Decoration of Rough Surfaces by Chain Grafting

Recently a considerable experimental and theoretical effort has been devoted to the study of the adsorption of block copolymers and end-functionalized chains. Although a remarkable progress in understanding the conformation of grafted or adsorbed layers has been achieved, some important issues need still to be elucidated. For instance, Tassin et al. have investigated the kinetics of adsorption of polystyrene–poly(vinyl-*L*-pyridine) diblock copolymers on silver substrates and reported the existence of a nonhomogeneous adsorbed layer.[1] They conjectured that, at short times, copolymer micelles adsorb on a surface and create regions with a high polymer density. On the other hand, Johner and Joanny argued that for copolymers in a selective solvent (good for the nonadsorbing block B and poor for the adsorbing block A) the potential barrier for direct adsorption of micelles is extremely high and only nonassociated chains can adsorb to the wall.[2] Then the question arises as to how the surface coverage may be so inhomogeneous. A possible explanation could be the existence of "surface micelles" at equilibrium with copolymers in the solution. We have shown that this might be the case when the blocks A tend to wet only partially the surface.[3] Here, we propose a more "trivial" mechanism of nonhomogeneous adsorption that is related to the roughness of the surface. We argue that contrary to the adsorption of homopolymers, which tend to smooth the defects of the surface,[4] the terminal anchoring of chains or adsorption of asymmetric copolymers should amplify the effect of surface roughness and result in an important nonhomogeneous surface coverage.

Indeed, let us consider chains with polymerization index N terminally anchored to a flat surface or to a spherical or cylindrical defect (bump) on a surface (Figure 1). Clearly, for nonadsorbing chains, the constraint imposed by grafting on chain conformation is different: for the same surface coverage, σ, the chain deformation energy is lower in the spherical geometry than the energy in the cylindrical geometry, which in turn is lower than that in the planar geometry. These geometrical effects have been studied extensively in the context of star molecules,[5,6] copolymer micelles,[7] and grafted layers.[6,8-10] Here, we deal with grafting of chains by adsorption of the chain end group on a curved defect or a flat surface.

At equilibrium, the chemical potential of chains in the solution in contact with the surface, μ_{ext}, is equal to the chemical potential of adsorbed chains $\mu_d(\sigma)$ (with d = 1–3 corresponding to the adsorption on a flat surface, a cylindrical defect, and a spherical defect, respectively). There are three main contributions to the chemical potential $\mu_d(\sigma)$:

$$\mu_{\text{ext}} = \mu_d(\sigma) = kT\{-\Delta + \ln \sigma + f_d(\sigma)\} \tag{1}$$

The first term is the free energy gain when a terminal end group is fixed to a surface. The second contribution comes from the translational entropy of chains in the adsorbed layer. The last term, $f_d(\sigma)$, represents the average chain deformation and excluded-volume energy different from that of a free chain in the solution because of constraints imposed by grafting.[11] The competition between the energy gained by anchoring the end groups and the entropic penalty (stretching and concentrating) when the grafting is dense governs the equilibrium grafting density, σ_d, in each geometry.

The geometrical effects will be particularly important when the curvature radius of the defect, ρ, is small. We use a simple blob picture introduced by Daoud and Cotton[5] for star molecules, which is particularly adapted to treat such an asymmetric situation. When grafted chains overlap, they stretch, but contrary to the flat case for spherical and cylindrical geometries, the correlation length, $\xi_d(\bar{r})$, and thus the blob size vary in space. We assume the spherical and cylindrical symmetry for the concentration profile in the d = 3 and d = 2 cases, respectively. Hence, grafted chains form radial branches, each branch consisting of a succession of nonoverlapping blobs that are self-avoiding portions of the chain (Figure 1). Since $\xi_d(\bar{r})$ may be viewed as a distance between adjacent chains on the flat, cylindrical, and spherical surface, we can write with the help of elementary geometry[8,12]

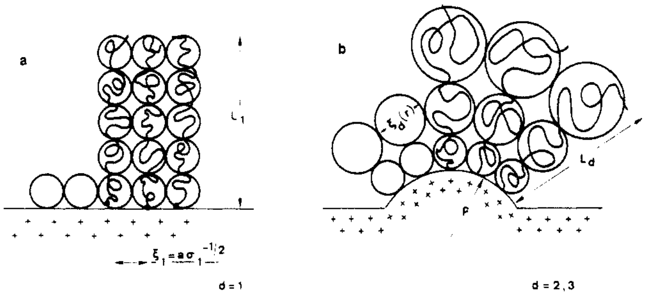

Figure 1. Blob model for a grafted layer (a) on a flat surface and (b) on a (cylindrical or spherical) defect of curvature radius, ρ.

