Grafting of Free Chains in the Presence of Preexisting Polymer Brushes

Heqing Huang,[†,§] Arthur Cammers,[‡] and Lynn S. Penn*[,†]

Department of Chemical and Materials Engineering and Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Received March 20, 2006; Revised Manuscript Received July 12, 2006

ABSTRACT: Experiments were conducted on the grafting of end-functionalized free chains from dilute solution to a solid bearing a preexisting polymer brush. The hypothesis was that grafting behavior would parallel the theoretical predictions made for penetration of a preexisting brush by free chains. Paralleling penetration theory, the grafting of free chains increased with concentration of the bulk solution and decreased with molecular weight of the free chains, although the decrease was less pronounced than predicted by theory. Free chains chemically identical to, but longer than, the chains in the brush did not become grafted. However, free chains longer but more flexible than the chains in the preexisting brush did become grafted. Contrary to penetration theory, which predicts an exponential decrease in penetration with grafting density of the preexisting brush, grafting of free chains (of three different molecular weights and two different chemical structures) appeared to have little to no sensitivity to density of the preexisting brush. This insensitivity, unexplained at present, suggests that there are aspects of penetration that have not been identified by theory and also suggests a direction for future experiments. One of the most surprising findings was the rapidity with which free chains penetrated the preexisting brush. They became grafted almost as rapidly as free chains diffuse to a bare surface to form a mushroom layer. This indicates that the preexisting brush does *not* constitute a strong barrier to diffusion of free chains but, instead, facilitates their diffusion to the surface.

I. Introduction

Our previous studies on the grafting of free chains from solution showed that free chains of any molecular weight could be readily grafted to a nonporous solid substrate containing a preexisting *mushroom* layer.[1] The present paper describes an experimental investigation of the grafting of free chains from solution to a solid substrate bearing a preexisting polymer *brush*.

Theorists have been interested in polymer brushes in contact with chemically identical free chains in the melt state (two-component systems) or chemically identical free chains in solution (three-component systems) for nearly three decades.[2−17] They have focused their attention on how the structure of the polymer brush would change in the presence of free chains[5−8] and on the extent of penetration of the brush by the free chains.[5,9−17] Theoretical studies on penetration are relevant to grafting because free chains must penetrate the preexisting brush to become grafted. Our hypothesis in the present investigation was that the grafting behavior of free chains would agree qualitatively with the predictions of penetration theory. Most theoretical studies have addressed free chains shorter than those comprising the brush and have predicted that penetration would decrease with grafting density of the preexisting brush,[11−14] would decrease with length of the free chains,[11−14] and would increase with solution concentration.[5,12−14] Free chains longer than those in the brush have been predicted to penetrate either not at all or only part way into the brush.[3,13,15,17] In practice, partial penetration would not lead to grafting.

Some of the theoretical studies cited above produced phase diagrams depicting distinct phase states of systems composed of free and grafted chains and sometimes solvent as a third species. Particularly pertinent to the present experimental investigation is the phase diagram shown in Figure 1 for a brush in contact with chemically identical free polymer chains dissolved in an athermal solvent and for systems in which the free chains are shorter than the chains in the brush. This diagram, which plots the reduced grafting density (σ) of the brush vs the volume fraction ($\Phi_{\mathrm{P}}^{\mathrm{bulk}}$) of free chains in the bulk solution contacting the brush, is dominated by three regimes, first designated as I, II, and III by Gast and Leibler[12] nearly two decades ago and later expanded upon by Zhulina, Borisov, and Brombacher.[13] Regime I is nominally a regime of no mixing, i.e., no penetration of the brush by free chains. In this regime, the volume fraction of free chains in the solution is lower than the volume fraction of the grafted chains within the brush, and as a result, the structural features of the brush are not modified to any extent by the free chains. Regime II also is nominally a regime of no mixing. In this regime, the volume fraction of free chains in the solution is higher than the volume fraction of the grafted chains within the brush, and the greater osmotic pressure of the solution causes the brush to contract, deterring the free chains from penetrating. Regime III is one in which the volume fraction of free chains in the solution is so much higher than the volume fraction of the grafted chains within the brush that, in contrast to regimes I and II, penetration of the brush by free chains occurs and is substantial. Regimes I, II, and III in Figure 1 correspond to the strongly stretched−unmixed, the weakly stretched−unmixed, and the weakly stretched−mixed regimes, respectively, originally developed by DeGennes[5] with scaling arguments. The mushroom regimes, corresponding to the unstretched−unmixed and the unstretched−mixed regimes defined by DeGennes, are not visible in Figure 1, as they are compressed into the *x*-axis due to their extremely low σ values.

