5806 *Macromolecules* **1993,** *26,* 5806–5808

Grafted Polymers in Poor Solvents: Shear-Induced Shrinkage

D. R. M. Williams

Laboratoire de la Matière, Condensée,† *Collège de France, 75231 Paris Cedex 05, France*

Received June 1, 1993
Revised Manuscript Received July 19, 1993

The grafting of polymer chains to surfaces has been much studied in recent years, both theoretically and experimentally and by simulation.[1–7] Grafting provides a method of studying polymer deformation and has applications in colloidal stabilization and the prediction of block copolymer microphases. Experimentally the conformations of grafted chains can be studied by use of neutron scattering and by the surface force apparatus.

Densely grafted polymers in *good* solvents swell and stretch away from the surface. This occurs because of excluded-volume interactions between monomers. At the equilibrium level of swelling these interactions are balanced by chain stretching, which favors less extended chains. Here we are interested in grafted chains in *poor* solvents.[8–13] Most of the static properties of undistorted brushes are now fairly well understood. The same cannot be said for distortions of a brush and for dynamical properties. One of the most interesting distortional properties of brushes in good solvents was described recently by Klein *et al.*[14] They inferred experimentally that a polymer brush in a good solvent subjected to a shear flow tends not only to tilt but also to swell normal to the grafting surface.[15] A "blob" picture for such sheared brushes was developed by Rabin and Alexander.[16] This blob picture was reanalyzed by Barrat,[17] who used the same free energy[16] and obtained a swelling under shear. The physics is as follows. Under shear, the blob number is determined by the shear strength and the number of blobs increases. These blobs repel each other like hard spheres, and the brush swells in the direction normal to the surface to relieve the osmotic pressure. The theory is able to reproduce the main result of the experiments. Independent of such experiments, swelling is, in itself, an interesting effect.[18]

Here we are interested in a similar system—the shearing of a polymer brush in a *poor* solvent. The stretching deformation of a brush in a poor solvent was first analyzed by Halperin and Zhulina, and following them we use a blob model.[9,10,19,20] The blobs are groups of monomers of radius 1 correlation length and attempt to be close-packed to minimize their surface energy.[21,22] Throughout the analysis we use the Alexander–de Gennes ansatz, that the chain ends are located at the brush surface,[23–25] and we ignore all numerical coefficients.

It is useful to compare this system with the good solvent brush. The blobs in a good solvent repel each other with an energy of kT per blob. Shearing increases the number of blobs and hence can induce swelling, which lowers the blob concentration. This swelling is however limited to about 25% of the original height.[17] In a poor solvent the blobs no longer repel but attract. Relative to the pure solvent each blob has a surface tension $\sim kT/\xi^2$. The blobs thus attempt to be close-packed, and there is no driving force for swelling. It is this close-packed behavior which causes brush shrinkage. At high shear the blob size is determined by the shear force, the blobs get smaller, and the brush height $H = Na^2\xi/d^2$ decreases. As we shall see, unlike the case of a good solvent brush, this change in height can be very large.

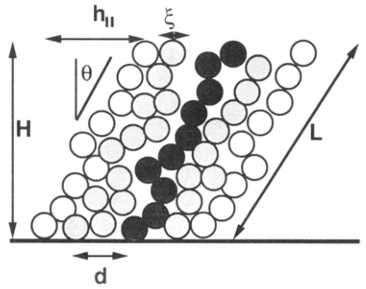

Figure 1. Geometry of the brush under shear. Here we show case i where the blob size, ξ, is smaller than the grafting distance, d. Each blob contains several monomers (not shown).