$$\xi_d(r) \simeq a\sigma_d^{-1/2}(r/\rho)^{(d-1)/2} \tag{2}$$

where a denotes the statistical segment length and r is the radial distance from the center, or the axis of the defect (for d = 3 and d = 2 cases, respectively). In the case of the flat surface, r is just the distance from the surface and ξ is a constant independent of r, which depends only on the grafting density σ_1.

The extension of the grafted layer, L_d, can be evaluated directly from blob construction. Indeed, the number of monomers per chain is obtained by summing the number of monomers in blobs

$$N = \int_\rho^{\rho+L_d} g_d(r)\frac{\mathrm{d}r}{\xi_d(r)} \tag{3}$$

with

$$g_d(r) = [\xi_d(r)/a]^D \tag{4}$$

being the number of monomers in a blob and $D \simeq 5/3$ being the fractal dimension of the excluded-volume chains. For the interesting case of strong geometrical effects, i.e., for very extended grafted layers for which $L/\rho \gg 1$, we get from eqs 2–4

$$L_d \simeq \alpha_d^{-\alpha_d}\left(\frac{Na}{\rho}\sigma^{(D-1)/2}\right)^{\alpha_d} \tag{5}$$

where the characteristic exponent equals

$$\alpha_d = \frac{2}{2 + (D-1)(d-1)} \tag{6}$$

For a flat surface $\alpha_d = 1$, which means that the chains are strongly stretched. For cylindrical and spherical defects, the grafted chains behave more like nonconstrained chains as $\alpha_2 \simeq 3/4$ and $\alpha_3 \simeq 3/5$, respectively.

These geometrical effects manifest themselves also in the free energy per chain, which can be obtained simply by the blob-counting argument since an energy of

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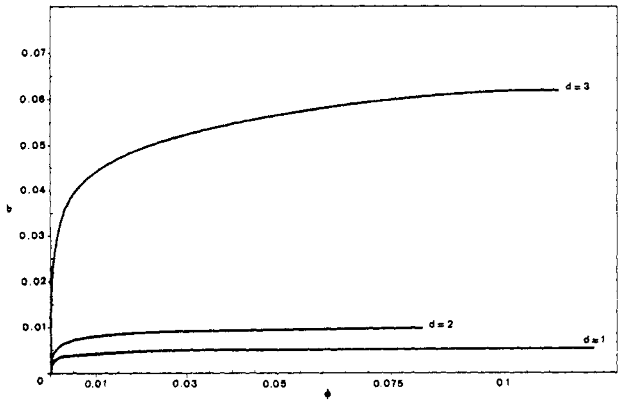

Figure 2. Dependence of adsorption isotherm surface coverage (σ) on the volume fraction of chains in solution (ϕ_0) for three different geometries. Polymerization index $N = 1000$; $\Delta = 10$ kT; $a = 5$ Å; $\rho = 100$ Å.

approximately kT is assigned per blob:

$$f_d = kT\int_{\rho}^{\rho+L_d}\frac{\mathrm{d}r}{\xi_d(r)} \tag{7}$$

For extended grafted layers with $L \gg \rho$, eqs 2 and 5–7 lead to

$$f_1/kT \simeq N\sigma_1^{5/6} = (R_f^{\,2}/\Sigma_1)^{5/6} \tag{8a}$$

$$f_2/kT \simeq 2\,(4/3)^{3/4}(R_F\rho/\Sigma_2)^{5/8} \tag{8b}$$

$$f_3/kT \simeq \left(\frac{\rho^2}{\Sigma_3}\right)^{1/2}\ln\left\{\left(\frac{5}{3}\right)^{3/5}\frac{R_F}{\rho}\left(\frac{\rho^2}{\Sigma_3}\right)^{1/5}\right\} \tag{8c}$$

where we use experimentally accessible quantities, the chain end-to-end distance $R_F = aN^{3/5}$ and $\Sigma_i = a^2\sigma_i^{-1}$ (i = 1–3), the surface area per chain.