---

* To whom correspondence should be addressed: Ph 859-257-7897; Fax 859-323-1929; e-mail penn@engr.uky.edu.

[†] Department of Chemical and Materials Engineering.

[‡] Department of Chemistry.

[§] Now at National Institute of Standards and Technology, Gaithersburg, MD.

10.1021/ma060623i CCC: $33.50

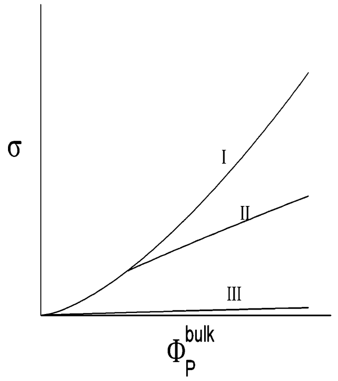

Figure 1. Reduced grafting density of brush, σ, vs volume fraction of free chains in the contacting solution, Φ_P^{bulk}. The boundary lines were computed with the equations in ref 17; because these lines shift with changes in lengths of grafted and free chains, the axes are not numbered. The dimensionless quantity, σ, is explained in detail in section III.B.

The experimental systems described in the present paper fall in regime I, where the solutions of free chains are *dilute*. Dilute solutions are important for the construction of polymer brushes that must have controlled ratios of chains with different molecular weights and/or chemical structures. Use of dilute solutions allows the experimenter to monitor precisely, and in real time, the number and identity of free chains leaving solution to become grafted and thereby confers experimental control of the grafting process and of the characteristics of the final brush.[1]

The description of regime I as a regime of no mixing (no penetration) is a qualitative one.[5] Closer examination of the details of the free energy analyses, scaling arguments, and self-consistent-field calculations reveals that regime I is predicted have in actuality an *exponentially small* amount of mixing rather than no mixing.[5,10−14] It is the nonvanishing mixing, however small, that makes this regime of great interest to experimentalists studying grafting.

The present paper reports results of three types of experiments. The first were control experiments in which the free chains were inert-ended and had no ability to become grafted. The second were experiments in which the free chains were end-functionalized (able to become grafted) and chemically identical to those of the preexisting brush. The third were experiments in which the free chains were end-functionalized but chemically different from those of the preexisting brush. This last type of experiment was motivated by our observation that free chains longer than, but chemically identical to, the chains in the brush did *not* become grafted; this prompted us to postulate that longer free chains *would* become grafted if they were more flexible than the chains in the preexisting brush. In our experiments, all of the preexisting brushes were polystyrene, and the free chains were either polystyrene or polyisoprene. Because all of the existing theoretical works on penetration stipulate no segmental adsorption to the wall for either grafted or free chains, we used toluene as the solvent throughout our investigation. In toluene, neither polystyrene nor polyisoprene exhibits any segmental adsorption to the substrate used in our work.

II. Experimental Section

A. Introduction of Reactive Sites to Surface of the Solid Substrate. The solid used as the substrate in the present work was silicate glass in the form of nonporous, spherical beads (Potters Industries, Cleveland, OH) of specific surface area equal to 0.24 m^2/g and a mean diameter of 10 μm. The spherical and nonporous geometry ensured that the total surface was accessible to solutions and solvents. Epoxide reactive sites were introduced to the surface of the glass beads by means of a derivatization procedure described in detail elsewhere.[1,18,19] This derivatization procedure results in 2.71 ± 0.24 epoxide groups/nm^2 of surface, a value well above that needed for grafting of polymer chains at the highest conceivable surface density.[20]

Table 1. Polymer Samples Used in the Investigation

polymer[a]	M_n, g/mol	M_w/M_n	polymer[a]	M_n, g/mol	M_w/M_n
PS−NH$_2$	90 000	≤1.04	PS[b]	20 000	≤1.05
PS−NH$_2$	44 000	≤1.04	PS[b]	45 000	≤1.05
PS−NH$_2$	14 500	≤1.04	PI[b]	75 000	≤1.05
PI−NH$_2$	45 000	≤1.04			

[a] PS means polystyrene and PI means polyisoprene. [b] Inert-ended polymer, used as free chains in control experiments.

