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Notes

Brush Adsorption from Polydisperse Solutions

N. Dan

Department of Materials and Interfaces,
Weizmann Institute of Science, Rehovot 76100, Israel

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Polymeric brushes are composed of chains that are densely attached by one end to a solid surface.[1] They are often formed by adsorption from solution, i.e., by bringing a solution containing end functionalized chains into contact with an interacting surface. The adsorbing, functional end could be a reactive group,[2] or the immiscible block of a copolymer.[3,4] Applicability to colloidal stabilization, surface modification, and adhesion has led to extensive study of the structure and properties of polymer brushes,[1] as well as brush adsorption from a solution of monodisperse chains.[2-6]

Most polymerization processes yield a continuous distribution of chains, rather than a monodisperse product.[7] Even systems with a nominally low polydispersity index (commonly defined as the ratio between the weight and number average molecular weight) may contain some chains that are either much shorter or much longer than the average molecular weight. Recent experiments have shown that the presence of a small fraction of very short chains in a solution of longer chains prevents adsorption of the longer species.[8,9] The properties of such a brush, adsorbed from a solution containing equivalent molar fractions of two largely disparate chains, were calculated by Milner.[10] At equilibrium, the surface density ratio of the short and long chains was predicted to be high, proportional to the product of the chain molecular weight ratio and the end adsorption energy to the $^3/_2$ power.[10]

In this paper, a self-consistent field model[13,14] is used to investigate this effect of solution polydispersity on the adsorbed, equilibrium brush. We find that the composition of the brush, i.e., distribution of chain molecular weights, is comparable to that of the solution only when the end adsorbing energy is very small (of order kT, where k is the Boltzmann coefficient and T the temperature). Increasing the end adsorption energy leads to preferential adsorption of the shorter chains. In the limit of high end adsorption energy, all but the shortest species are excluded from the brush, irrespective of solution composition and the width of the molecular weight distribution. The adsorption process may be thus utilized, not only to tailor brush structure but also in distinguishing and separating chains of similar molecular weights.[8]

Consider a polydisperse solution of end-functionalized chains, containing J types, or species, of chains that differ only by their molecular weight. For simplicity we discuss dilute solutions in a good solvent, where the osmotic pressure is negligible. The solution free energy, per unit volume, is dominated by the translational entropy of the chains;[7,11,12]

$$F_s = \sum_{j=1}^{J} x_j \ln x_j \tag{1}$$

where x_j is the number of chains, per unit volume, of species j. The monomer concentration, ϕ_j, of chains of molecular weight N_j scales, therefore, as x_jN_j. All volume, area, and length scales are taken to be dimensionless throughout this paper, normalized, respectively, by the volume, area, and length of a monomer unit. Energies are given in units of kT.

The free energy (per unit area) of an end-adsorbed brush can be written as the sum of three contributions: the translational entropy of the chains on the surface, the adsorption energy of the functional chain ends, and the stretching energy of the chains

$$F_B = \sum_{j=1}^{J} \sigma_j \ln \sigma_j - \Delta\sigma_T + F_{st} \tag{2}$$

σ_j is the dimensionless surface density of species j, Δ is the adsorption energy, per end (in units of kT), and $\sigma_T \equiv \sum_j \sigma_j$ is the overall number of chains, per unit area.

F_{st} has been calculated, using a self-consistent field model, by Milner et al.[13] and Birshtein et al.[14] for an arbitrary surface density (σ_j) and molecular weight (N_j) distribution;

$$F_{st} = \frac{3}{5}\beta\{N_1\sigma_T^{5/3} + \sum_{j=1}^{J}(N_{j+1} - N_j)(\sigma_T - \sum_{i=1}^{j}\sigma_i)^{5/3}\} \tag{3}$$

where β is a constant of order 1.[15] We use the convention that $N_j > N_{j-1}$, so that N_1 is the molecular weight of the shortest chains. Equation 3 may be derived, in a simplified manner, by dividing the polydisperse brush into J regions; the first region, nearest to the surface, contains σ_T chains that are N_1 long. The free energy of such a brush scales,[13,14] in a good solvent, as $N_1\sigma_T^{5/3}$. On top of this brush there is another region, now containing $\sigma_T - \sigma_1$ chain sections of $N_2 - N_1$ molecular weight, whose energy scales as $(N_2 - N_1)(\sigma_T - \sigma_1)^{5/3}$. The energy of the following region, of $N_3 - N_2$ long sections at a density $\sigma_T - (\sigma_1 + \sigma_2)$, scales as $(N_3 - N_2)(\sigma_T - (\sigma_1 + \sigma_2))^{5/3}$. Thus F_{st} is constructed.