Adsorption isotherms can now be calculated from eqs 1 and 8. When the bulk solution is dilute and end-functionalized chains do not form micelles $\mu_{\text{ext}} \simeq \ln\phi$, where ϕ is the monomer concentration in the solution. In Figure 2 we show the variation of the surface coverage on a flat surface (d = 1), a cylindrical defect (d = 2), and a spherical defect (d = 3) for typical molecular parameters $N = 1000$, $a = 5$ Å, $\Delta = 10$, and $\rho = 100$ Å. We note that the effect of preferential adsorption on spherical bumps may be quite important and should be much less pronounced for cylindrical defects for which chains are still strongly constrained in one direction even when ρ is small.

It should be remarked that the blob model does not give precise estimates of prefactors in the free energy of constrained chains. Still, the blob model usually predicts a correct order of magnitude and correct scaling laws and we expect that it describes well the essential features of grafting on rough surfaces, namely the prediction that chains will preferentially graft on spherical bumps with high curvature (ρ small). This effect is illustrated on Figure 3 where the value at the adsorption plateau is plotted as a function of the radius of the defect. Indeed, there is a crossover value of the radius ρ_c above which the surface coverage σ_1* on the flat portion of the surface is essentially equal to σ_2* and σ_3*, the surface coverage on defects. For a given solution concentration ϕ the crossover value, ρ_c, is obtained by requiring $f_1(\sigma_1^*) = f_2(\sigma_2^*) = f_3(\sigma_3^*)$, which leads to the condition:

$$\rho < \rho_c \simeq L_1^* = N\sigma_1^{*1/3} \tag{9}$$

Hence, we find that the grafting density will be enhanced on bumps with the radius of curvature ρ smaller than the thickness of the grafted layer on flat portions of the surface.

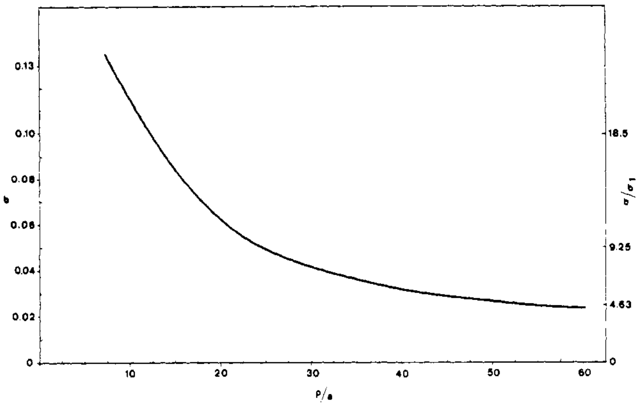

Figure 3. Dependence of the plateau surface coverage on the curvature radius for a spherical bump defect ($N = 1000$; $\Delta = 10$ kT; $a = 5$ Å; $\phi_0 = 0.1$).

The condition (9) ensures also that, for bumps with $\rho < \rho_c$, the thicknesses L_2 and L_3 are much bigger than ρ and that calculations of layer thickness and deformation energy by the blob-counting argument are consistent. The situation for adsorption by one end is thus very different from that of the standard adsorption when any monomer can adsorb in which no such effect is expected. We also want to stress that "bumps" and "hollows" have a very different effect on grafting density. Indeed, although for hollows the grafting density should be decreased with respect to a flat surface, the decrease will be very small as there is no reason why chains should adopt a symmetry of the defect for the concentration profile in the case when this causes an energy penalty. The chain conformation for chains grafted onto a hollow should be essentially the same as that for chains grafted on a flat surface.

Eventually, we note that kinetics of the process favors the nonhomogeneous grafting. In fact, in a recent paper, we have shown that, in late stages, the grafting kinetics is controlled by an activation barrier since adsorption requires penetration through a grafted layer.[13] The barrier is essentially of the order of magnitude of the chain deformation energy. This implies that chains will adsorb much faster on defects than on flat portions of the surface.

We note that roughness effects should not be important for modification of liquid surfaces for which the curvature of the defects is of the order of capillary length and thus much too high. On the other hand, the curvature effects described here may play an important role also for equilibrium grafting on small spheres or liquid droplets or on fibers. For small radiuses of curvature, the adsorption plateau will be much higher than for large objects. These effects may be of interest for suspension or emulsion copolymerization processes.

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