Chemistry C3102-2006: Polymers Section

Dr. Edie Sevick, Research School of Chemistry, ANU

4.0 Polymers at interfaces

In this section, we begin to investigate the conformation at interfaces, including multiplechains at interfaces. A polymer brush is a system of polymer chains that are densely endtethered or end-grafted onto a surface. Such brushes are important in a number of applications, most notably surface modification and colloidal stabilisation. We will address planar brushes only; however brushes grafted onto curved surfaces are also very important. Examples include polymers grafted to the interior pores of membranes, the exterior surface of colloidal particles, hairy-rod polymers and molecular bottlebrushes.

The most fundamental and easily measured property of a polymer brush is its height. In colloidal stabilisation applications, the brush height determines the hydrodynamic radii of the brush-coated particles and increases the range of repulsive interactions between the particles, thereby reducing colloidal aggregation. In good solvent and where the surface is "inert", the brush height is determined by a balance of monomer-monomer repulsion (or osmotic pressure of the monomers), which favours large brush heights, and the entropic stretching of the chains, which favours small heights. The grafting density, σ , is the number of grafted chain ends per unit area substrate, given by

$$\sigma \equiv \frac{1}{(D/a)^2} \tag{1}$$

where D is the distance between grafting points in units of monomer size. The grafting density is an important parameter in determining the properties of a brush. If σ is too small,

then the chains are effectively isolated from one another and act independently of one another: there is no additional osmotic pressure causing the chains to stretch away from the surface, and the chains form isolated islands or "mushrooms". In the following section, we explore first, the "mushroom-regime", where the grafting is too small for brush formation and second, the "brush" regime of higher grafting densities

4.1 The "mushroom" regime of polymers endgrafted to a substrate

Consider chains that are end-grafted in a dilute manner on an inert surface, in a good solvent, figure 1. The size of an isolated chain in good solvent is given by the Flory radius:

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



Figure 1: Schematic of solvent-swollen chains end-grafted to an inert substrate with distance D between grafting points. The grafting distance is larger than the radius, $R_F \sim a N^{3/5}$ so that the chains are isolated from one another and form "mushrooms" on the surface

so that, if tethered dilutely, the size of a single-chained mushroom is also R_F . The critical grafting density, σ^* , that delineates the mushroom and brush regime occurs at a grafting density where the mushrooms are just touching each other, or when the grafting distance D is approximately R_F :

$$\sigma^* \equiv \frac{1}{(\frac{D}{a})^2} \sim \frac{a^2}{R_F^2} \sim N^{-6/5}$$

Thus, the longer the chains, the more dilute the surface tethering must be in order to remain in the mushroom regime. Alternatively, consider a substrate with a prescribed array of reactive tether sites, at which monomers are incorporated to form "growing polymers". At the early stages of polymerisation, when the number of monomers in each growing chain is small, the surface is spotted with isolated polymer mushrooms. But as the chains grow longer, each mushroom grows in size until they impinge upon one another and finally begin to form a polymer brush.

EXAMPLE PROBLEM

•• Using simple geometrical arguments, describe the profile of monomer concentration of end-tethered chains in the mushroom regime?

First, consider the boundaries of a mushroom as a shell of size R_F that circumscribes each isolated end-grafted chain. The volume fraction of monomers within the mushroom is approximately N/R_F^3 as there are N monomers per chain. Now consider a plane, parallel to the grafting surface, located an arbitrary distance z from the substrate. The concentration or volume fraction of monomers located in a plane at $z > R_F$ must vanish. However, the volume fraction of monomers in planes $z < R_F$ is non-zero as these planes must bisect the mushrooms. The z = a plane has a minimal, non-zero volume fraction of monomers that is roughly equal to the grafting density

$$\phi(z=a) = \sigma. \tag{2}$$

The plane of maximum volume fraction should be located roughly $z \sim R_F$ or at z of order R_F . The volume fraction at $z \sim (\mathcal{O})R_F$ can be simply estimated as the fraction of the plane that bisects mushrooms, or the area of the mushroom, πR_F^2 , times the number of mushrooms per grafting area, estimated by the grafting density:

$$\phi(z \sim R_F) \sim \frac{N}{R_F^3} \times R_F^2 \sigma.$$
(3)

This can be re-expressed in quantities of grafting density and number of monomers per chain to yield

$$\phi(z \sim R_F) \sim \sigma N^{2/5},\tag{4}$$

indicating that the maximum concentration depends upon the size of the chains that are grafted. Now these two estimates, $\phi(z = a) = \sigma$ and $\phi(z \sim R_F) = \sigma N^{2/5}$ describe the minimum and maximum concentrations in the profile. There is no reason to assume discontinuities in the profile, or a non-monotonic concentration profile. So we can fit these two values of ϕ to a profile of the form

$$\phi(z) \sim \sigma(z/a)^m. \tag{5}$$



z/a, dimensionless distance from substrate

Figure 2: Volume fraction of monomer, scaled with grafting density, ϕ/σ , versus scaled distance above grafting plane, z/a, for Flory chains end-grafted to an inert substrate in the mushroom regime. The concentration of monomers s simple ansatz is given in full line and is $\phi \sim \sigma (z/a)^{2/3}$ spanning $\phi \sim \sigma$ at z = a and $\phi \sim \sigma (R_F/a)^{2/3} = \sigma N^{2/5}$ at $z = R_F$. For $z > R_F$, the monomer concentration should fall smoothly to zero over a distance less than R_F . There should be no discontinuity in this profile or its slope - discontinuous slope is due to graphing program, to be fixed later. Problem based upon De Gennes, P.G., "Conformations of Polymers Attached to an Interface", *Macromolecules* **13**, 1069-1075 (1980).