The overall free energy of a polydisperse solution, in equilibrium with an adsorbed brush, is

$$F_T = VF_s(x_j) + AF_B(\sigma_j,N_j) \tag{4}$$

where V is the volume of the solution and A is the surface area of the brush. In any finite system there exists a conservation requirement on the number of chains of each species j, i.e., $Vx_j + A\sigma_j$ = constant. Note that x_j is the concentration of unadsorbed chains, at equilibrium with the brush. However, in systems where $V/A \gg 1$, this concentration is similar to the solution concentration prior to adsorption.

The equilibrium brush structure, as a function of the solution composition, is determined by minimization of F_T with respect to each of the $\{\sigma_j\}$, under the conservation constraint. We find

$$-\Delta + [\ln \sigma_j - \ln x_j] + \beta\{N_1\sigma_T^{2/3} + \sum_{m=1}^{j-1}(N_{m+1} - N_m)(\sigma_T - \sum_{i=1}^{m}\sigma_i)^{2/3}\} = 0 \tag{5}$$

A self-consistent, exact solution requires a numerical

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procedure. However, an analytical solution is obtainable in the limit where the end adsorption energy is high, so that $|\ln \sigma_j| \ll (\Delta + \ln x_j)$;

$$\sigma_1 \approx \left\{\frac{\Delta + \ln x_1}{\beta N_1}\right\}^{3/2} - \left\{\frac{\ln[x_2/x_1]}{\beta(N_2 - N_1)}\right\}^{3/2} \tag{6a}$$

and, for $j \geq 2$,

$$\sigma_j \approx \left\{\frac{\ln[x_j/x_{j-1}]}{\beta(N_j - N_{j-1})}\right\}^{3/2} - \left\{\frac{\ln[x_{j+1}/x_j]}{\beta(N_{j+1} - N_j)}\right\}^{3/2} \tag{6b}$$

Because only σ_1 depends on the end adsorption energy, increasing Δ will increase only the surface density of the shortest chains; σ_j is much smaller than σ_1 unless $(N_j - N_1)/N_1 < \ln[x_j/x_1]/\Delta \ll 1$. The brush composition is thus dominated, in this limit, by the *shortest* species in the solution, irrespective of the molecular weight distribution.

If $x_j < x_{j-1}$, the expression in eq 6b is complex, and the surface density of species j is zero. A brush adsorbed from a solution where $x_j(N_j)$ is centered around an average molecular weight (single peak distribution) should not contain, therefore, chains longer than the average.

Polymer polydispersity may take various forms, of which we examine two representative cases: (i) a solution characterized by a Gaussian distribution, $x_j = x_0 \exp[\delta(N_j - \bar{N})^2]$, where $\bar{N}$ is the average molecular weight of chains in the system and δ is the distribution width, and (ii) the distribution obtained in condensation[7] polymerizations, $x(N_j) = x_0 q^{N_j}$, where q is the probability of reaction and $\bar{N} = 1/(1-q)$. The solutions contain only a fraction of the overall distribution, centered around the average chain molecular weight. Their polydispersity indices are, therefore, low.[16] In both distributions, x_j decreases with molecular weight when N_j is larger than $\bar{N}$, so that chains longer than the average molecular weight are not expected to adsorb in the limit of high end adsorption energy (eq 6).

