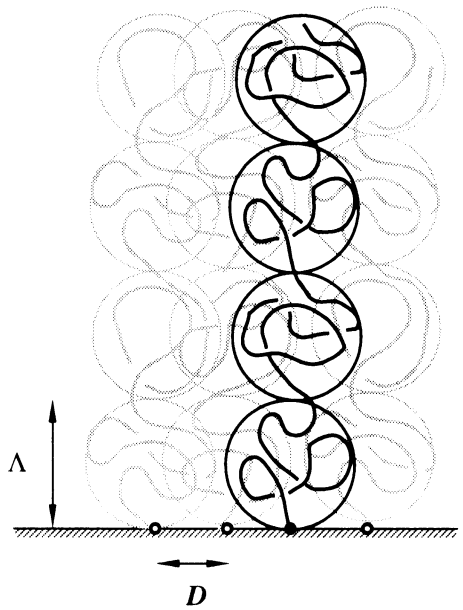

Figure 2. Schematic representation of a brush in region 3b. Each chain can be pictured as a string of nonoverlapping spherical subunits of size $\Lambda > D$, almost fully stretched along the normal to the wall. In a plane parallel to the wall, subunits of different chains overlap.

$$L \cong (N/g_\Lambda)\Lambda \cong aNP^{-1/3}\sigma^{1/3} \tag{6}$$

in agreement with the Flory result. The kT per subunit ansatz leads to a free energy per chain

$$\frac{F}{kT} \cong \frac{N}{g_\Lambda} \cong NP^{-2/3}\sigma^{2/3} \tag{7}$$

Note that eqs 6 and 7 are in accordance with the predictions of RFP. The present approach is more satisfactory from the physical point of view, however.[16]

We now consider what happens at larger grafting densities $\sigma > P^{-1/2}$ (region 5). In this regime the P chains are almost completely expelled from the brush and the thickness L is related to the grafting density σ by the requirement $\phi \cong Na\sigma/L \cong 1$. This leads to $L \cong aN\sigma$. The free energy per chain consists merely of an elastic term

$$\frac{F}{kT} \cong \frac{L^2}{a^2N} \cong N\sigma^2 \tag{8}$$

It is of some interest to build up a scaling picture for this high-coverage regime. As in region 3b, each chain can be viewed as a string of subunits of size Λ larger than D almost fully stretched along the normal to the wall; at a scale smaller than Λ, the chain behaves like an ideal chain (the corresponding number of monomers is given by $g_\Lambda \cong (\Lambda/a)^2$). Within a given subunit, there is on average a number $(\Lambda/D)^2$ of other chains. The subunit size Λ can be determined as follows. For $\sigma \cong P^{-1/2}$, Λ is given by $aP^{1/2}$ (see eq 4). Assuming the scaling form $\Lambda \cong aP^{1/2}(\sigma/P^{-1/2})^m$ and imposing the condition that Λ is independent of P, we find $m = -1$. This leads to

$$\Lambda \cong a(D/a)^2 \tag{9}$$

Note that the kT per subunit ansatz leads to a free

energy per chain $F/kT \cong N/g_\Lambda \cong N(a/D)^4$, in agreement with eq 8. The result (9) might be of some relevance in the study of the structures formed by diblock copolymers.[17]

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