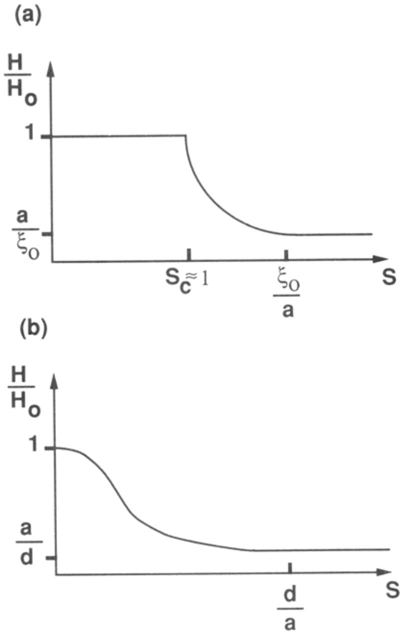

Figure 2. Plots of the brush height, H, in terms of the unsheared brush height, H_0, as a function of dimensionless shear stress, S. In a the grafting density is low (or the solvent fairly poor), so the blob size ξ_0 is less than the grafting distance. At low shears there is no decrease in the brush height. At a critical shear stress $S_c \approx 1$ the brush forms Pincus blobs and begins to collapse with $H \propto 1/S$. At very large shears, $S \approx \xi_0/a$ we enter the melt regime and the brush remains at its melt height, $H = H_0 a/\xi_0$. In b the grafting density is high (or the solvent only marginally poor). The brush begins to shrink as soon as shear is applied.

We begin by considering the unsheared brush in a poor solvent. In a poor solvent the monomers inside each blob behave as if they were under Θ conditions. The radius of each blob is thus given by $\xi \sim (N/N_b)^{1/2}a$, where a is a monomer size, N is the number of monomers in a chain, and N_b is the number of blobs per chain. For an unsheared brush there are two different regimes:

(i) If the grafting density is low, then the blob size is determined by excluded-volume interactions, the number of monomers per blob is $N/N_b \sim (\theta/\Delta T)^2$, and the blob size in the unsheared brush is $\xi_0 = a\theta/\Delta T$. Here θ is the Θ temperature of the polymer and ΔT is the degree of cooling below it. Inside each blob, monomer–monomer interactions are unimportant and the chain is ideal. On length scales larger than a blob, monomer–monomer interactions become significant and are attractive.

(ii) If the grafting density is high, then the grafting distance d controls the blob size and $\xi_0 = d = a(N/N_b).^{1/2}$.

The crossover between these two regimes occurs at $d = a\theta/\Delta T$. The unsheared brush height, H_0, can be obtained

---

† Unité de Recherche Associée no. 792 du CNRS.

0024-9297/93/2226-5806$04.00/0

by computing the volume occupied by the close-packed blobs, $d^2H_0 = N_b\xi_0^3 = Na^2\xi_0$.

We begin by discussing the first regime. The brush is effectively a grafted melt of blob monomers of size $\xi_0 = a\theta/\Delta T$. At small deformations, where the blob size is unperturbed by shear, we can thus use the known deformational properties of melt brushes. For planar brushes these have been studied by Fredrickson *et al.*[26,27] They argue that a melt brush has a shear modulus $\mu \sim kTad^{-4}$. In our case the monomer size a is replaced by the blob size ξ so the shear modulus of our brush is $\mu \sim kTd^{-4}a\theta/\Delta T$. Note that since $\xi > a$ the modulus of a brush in a poor solvent is actually larger than that of a melt brush. This is because a bad solvent brush has fewer effective monomers. We now shear the brush weakly. For weak shears the blob structure is unperturbed, as is the modulus. There will be no change in the brush height, H_0. The blob size remains at it zero-shear value $\xi_0 = a\theta/\Delta T$. The chains tilt through an angle $\theta = \tan^{-1} h_\parallel/H_0$, where $h_\parallel$ is the parallel displacement of a chain end. The deformation energy per unit area is $u = (1/2)\,\mu H_0 \tan^2\theta = (1/2)\,\mu h_\parallel^2/H_0$. The shear stress is $\sigma = \partial u/\partial h_\parallel = \mu h_\parallel/H_0$. Note that for a given shear stress the parallel extension of the chains is $h_\parallel = (kT)^{-1}\sigma Na^2d^2$, which is independent of the solvent quality. Thus although a poor solvent brush has a larger shear modulus than a melt brush it undergoes the same parallel extension. The end-to-end length of each chain is $L = (H_0^2 + h_\parallel^2)^{1/2}$. When this length is equal to $N_b\xi = Na\theta/\Delta T$, the chain of blobs is fully extended and can extend no further without modifying the internal structure of the blobs.[9,10,19,20] This corresponds to a critical shear stress of

$$\sigma_c = \frac{kT}{d^2a}\frac{\Delta T}{\theta}\left[1 - \left(\frac{a\theta}{d\Delta T}\right)^2\right]^{1/2} = \frac{kT}{d^2\xi_0}[1 - (\xi_0/d)^4]^{1/2} \quad (1)$$

