Suppressing Autophobic Dewetting by Using a Bimodal Brush

S. R. Edgecombe, J. M. Gardiner, and M. W. Matsen*

Polymer Science Centre, University of Reading, Whiteknights, Reading RG6 6AF, United Kingdom

Received March 25, 2002
Revised Manuscript Received May 22, 2002

Grafting a polymer brush to an inorganic substrate is a simple cost-effective method of modifying its surface properties. In particular, it offers a natural way of preventing the dewetting of a homopolymer film. By bonding a microscopic monolayer of polymer chains to the substrate, the homopolymer film is shielded from the unfavorable enthalpic interactions that generally cause it to dewet. Unfortunately, even when the brush is chemically identical to the homopolymer, there remains an unfavorable entropic interaction, albeit usually much smaller, that still causes the homopolymer to dewet.[1−3] This surprising behavior, referred to as autophobic dewetting, is now well understood.[4−7] It can be suppressed either by lowering the molecular weight of the homopolymer film or by reducing the grafting density of the brush. However, the intended application will generally prevent the homopolymer from having too low of a molecular weight, and the need to shield the homopolymer from the substrate will limit the grafting density.[8] Thus, an alternative remedy would be useful.

The principal cause of autophobic dewetting is the loss of entropy associated with the homopolymer interface.[4,5] In short, the presence of an interface requires the homopolymer molecules to deviate from the preferred random-walk statistics, thus lowering their configurational entropy. In the high-molecular-weight limit, the entropy loss is given by[9]

$$S_{\mathrm{h,conf}} = -\frac{a^2\rho_0 k_{\mathrm{B}}}{24}\int\frac{|\nabla\phi_{\mathrm{h}}(\mathbf{r})|^2}{\phi_{\mathrm{h}}(\mathbf{r})}\,\mathrm{d}\mathbf{r} \qquad (1)$$

where $\phi_{\mathrm{h}}(\mathbf{r})$ is the homopolymer profile, ρ_0^{-1} is the volume of a polymer segment, and a is the statistical segment length. Thus, the entropy lost by the homopolymer is proportional to the average gradient of its profile squared times the width, w, of the brush/homopolymer interface. Since the gradient, $|\nabla\phi_{\mathrm{h}}(\mathbf{r})|$, is inversely proportional to w, it follows that $S_{\mathrm{h,conf}} \propto w^{-1}$. Hence, the key to suppressing autophobic dewetting is to broaden the brush/homopolymer interface, which might be accomplished by using brushes with a wide distribution of chain lengths.

Here, we test this hypothesis by calculating the entropic tension, γ, from a bidisperse brush and comparing it with the tension, γ_0, from a monodisperse brush of the same thickness, d_0, and grafting density, σ. The bidisperse brush will consist of $A\sigma_{\mathrm{s}}$ short chains of N_{s} segments each and $A\sigma_{\mathrm{l}}$ long chains of N_{l} segments each, where A is the total area of the brush. For simplicity, we restrict our attention to the limit of infinite homopolymer molecular weight, for which the entropic tension is highest.[4] In this case, the system is characterized by just three parameters: the molecular weight ratio, $\alpha \equiv N_{\mathrm{s}}/N_{\mathrm{l}}$, the brush composition, $\beta_{\mathrm{s}} \equiv \sigma_{\mathrm{s}}/\sigma$, and the brush thickness, $d_0/aN^{1/2} = \sigma N^{1/2}/a\rho_0$, where $\sigma \equiv \sigma_{\mathrm{s}} + \sigma_{\mathrm{l}}$ is the total grafting density and $N \equiv (\sigma_{\mathrm{s}}N_{\mathrm{s}} + \sigma_{\mathrm{l}}N_{\mathrm{l}})/\sigma$ is the number-averaged degree of polymerization.

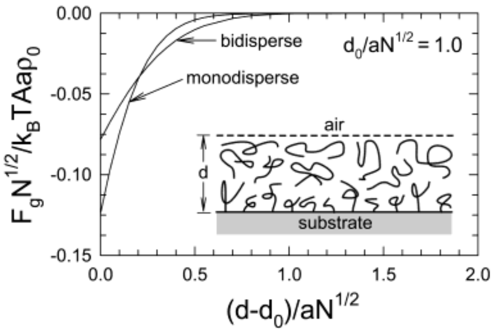

Figure 1. Grand canonical free energy, F_{g}, of brush/homopolymer films as a function of their thickness, d. Both curves correspond to brushes of the same thickness $d_0/aN^{1/2} = 1.0$, but one is for a bidisperse brush ($\alpha = 0.125$ and $\beta_{\mathrm{s}} = 0.5$) whereas the other is for a monodisperse brush ($\alpha = 1$). Note that the curves have been shifted vertically such that F_{g} approaches zero as d diverges. Based on the minimum in F_{g}, the tension of the bidisperse brush ($\gamma N^{1/2}/k_{\mathrm{B}}Ta\rho_0 = 0.078$) is significantly less than that of the monodisperse brush ($\gamma_0 N^{1/2}/k_{\mathrm{B}}Ta\rho_0 = 0.124$).