As shown in Figure 1,[17] the distribution of chains in the adsorbed brush is similar to the distribution in solution only when the end adsorption energy is of the order kT. In this limit, the overall surface density is small, and the brush energy is dominated by the translational entropy term.[18] Hence, $\sigma_j \approx x_j \exp \Delta$. As the end adsorption energy increases, so does the energetic gain due to chain adsorption. Brush energy is dominated then by the stretching term, F_{st}, which decreases with the fraction of long chains. The longer chains are thus excluded from the adsorbed brush, irrespective of solution composition. As demonstrated in Figure 1C, the composition of a brush adsorbed from a Gaussian solution and the composition of a brush adsorbed from a condensation one are similar when $\Delta \gg 1$. In both systems the surface density of any species longer than $\bar{N}$ is negligible, in agreement with eq 6b.

Bimodal brushes are of special interest, as they offer unique ways of tailoring brush properties.[8,9,13,14,19,20] The composition of a brush adsorbed from a bimodal solution has been shown to bear little resemblance to the solution composition.[19] Moreover, the presence of a small fraction of shorter chains in the solution was found to inhibit the adsorption of the longer species.[8,9] It is therefore of interest to examine, in detail, the relationship between the composition of a two component solution and the adsorbed brush.

The bimodal brush is adsorbed from a solution containing x_1 and x_2 chains of N_1 and N_2 molecular weight, respectively. In the limit where $N_2 \gg N_1$, the surface densities of the short and long chains are given by