As the solvent is made poorer ξ_0 decreases and the critical shear stress increases. Note that in the crossover regime between i and ii we have $\xi_0 = d$ and the critical shear stress is zero. When the chain of blobs is fully extended, the force, f, on the chain, parallel to the end-to-end vector, is $f = kTL/(N_b\xi_0^2) = kT/\xi_0$. At larger shears, the blob size is determined by $\xi = kT/f < \xi_0$ and we have a series of Pincus blobs.[9,10,19,20] The size of the blobs can now vary, and there is no reason for the height of the brush to remain constant. The end-to-end length of the chain is $L = N_b\xi = Na^2/\xi = Na^2f/kT$. Taking components of the force gives $f \sin\theta = \sigma d^2$ so we have $L = Na^2\sigma d^2/(kT \sin\theta)$. Since the brush is a series of closely packed blobs, we have $Hd^2 = N_b\xi^3 = NkTa^2 \sin\theta/(\sigma d^2)$. Finally we have the geometrical relation $H = L\cos\theta$. Solving these equations yields the tilt angle

$$\sin^2\theta = \frac{1}{2}\left(\frac{\xi_0}{dS}\right)^{-4}\left[\left[1 + 4\left(\frac{\xi_0}{dS}\right)^4\right]^{1/2} - 1\right]$$
$$\left(\approx 1 - \left(\frac{\xi_0}{dS}\right)^4 \text{ for } \frac{\xi_0}{dS} \ll 1\right) \quad (2)$$

and the brush height is

$$H = (H_0/S)\sin\theta \quad (3)$$

Here we have introduced $S \equiv \sigma d^2\xi_0/kT$ which is a dimensionless measure of the shear stress. From (1) it has a critical value $S_c = [[1 - (\xi_0/d)^4]]^{1/2}$, which is roughly 1 when the blob size in the unsheared brush is small compared to the grafting distance. Two facts are to be noted. First, the height decreases with increasing shear, roughly as $1/S$. Second, if $\xi_0 \ll d$, at the critical shear stress the brush is very strongly tilted, i.e., $\theta \approx \pi/2$. At this point we have $L/H_0 \approx (d/\xi_0)^2$ and the chain is stretched further in the parallel direction than in the perpendicular direction. Note also that at $S = S_c$ we have $\sin\theta = S$ so the collapse is continuous. The blob size as a function of shear is $\xi = kT/f = \xi_0 \sin\theta/S$. The shear steadily decreases the blob size and the brush height but cannot do this indefinitely. When the blob size is on the order of a monomer size, $\xi \sim a$, the brush is a melt, further compression is impossible, and the height of the brush is constant at its melt value $H_m = Na^3/d^2$. This occurs at a rather extreme shear stress $S = \xi_0/a = \theta/\Delta T$.

Now we look at regime ii where the blob size is originally set by the grafting distance, so $\xi_0 = d$.[28-30] In this case brush shrinkage begins immediately upon application of shear. Equations 2 and 3 still hold. For weak shear, $S \ll 1$, (2) gives $\sin\theta = S[1 - S^2/4]$ and the brush height is $H = H_0(1 - S^2/4)$. The brush height thus decreases weakly with shear. At large shear stresses, $S > 1$, we have $\sin\theta = 1 - (1/2)S^{-4}$ and $H = H_0/S$, and the decrease in height becomes very rapid. Again, beyond a maximum shear of $S = d/a$, we have a melt brush and the brush height remains constant.

The situation for brush shear is then as follows. In good solvents the brush should expand, albeit by a limited amount. In poor solvents a brush at low grafting density will show no expansion at weak shear but will shrink at high shear. In the intermediate case of a Θ solvent, if we neglect three-body interactions, there should be no change in the brush height. Three-body interactions, which are usually repulsive, should, however, produce some slight expansion.