B. Source of Monodisperse Polymers. Monodisperse, primary amine-end-functionalized polymer samples were prepared in the laboratory of Prof. Roderic P. Quirk, University of Akron, as described elsewhere.[21] Monodisperse, inert-ended polymer samples were purchased from Polymer Source, Dorval, Quebec, Canada. All polymers were prepared by living anionic polymerization. Both the functional-ended and the inert-ended polyisoprene were >95% 1,4-addition. The molecular weights, M_n, and the polydispersities, M_w/M_n, are listed in Table 1.

C. Preparation of Preexisting Brushes. Monodisperse, primary amine-end-functionalized polystyrene chains of $M_n = 90\,000$ g/mol were grafted from solution to the surface of the epoxide-derivatized beads. Final grafting density of each brush was controlled by reaction time and solvent quality. As described in previous publications, brushes of low grafting density are produced when the grafting reaction is conducted in a good solvent (one that does not allow segmental adsorption to the grafting surface),[19,21] while brushes of higher grafting density can be produced by grafting from poor solvent.[18,22] Random variation in grafting density among replicate preexisting brushes, prepared in separate reactions, increased with grafting density, ranging from ~5% for lowest grafting density to ~11% for highest grafting density.[22] The average lateral radius of a grafted chain in a given preexisting brush was obtained by inverting the experimental value for chains/nm^2, equating to πR^2 and solving for R.

D. Experiments on Grafting of Free Chains. For each experiment, a weighed amount of beads containing a preexisting polymer brush of known grafting density was exposed to a solution of free chains. Solution concentrations of free chains ranged from 0.130 to 0.530 mg/mL of solvent. Specific gravities of polystyrene and polyisoprene (1.05 and 0.940 g/mL, respectively) were used to convert values expressed as mg/mL to volume fraction. These concentrations, although low, were more than sufficient for accurate measurement of solution depletion. In all grafting experiments, the solvent was toluene, which has been shown *not* to allow segmental adsorption of either polystyrene or polyisoprene to the epoxide-derivatized substrate.[19]

The ratio of beads to total amount of polymer solution was balanced so that grafting would not be limited by exhaustion of the free chains from the solution. In a typical grafting experiment, ~50 mass % of the polymer is depleted from solution, and this extent of depletion does not affect the process or the end-point of grafting. In addition, the density of reactive sites (see section II.A) remaining on the substrate surface after some sites have been consumed in preparation of the preexisting brush is far in excess of that needed for grafting of additional chains.[20]

E. Quantitative Analysis of Number of Chains Grafted. A solution depletion method[1,18−22] based on size exclusion chromatography was used to quantify the number of free chains leaving solution to become grafted to the solid surface. This method involves taking aliquots from the reaction mixture, removing the beads from each aliquot with a syringe filter, and injecting the supernatant portion of the aliquot into a size exclusion chromatograph (Waters LC, Waters Corp., Milford, MA) equipped with ultraviolet and refractive index detectors. The constituents of the injected supernatant are quantified by the detectors as they emerge

Table 2. Results of Screening Study on Different Molecular Weights of Polystyrene[a]

M_n of preexisting brush, g/mol	R_g in toluene, nm	grafting density of preexisting brush, chains/nm^2	grafting of free chains ($M_n = 14\,500$ g/mol)	grafting of free chains ($M_n = 44\,000$ g/mol)	grafting of free chains ($M_n = 90\,000$ g/mol)
14 500	4.28	0.026	yes	no	no
44 000	7.80	0.020	yes	no	no
90 000	11.7	0.0042	yes	yes	no

[a] Concentration of free chains in toluene was 0.255 mg/mL (volume fraction of 2.43×10^{-4}).