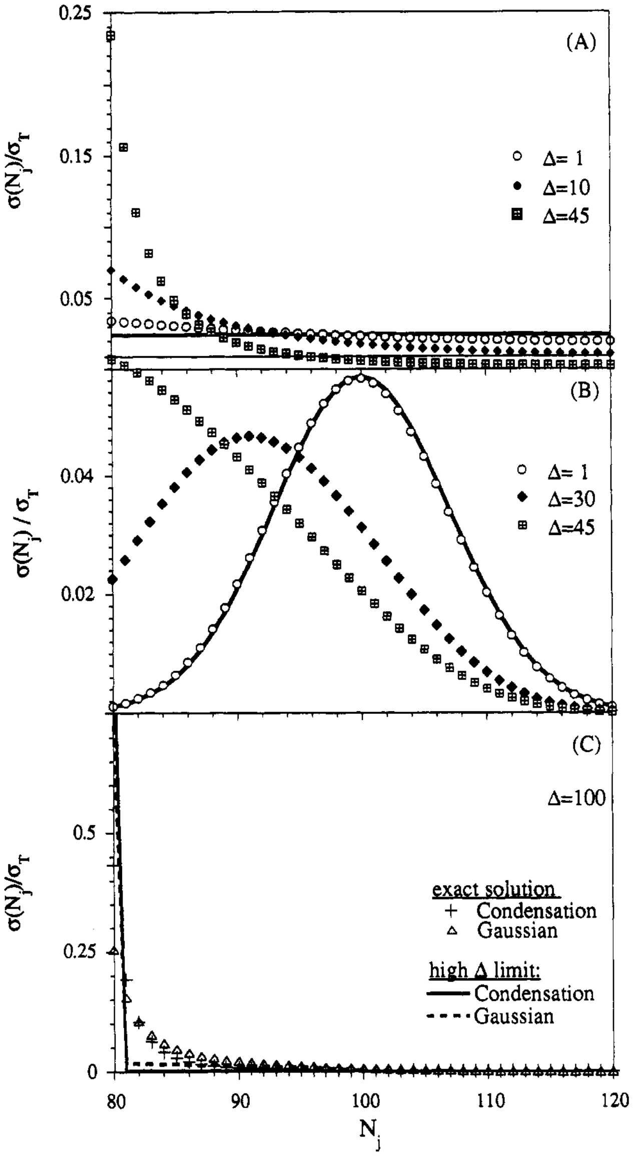

Figure 1. Surface density distribution, σ_j/σ_T, of a polydisperse brush adsorbed from condensation and Gaussian solutions. Both distributions are characterized by $N_1 = 80$, $N_J = 120$, and $\bar{N} = 100$. $x_0 = 10^{-5}$. The overlap surface density for $\bar{N}$ is $\sigma^* = 0.004$. (A) Brush adsorbed from a solution characterized by a fraction of a condensation distribution, where $q = 0.99$. The line denotes the solution composition, $x_j/\sum x_j$. For $\Delta = 1$, $\sigma = 0.7\sigma^*$; for $\Delta = 10$, $\sigma = 5\sigma^*$; and for $\Delta = 45$, $\sigma = 53\sigma^*$. (B) Brush adsorbed from a solution characterized by a fraction of a Gaussian distribution, where $\delta = 0.01$. The line denotes the solution composition, $x_j/\sum x_j$. For $\Delta = 1$, $\sigma = 0.07\sigma^*$; for $\Delta = 30$, $\sigma = 10\sigma^*$; and for $\Delta = 45$, $\sigma = 42\sigma^*$. (C) Comparing the exact (eq 5) and high Δ limit (eq 6) predictions, for $\Delta = 100$ and the solution distributions defined in (A) and (B). The surface density of the condensation brush is $199\sigma^*$ and, of the Gaussian, $170\sigma^*$.

$$\sigma_1 \approx \left(\frac{\Delta}{\beta N_1}\right)^{3/2}\left\{1 + \frac{1}{\Delta}\left(\ln x_1 + \frac{3}{2}\ln\frac{\beta N_1}{\Delta}\right)\right\}^{3/2} \tag{7a}$$

$$\sigma_2 \approx \left(\frac{1}{\beta N_2}\right)^{3/2}\left\{\ln\frac{x_2}{x_1} + \frac{3}{2}\ln\frac{\Delta N_2}{N_1}\right\}^{3/2} \tag{7b}$$

When the number of long and short chains in the solution is comparable, $\sigma_1/\sigma_2 \sim (N_2\Delta/N_1)^{3/2} \gg 1$, in agreement with Milner's analysis.[10] However, as σ_1 decreases with $\ln x_1$, the fraction of short chains in a brush adsorbed from an equimolar solution will decrease with overall chain concentration. The surface density of the longer chains, which increases with $\ln x_2/x_1$, may become comparable to

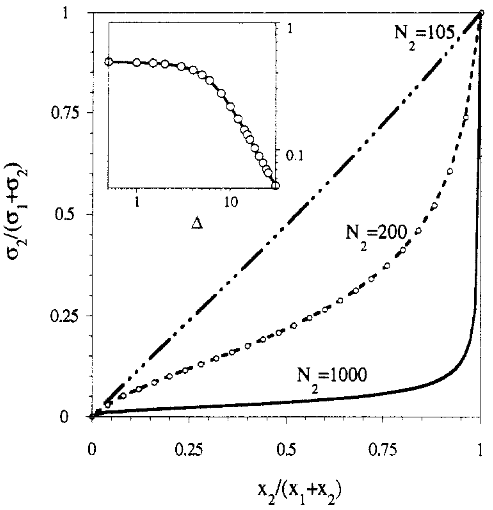

Figure 2. Composition of a two component (bimodal) brush, adsorbed from solution. Fraction of long chains in the brush, as a function of the fraction of long chains in solution. $N_1 = 100$, $\Delta = 10$, and $x_1 + x_2 = 10^{-5}$. The inset shows the fraction of long chains in the brush, $\sigma_2/(\sigma_1 + \sigma_2)$, as a function of the end adsorption energy. $N_1 = 100$, $N_2 = 200$, and $x_1 = x_2 = 5 \times 10^{-6}$.

that of the shorter species when $x_2 \sim x_1 \exp(\Delta N_2/N_1)$, despite the large difference in molecular weights.

When the molecular weights of the two chains are similar ($N_2 \sim N_1$), we find

$$\sigma_1 \approx \left(\frac{\Delta}{\beta N_1}\right)^{3/2} \frac{x_1/x_2}{(1 + x_1/x_2)}\left(1 + \frac{(N_2 - N_1)\Delta}{N_1(1 + x_1/x_2)^{2/3}}\right) \tag{8a}$$

$$\sigma_2 \approx \left(\frac{\Delta}{\beta N_1}\right)^{3/2} \frac{1}{(1 + x_1/x_2)} \tag{8b}$$

As may be expected, the ratio between σ_1 and σ_2 is roughly proportional to the ratio x_1/x_2. However, in the limit of high end adsorption energy, the small differences in species molecular weight are sufficient to induce enhanced adsorption of the shorter chains.

