Macromolecules **2008**, *41*, 2747–2748

Polymer Brushes Are Not Always Barriers to Diffusion

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Received August 20, 2007
Revised Manuscript Received January 26, 2008

The behavior of three-component systems of brush, solvent, and free chains has been the subject of numerous theoretical studies that have addressed the conditions under which the free chains in solution would penetrate the brush. Scaling theory, self-consistent-field theory, and simulations have predicted *partial* penetration of the brush by free chains in solution whose volume fraction approaches that of the grafted chains in the brush layer.[1–10] This interesting and potentially useful behavior has been confirmed experimentally.[11] By contrast, theory predicts exponentially small amounts of penetration for brushes in contact with very dilute solutions of free chains in good solvent.[1–10] This situation has received very little attention experimentally.

In a recent paper, we reported the unexpected experimental observations that polymer chains in very dilute solution diffused completely through the pre-existing polymer brush and became grafted to the underlying solid surface.[12] Because that experimental study was focused only on whether penetration of the brush leading to grafting was possible, we did not determine the kinetics of the process. The purpose of the present Note is to report results revealing that diffusion of free chains through a brush to the underlying surface is extremely facile.

The polymer brushes used in the present study were composed of monodisperse polystyrene chains (M_n = 44 000 g/mol; $M_w/M_n \le 1.04$) grafted to the surface of silicate glass. The preparation of the brushes is described in detail elsewhere.[12–15] Briefly, polystyrene chains, synthesized by anionic living polymerization and each terminated with a primary amine group,[16] were grafted to the surface of epoxide-derivatized silicate glass by means of a chemical reaction between the primary amine and the epoxide groups. This reaction attached each chain to the surface by means of a permanent, covalent bond. Final surface attachment densities of the pre-existing grafted layers were 0.0051 and 0.010 chains/nm^2.

The question of brush status for the above grafted layers can be addressed by considering the ratio of πR_g^2 to πR^2, where R_g is the radius of gyration of an isolated chain in solution and R is the radius of the lateral area occupied by the same chain attached by one end to a surface. For the surface attachment densities stated above, these ratios are 1.24 and 2.43, respectively. Carignano and Szleifer[17] showed by modeling that grafted chains start to interact unfavorably with each other and begin to stretch away from the surface at $\pi R_g^2/\pi R^2$ values lower than 1.0. However, they reserved the term brush for grafted chains with $\pi R_g^2/\pi R^2$ values >8.0, based on the results of their modeling, which showed a lower rate of stretching below and a slightly higher rate above $\pi R_g^2/\pi R^2 = 8$. An alternative and commonly used criterion for brush status is when the average distance between chain attachment points is less than $2R_g$ or, equivalently, when $\pi R_g^2/\pi R^2 > 1.0$. The grafted layers used as the pre-existing brushes in the present study meet both of these criteria. Finally, the formation process for the grafted layers used in this study followed the usual three-regime kinetics, described in detail in ref 18. This three-regime kinetics establishes the end result of the grafting process as distinct from the mushroom layer and also as distinct from (and beyond) a layer that is in transition from the mushroom to the brush, as follows. The formation of the mushroom layer composes a distinct first regime of fast grafting. This is followed by a second regime of negligible grafting and, finally, by a relatively rapid transition from mushroom to brush during which the surface attachment density doubles. The third regime ends when the transition from mushroom to brush is complete and grafting ceases spontaneously. The clear delineation of these stages in the formation of a grafted layer establishes the final product as a brush, separate and distinct from a mushroom layer.

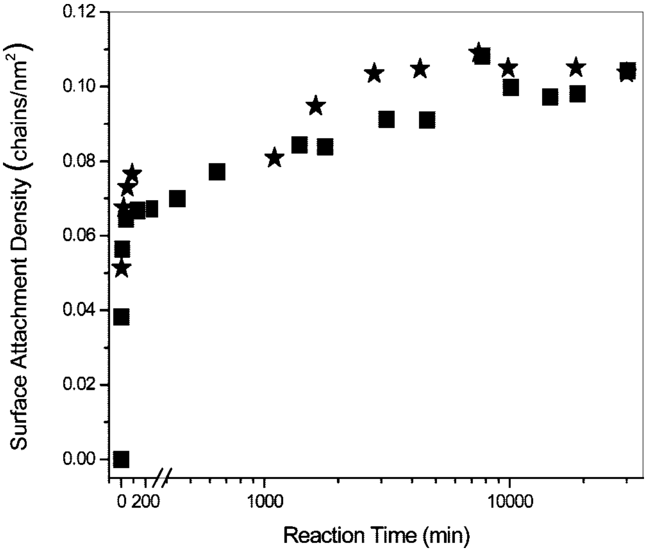

Figure 1. Grafting of free chains (end-functional polystyrene, 4000 g/mol) from dilute solution to surface underlying pre-existing brush (polystyrene, 44 000 g/mol, surface attachment density of 0.0051 chains/nm^2). Two different symbols represent replicate grafting experiments.