Substituting the expressions for ϕ at z = a and $z \sim R_F$ provides m = 2/3. So that a first estimate of the concentration profile $a < z < R_F$ is $\phi(z) = \sigma(z/a)^{2/3}$. For $z > R_F$, the concentration of monomers falls away to zero.

4.2 The brush regime of polymers end-grafted to a substrate

A first-principles approach to polymer brushes is the Alexander-de Gennes ansatz: this brush description ignores the detailed structure of the brush and assumes that all the chain ends are located at the brush edge. A physical picture of the model, shown in figure 3, is based around "blobs", whose size is the grafting distance, D. Within the blob, or at lengthscales smaller than D, the monomers "feel" only those local monomers within the same chain. The monomers within a blob effectively feel as if they belong to an isolated chain in a good solvent and their monomermonomer correlations are dominated by excluded volume effects. Within the volume circumscribed by the blob of size D, there are g_D monomers related to the size of the blob by



Figure 3: Schematic of an Alexander-de Gennes solvated brush

$$D \sim a g_D^{3/5}$$

The blobs act as hard, impenetrable spheres that fill space; in this way, the blob construct qualitatively captures the interactions between monomers that are widely spaced along the contour, or that are on different chains, and that hardly ever come into close contact. The volume fraction of monomers in the body of the brush, D < z < L, expressed in terms of the grafting density is thus,

$$\phi \sim \frac{g_D}{D^3} \sim \sigma^{2/3}.\tag{6}$$

The height or thickness of the brush, L, is found by equating ϕ with the number of monomers in a chain contained in a column of area $(D/a)^2$ and height L/a,

$$\phi \sim \frac{Na^3}{D^2L},\tag{7}$$

or recasting with $\sigma^{-1/2} \equiv D/a$ and eqn 6,

$$L \sim a N \sigma^{1/3} \tag{8}$$

Thus, in the high grafting limit, the chains are effectively modelled by a series of hard-core blobs that, in general, extend in a direction normal to the grafting plane.

The "physics" of this end-grafting of chains on the surface is entirely summarised by understanding that, as the density of grafting increases, the lengthscale over which Flory correlations persist, diminishes. By "Flory correlations" we mean the correlations that exist between the positions of pairs of monomers. Consider two monomers, labelled i and i + a along the contour of a single chain. The distribution of monomer-monomer distances between these monomers will not differ appreciably in an isolated chain, and in a mushroom. Indeed, that is true for all values of 1 < a < N in both an isolated Flory chain and a solvated mushroom. One can think of the circumscribing sphere of radius R_F that we draw about the Flory chain and the mushroom as a "blob", a demarcation that says all monomers contained in the blob follow isolated-chain, SAW statistics. However, this is not the case in a brush: monomers separated along a chain contour by 1, 2, 3, . . . , up to *a* monomers may have unchanged monomer-monomer correlations; but those monomers separated by greater than *a* monomers will not follow isolated-chain, SAW statistics, simply by virtue of the excluded volume interactions with other monomers of other chains. Again, the blob is a fictitious demarcation of where the isolated-chain, SAW statistics fail. The crux of the Alexander & de Gennes model is the specification of how the blob size varies with grafting density. Recognising that the blob size is constant at R_F in the mushroom regime until $D = R_F$, they simply equated the blob size with D for brush grafting densities. That is:

$$R_F = \text{ blob size } \quad \text{for } \sigma < \sigma^*$$
$$R_F = \text{ blob size } = D \quad \text{for } \sigma = \sigma^*$$
$$\text{ blob size } = D \quad \text{for } \sigma > \sigma^*$$

The introduction of blobs is a useful but simplistic theoretical tool and it captures the essential physics of the problem. It is a way to simply describe the Flory correlations that persist at all chain lengthscales that persist in the mushroom regime, and below a critical lengthscale, D, in the brush regime.

EXAMPLE PROBLEM

•• Using simple geometrical arguments, describe the profile of monomer concentration of end-tethered chains in the brush regime from a < z < L?

The body of the brush has a volume fraction $\phi(D < z < L) \sim \sigma^{2/3}$, that is it is constant over z from D to L. The volume fraction will NOT be constant over the distance a < z < Dand to consider this part of the profile, we simply need to consider the brush of figure 3, where each grafted chain is "snipped" after the first blob. According to the model, uch a chop does not affect the chain conformations as the monomers within each blob are correlated only amongst themselves. This "haircut" results in a surface covered with isolated mushrooms that are just touching. From section 4.1, we found the profile of a mushroom regime varied from $\phi(z = a) = \sigma$ to a maximum ϕ of $\sigma N^{2/5}$. For the "haircut" case, the profile will be that of a mushroom: $\phi(z = a) = \sigma$ to a maximum ϕ of $\sigma g^{2/5} = \sigma^{2/3}$.



Figure 4: Volume fraction of monomer, scaled with grafting density, ϕ/σ , versus scaled distance above grafting plane, z/a for Flory chains end-grafted to an inert substrate in the brush regime.

In recent years a more popular approach, self-consistent field (SCF) theory, has been used to construct more detailed and more accurate predictions of brush structure than that possible with the Alexander-de Gennes ansatz. However, it is more complex to use. Moreover, although the simpler ansatz was first introduced and exploited for its intuitive description and theoretical simplicity, it is now possible to construct a true Alexander-deGennes brush. Many different formulations of an Alexander-deGennes brush is possible: the first such "model" brush used water-soluble polymers with graftable stickers at one end, that form the root of the brush, and lipid molecules at the other end that self-assemble into a flat membrane at the brush edge.