In Figure 2[17] the fraction of long chains in a bimodal brush, of moderate end adsorption energy, is plotted as a function of the solution composition. When the difference in molecular weights is small, brush composition is nearly identical to that of the solution (eq 8). As the molecular weight disparity increases, the surface density of longer chains in the brush decreases; $\sigma_2/(\sigma_1 + \sigma_2)$ is small, unless $x_2 \gg x_1$ (eq 7).

Above a threshold value, the fraction of long chains in the brush decreases sharply with the chain end adsorption energy (Figure 2 inset). Below this critical value, brush energy is dominated by the surface entropy term, so that brush composition is equal to the solution composition. Exclusion of longer chains from the brush begins with F_{st} is comparable to the surface entropy, thus defining the crossover value of the adsorption energy, Δ_c, by $\exp(2\Delta_c/3)/\Delta_c \approx \beta N_1 x_1^{2/3}$. For the system discussed in Figure 2, $\Delta_c \sim 8$.

Experiments have shown that the weight fraction of much *shorter* chains in a bimodal brush was negligible when their weight fraction in the solution was 100 times lower than that of the long chains.[8,9] In solutions where the ratio of long to short weight fraction was lower, the *longer* chains were excluded from the brush.[8] Our calculations agree, within experimental error, with these results: in the first case, we find that the brush contains about 80% weight fraction of long chains, while decreasing the weight fraction appreciably reduces the weight fraction of longer chains in the brush.[21]

In conclusion, we show that the composition of a brush adsorbed from a polydisperse solution is not proportional to the solution composition. The fraction of the shorter species is, as a rule, much higher in the brush than in the solution. Preferential adsorption of the short chains becomes more pronounced with increasing end adsorption energy.

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References and Notes

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(12) The reference state is that of solvated chains at infinite dilution. Therefore, the appropriate expression for the entropy of a chain[11] is $\ln x_j$, and not the Flory–Huggins[7,11] mixing entropy, $\ln x_j N_j$.
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(15) $\beta = 3/2(\pi^2/12)^{1/3} \approx 1.4$, as shown by Milner et al.[13]
(16) We assume that no chains shorter than $N_1 = 80$ or longer than $N_J = 120$ are present ($\bar{N} = 100$ for both distributions). The polydispersity indices are 1.01 for the condensation distribution and 1.005 for the Gaussian.
(17) The set of J equations (eq 5 for each species) were solved using a simple numerical procedure. Iterations were stopped when the value in eq 5, for every j, was less than $10^{-4}\Delta$.
(18) σ_{T} is smaller than the overlap value when Δ is of order kT, in both distributions (the condition for overlap of the shortest chains is that $\beta/\Delta < N_1^{-1/5}$). The form of F_{st} is no longer applicable. However, due to the dominance of the entropy term in this limit, the corrections to brush composition are expected to be minor.
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(21) Experiments were conducted on three solutions where $N_1 = 26$ and $N_2 = 375$: (i) $x_2 = x_0$, $x_1 = x_0 N_2/100 N_1$; (ii) $x_2 = x_0$, $x_1 = x_0 N_2/N_1$ (i.e., equal weight fractions); and (iii) $x_2 = 50 x_0$, $x_1 = x_0 N_2/N_1$. We use in our calculation $\Delta = 6kT$[8] and $x_0 = 10^{-4}$ and find for the three cases (i) $\sigma_2/(\sigma_1 + \sigma_2) = 0.19$, i.e., 80% weight of the long chains, (ii) $\sigma_2/(\sigma_1 + \sigma_2) = 0.01$, i.e., 12% weight of the long chains, and (iii) $\sigma_2/(\sigma_1 + \sigma_2) = 0.026$, i.e., 35% weight of the long chains.