In the past, γ has been calculated by either strong-stretching theory (SST)[4,6] or self-consistent-field theory (SCFT).[4,5,7] Both theories are based on the same underlying model, but SCFT represents an exact mean-field treatment whereas SST is an approximation obtained by assuming the brush chains are strongly stretched. As a result, SCFT is unarguably more accurate, but on the other hand, SST is capable of analytical predictions. However, on the delicate issue of autophobic dewetting, SST has been inaccurate by close to an order of magnitude,[4] and based on a detailed examination of the free energy contributions, this problem is much more than a simple scaling factor. We also note that SST becomes far more complicated when dealing with bidisperse brushes,[10] and thus we could no longer expect analytical predictions. In contrast, the extension from monodisperse to bidisperse brushes is trivial in SCFT.

For the reasons above, we implement the SCFT following the algorithm detailed in ref 4. This procedure starts by evaluating the grand canonical free energy, $F_{\mathrm{g}}(d)$, of a brush/homopolymer film as a function of its overall thickness, d. From that, the tension of the brush/homopolymer interface is given by

$$\gamma = \frac{F_{\mathrm{g}}(\infty) - F_{\mathrm{g}}(d_{\mathrm{min}})}{A} \qquad (2)$$

where d_{min} is the thickness corresponding to minimum energy. In the present case where the homopolymer molecular weight is set to infinity, the minimum occurs at $d_{\mathrm{min}} = d_0$, which corresponds to a completely dry brush. Figure 1 shows an example where the free energy curve of a bidisperse brush is compared to that of a monodisperse one, and as expected, the bidisperse brush results in a significantly lower tension.

In the interest of finding the optimal condition that minimizes the tension, Figure 2 plots the relative

10.1021/ma020476y CCC: $22.00

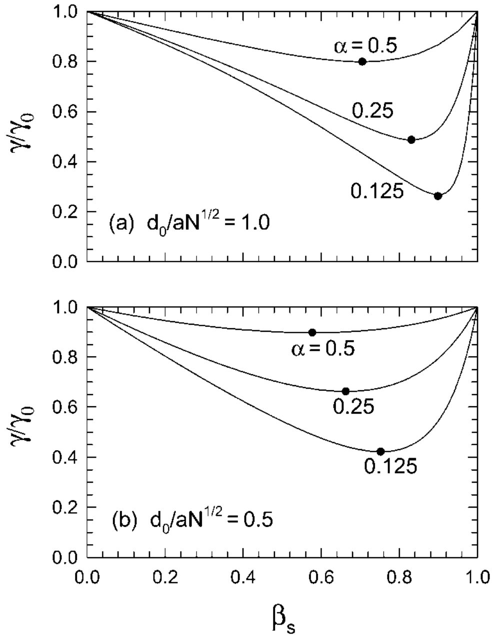

Figure 2. Entropic tension, γ, of a bidisperse brush as a function of its composition, β_s, plotted relative to the tension, γ_0, of a monodisperse brush. Plots (a) and (b) show results for thick ($d_0/aN^{1/2} = 1.0$ and $\gamma_0 N^{1/2}/k_B T a\rho_0 = 0.124$) and thin ($d_0/aN^{1/2} = 0.5$ and $\gamma_0 N^{1/2}/k_B T a\rho_0 = 0.068$) brushes, respectively, at various levels of bidispersity, α.

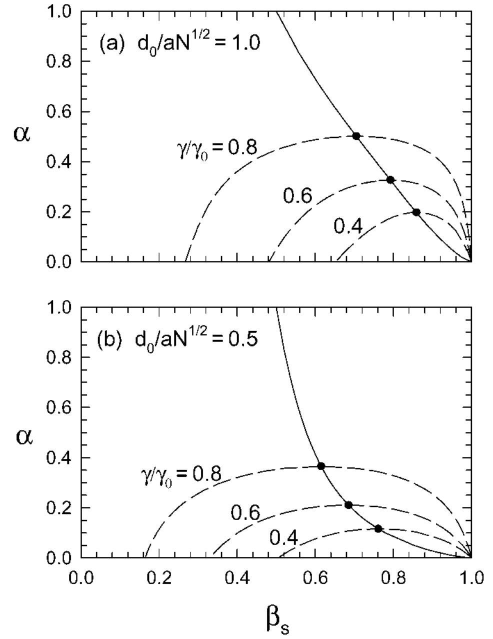

Figure 3. Optimum composition, β_s, corresponding to the lowest tension for a given degree of bidispersity, α, calculated for both (a) thick and (b) thin brushes. The dashed curves denote contours of constant entropic tension, γ.