There are at least three experimental means of testing our predictions. The most direct would be to use telechelic polymers end grafted to both surfaces in a force machine. The plate separation is chosen such that the chains are at their equilibrium height, and the normal force between the plates is then zero. Relative motion of the surfaces should produce negligible normal force between the plates until a certain critical angle, given by (2), is reached. At this point a normal force should act to pull the plates together. Of course, if the solvent is only marginally poor, then ξ_0 is set by d and the normal force will be felt immediately upon shearing.[31] A second, more difficult method would be to use a single brush in a shear flow. A more macroscopic, and possibly more dramatic, demonstration involves the use of triblock copolymer lamellar mesogels[32,33] with a high bridging fraction. The central block should be a flexible polymer in a poor solvent, and the outer blocks should be glassy. If a slab of this mesogel is placed in a bath of poor solvent and sheared above the critical shear, we expect a rapid decrease in the thickness of the gel or, alternatively, a normal force tending to contract the gel. Thus, the shrinkage predicted here can have macroscopic consequences. The most favorable situation for this is when the solvent is marginally poor, so that ξ_0 is only slightly smaller than d. In this case the shear need not be extreme. We note in passing that this procedure can also be used to test the swelling predicted by Barrat in a good solvent.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 33.
(2) Milner, S. T. *Science* **1991**, *905*, 251.
(3) Lai, P.-Y.; Binder, K. *J. Chem. Phys.* **1992**, *97*, 586.
(4) Chakrabarti, A.; Toral, R. *Macromolecules* **1990**, *23*, 2016.
(5) Murat, M.; Grest, G. S. *Macromolecules* **1989**, *22*, 4054.
(6) Lai, P.-Y.; Binder, K. *J. Chem. Phys.* **1992**, *91*, 586.

(7) Auroy, P.; Auvray, L. *Macromolecules* **1992**, *25*, 4134.
(8) Ross, R. S.; Pincus, P. *Europhys. Lett.* **1992**, *19*, 79.
(9) Halperin, A.; Zhulina, E. B. *Macromolecules* **1991**, *24*, 5393.
(10) Halperin, A.; Zhulina, E. B. *Europhys. Lett.* **1991**, *15*, 417.
(11) Zhulina, E. B.; Borosiv, O. V.; Pryamitsyn, V. A.; Birshtein, T. M. *Macromolecules* **1991**, *24*, 140.
(12) Halperin, A. *J. Phys. Fr.* **1988**, *49*, 547.
(13) Williams, D. R. M. *J. Phys. Fr.*, in press.
(14) Klein, J.; Perahia, D.; Warburg, S. *Nature* **1991**, *143*, 352.
(15) For a totally different interpretation of the experiments, see: Sekimoto, K.; Leibler, L. *Europhys. Lett.*, in press.
(16) Rabin, Y.; Alexander, S. *Europhys. Lett.* **1990**, *13*, 49.
(17) Barrat, J.-L. *Macromolecules* **1992**, *25*, 832.
(18) For a recent and different theory of brush swelling, see: Kumaran, V. *Macromolecules* **1993**, *26*, 2464.
(19) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(20) Pincus, P. *Macromolecules* **1976**, *9*, 386.
(21) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 483.
(22) Lifshits, I. M.; Grosberg, A. Y.; Khokhlov, A. R. *Rev. Mod. Phys.* **1978**, *50*, 683.
(23) Alexander, S. *J. Phys. Fr.* **1977**, *38*, 977.
(24) de Gennes, P.-G. *J. Phys. Fr.* **1976**, *37*, 1443.
(25) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(26) Fredrickson, G. H.; Ajdari, A.; Leibler, L.; Carton, J.-P. *Macromolecules* **1992**, *25*, 2882.
(27) Williams, D. R. M. *Macromolecules*, in press.
(28) Raphael, M.; Pincus, P. *J. Phys. II Fr.* **1992**, *2*, 1341.
(29) Raphael, M.; Pincus, P.; Fredrickson, G. H. *Macromolecules* **1992**, *26*, 1996.
(30) Ross, R. S.; Pincus, P. *Macromolecules* **1992**, *25*, 2177.
(31) In the case of telechelics with large numbers of blobs there will be trapped entanglements present in the system. Since the brush is assumed to be sheared uniformly, the entanglement points are also sheared uniformly and may make little difference. However, their exact effect is far from obvious.
(32) Zhulina, E. B.; Halperin, A. *Macromolecules* **1992**, *25*, 5730.
(33) Halperin, A.; Zhulina, E. B. *Prog. Colloid Polym. Sci.* **1992**, *90*, 156.