For the study of the kinetics of penetration, the solid containing the pre-existing brush was exposed to a very dilute solution of free chains in toluene (0.255 mg/mL, or volume fraction of ~10^{-4}), a good solvent for polystyrene. The free chains used were monodisperse, primary-amine-end-functionalized polystyrene of M_n = 4000 g/mol ($M_w/M_n \le 1.04$), a lower molecular weight than the chains comprising the brush. The amine functional group at the end of each free chain allowed those that penetrated the brush completely to become grafted by reaction with the epoxide active sites populating the underlying surface. The dilute solution in contact with the brush was monitored versus time for disappearance of free chains. Small aliquots, taken periodically, were passed through a size exclusion chromatograph, and the eluting species were measured with the attached ultraviolet and refractive index detectors. An

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10.1021/ma0718797 CCC: $40.75

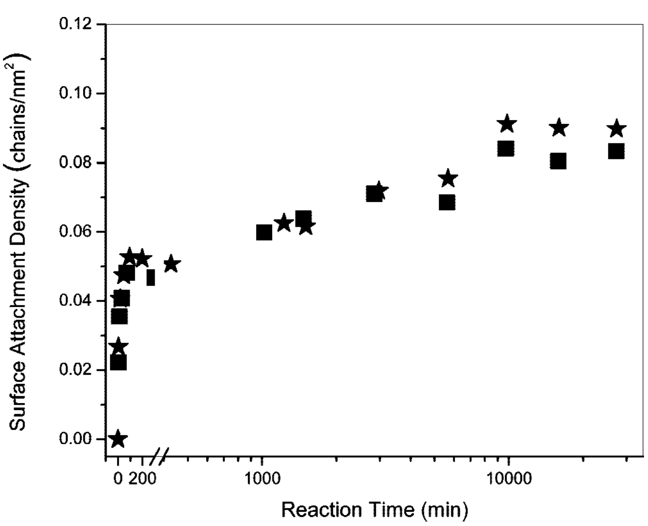

Figure 2. Grafting of free chains (end-functional polystyrene, 4000 g/mol) from dilute solution to surface underlying pre-existing brush (polystyrene, 44 000 g/mol, surface attachment density of 0.010 chains/nm^2). Two different symbols represent replicate grafting experiments.

internal standard made the method analytically quantitative.[14] The mass of species of $M_n = 4000$ g/mol depleted from solution was converted to number of free chains grafted. This method also enabled verification that the chains of the pre-existing brush were not released into solution, since no species of $M_n = 44\,000$ g/mol appeared in solution at any time during the process.

The results for free chains penetrating the brush and becoming grafted are shown in Figures 1 and 2, in which the surface attachment density of free chains is plotted versus time. Each figure contains data from two replicate grafting reactions (two different symbols) to show reproducibility. As can be seen from the figures, grafting of the free chains took place immediately and rapidly, with the majority being grafted within 1 h, after which a few more chains were grafted over a much longer time until the process came to a halt. (Grafting stopped spontaneously, without exhausting the supply of free chains in solution or the epoxide reactive sites on the solid surface.) The high rate of grafting during the first hour is similar to the rate at which a mushroom layer is formed on a bare surface.[18] This is surprising in view of the fact that the penetration of a brush contacted by free chains in very dilute solution is predicted to be exponentially small.

The rapidity of the diffusion of the free chains all the way through the brush to the underlying surface shows that the brush presents no barrier whatsoever to the diffusion of individual free chains. In contrast, the speed of grafting suggests that the anisotropy of the brush environment may even facilitate the diffusion to the surface. (A similar facilitated diffusion was postulated for the transition from mushroom to brush, when free chains have to make their way to the surface through an ever denser layer of grafted chains.[18]) The diffusion of species through various grafted layers is the focus of our ongoing research.

Acknowledgment. This work was supported in part by NSF Grant CTS 0650760.

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MA0718797