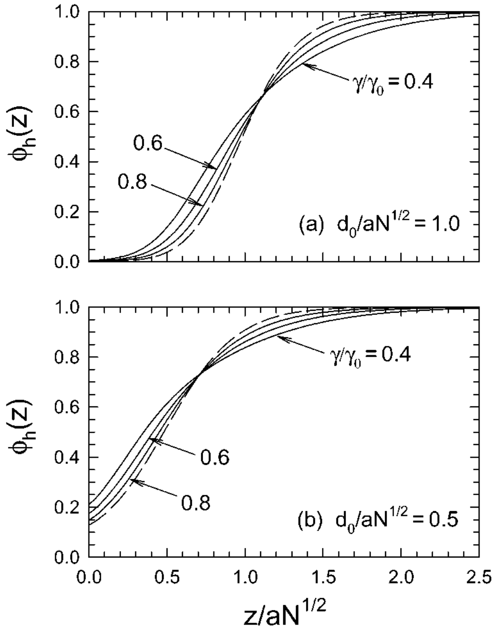

Figure 4. Homopolymer profiles, $\phi_h(z)$, plotted as a function of distance, z, from the substrate. The dashed curves are profiles from monodisperse brushes, whereas the solid curves correspond to the bidisperse brushes denoted by the solid dots in Figure 3.

tension, γ/γ_0, of a bimodal brush as a function of its composition, β_s, for several levels of bidispersity, α. Notice that, in all cases, the bidispersity reduces the entropic tension (i.e., $\gamma/\gamma_0 \leq 1$ for all α and β_s). The optimum composition, which is denoted with solid dots in Figure 2, starts at $\beta_s \approx 0.5$ for low degrees of bidispersity (i.e., $\alpha \approx 1$) and shifts toward brushes with fewer and fewer long chains (i.e., $\beta_s \rightarrow 1$) as the bidispersity increases (i.e., $\alpha \rightarrow 0$). Figure 3 displays this dependence on bidispersity more clearly. The solid curves indicate the optimum composition, β_s, as a function of bidispersity, α, and the dashed curves show contours of constant γ/γ_0 in the $\alpha-\beta_s$ plane.

Our hypothesis predicts that the reduction in tension observed in Figures 2 and 3 is a result of a broadened brush/homopolymer interface. To confirm this, Figure 4 compares the homopolymer profile, $\phi_h(z)$, from the monodisperse brush (dashed curves) to that from the bidisperse brush (solid curves) for those conditions denoted by solid dots in Figure 3. Exactly as expected, the reduction in tension corresponds with a reduction in the slope of the homopolymer profile.

Experiments by Reiter et al.[1] have already examined autophobic dewetting from bimodal brushes ($\alpha = 0.21$ and 0.073), and in particular they focused on brushes containing a small number of long chains, the condition for which we predict a significant reduction in γ. Consistent with our prediction, their dewetting kinetics showed a substantial slowing down as a small number of longer chains were introduced into the brush. However, Reiter et al. hypothesized that this was due to so-called *pull-out* forces preventing the extraction of the longer brush chains, referred to as *connectors*, from the homopolymer film. Nevertheless, on the basis of the previous success[4] of the SCFT in quantitatively modeling autophobic dewetting,[2] it seems likely that our predicted reduction in γ may be the dominant mechanism suppressing the kinetics. Ultimately, the best way of confirming a reduction in tension would be to perform static contact angle measurements,[2] for which frictional-type forces have no effect.

In conclusion, we have shown that the tendency for autophobic dewetting can be substantially suppressed by creating bimodal brushes containing a small number of long chains. The prediction is consistent with experiment and is attributed to the fact that a bidisperse brush results in a more gradual brush/homopolymer interface compared to a monodisperse brush. Naturally, this result should be general to all polydisperse brushes, and thus perhaps other molecular weight distributions could even be more effective at suppressing autophobic dewetting.

Acknowledgment. This work was supported by the EPSRC (GR/M61160).

References and Notes

(1) Reiter, G.; Schultz, J.; Auroy, P.; Auvray, L. *Europhys. Lett.* **1996**, *33*, 29. Reiter, G.; Auroy, P.; Auvray, L. *Macromolecules* **1996**, *29*, 2150.

(2) Reiter, G.; Khanna, R. *Phys. Rev. Lett.* **2000**, *85*, 5599.

(3) Liu, Y.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A.; Zhong, X.; Eisenberg, A.; Kramer, E. J.; Sauer, B. B.; Satija, S. *Phys. Rev. Lett.* **1994**, *73*, 440.

(4) Matsen, M. W.; Gardiner, J. M. *J. Chem. Phys.* **2001**, *115*, 2794.

(5) Shull, K. R. *Faraday Discuss.* **1994**, *98*, 203.

(6) Leibler, L.; Ajdari, A.; Mourran, A.; Coulon, G.; Chatenay, D. In *OUMS Conference on Ordering in Macromolecular Systems*; Teramoto, A., Kobayashi, M., Norisuje, T., Eds.; Spinger-Verlag: Berlin, 1994; p 301.

(7) Leibler, L.; Ajdari, A.; Mourran, A.; Coulon, G.; Ferreira, P. G.; Ajdari, A.; Leibler, L. *Macromolecules* **1998**, *31*, 3994.

(8) Voronov, A.; Shafranska, O. *Langmuir* **2002**, *18*, 4471.

(9) Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L. *Macromolecules* **1990**, *23*, 132.

(10) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1989**, *22*, 853.

MA020476Y