Table 3. Characteristics of Typical Brushes of $M_n = 90\,000$ g/mol

chains/nm^2	R, nm	πR^2, nm^2	$(\pi R_g^2/\pi R^2)^a$	σ^c
0.002 33[a]	11.7	430	1.00	0.000 819
0.003 74[b]	9.23	268	1.61	0.001 32
0.006 48[b]	7.01	154	2.79	0.002 29
0.014 4[b]	4.70	69.4	6.20	0.005 08
0.025 5[b]	3.53	39.2	11.0	0.009 00

[a] Included for comparison only, values in this row are for a mushroom layer, i.e., nonoverlapping, unstretched chains in good solvent, for which $R = R_g = 11.7$ nm. [b] Variability among replicates ranged from ∼5% for smallest σ to ∼11% for highest σ. [c] $\sigma = a^2/D^2$, where a is the monomer size of 0.670 nm and $D = 2R$.

separately from the column. Although SEC is not usually associated with quantitative analysis, careful control over operating conditions, use of the appropriate (inert) internal standard, and careful calibration of the detectors render it quantitative. Linearity of both detectors was verified on polymer solutions of six different concentrations that spanned the range used in the grafting experiments. Instrument drift over long times contributed an increase of 1−2% to experimental measurements over a 24 h period. The UV and refractive index (RI) detectors analyzed for polystyrene and polyisoprene, respectively. Because the detectors were calibrated with respect to the all analytes and internals standards used and because the mass of the (inert) internal standard present did not change, *the area ratio of the elution band of the analyte to that of the internal standard in the chromatogram was proportional to the mass ratio of analyte to internal standard.* Division of mass of polymer grafted by its M_n and multiplication by Avogadro's number yielded the number of chains grafted, which was divided by the known surface area of the substrate to yield the grafting density, expressed as number of chains per unit surface area, chains/nm^2. We have previously established that values for chains/nm^2 obtained by the solution depletion method just described agree within 3% with values obtained by thermogravimetric analysis.[21]

This method was used for three different purposes: (a) to establish the grafting density of the preexisting brushes during their construction, (b) to quantitatively monitor the grafting of end-functionalized free chains to surfaces containing preexisting brushes, and (c) to check for possible disappearance by entanglement of inert-ended free chains exposed to preexisting brushes.

III. Results and Discussion

A. Screening Study for Selection of Systems. The scope of our investigation was constrained by the limited availability of monodisperse polymer with the appropriate functional end groups. To use the available material wisely, we conducted a screening study to identify fruitful combinations of molecular weight for free chains and preexisting brushes in subsequent experiments.

Table 2 shows the results of the screening study, in terms of whether or not grafting of the free chains occurred in the presence of the preexisting brush. The table reveals that grafting occurred only when the free chains were shorter than those in the brush, the single exception being the brush of lowest molecular weight, in the presence of which free chains of shorter *and* equal length were grafted. This preliminary study suggested that the best systems for further study would be those in which the identical free chains were shorter than the brush chains. Therefore, subsequent experiments involved preexisting brushes of $M_n = 90\,000$ g/mol and free chains of $M_n = 14\,500$ g/mol and, in a few cases, 44 000 g/mol. The screening study also established that grafting of free chains in the presence of a preexisting brush reached its final level well within 2 h; therefore, subsequent grafting experiments were run for 24 h, more than long enough to ensure completion. This surprising rapidity of grafting will be discussed later.

B. Description of Experimental Systems in Terms of Theoretical Quantities. To discuss our experimental results in the context of existing theoretical studies, we need to express the experimental quantities in the forms used in the theoretical studies. Theorists typically use the following dimensionless quantities: Φ_P^{bulk}, volume fraction of free chains in solution; N, degree of polymerization of grafted chains; P, degree of polymerization of free chains; and σ, reduced grafting density. Of all these, only σ requires discussion because it has also been used to designate nonreduced grafting density, i.e., chains/nm^2. When used in theoretical works to designate reduced grafting density, it is defined[5] as $\sigma = a^2/D^2$ and is dimensionless, running from 0 to 1.0. This definition is based on a chain-on-lattice model, in which a is the length of the basic lattice unit and D is the distance between grafting points. The value of the basic lattice unit is arbitrary and is typically taken to be a characteristic dimension within the polymer chain; we let $a = 0.670$ nm, the statistical segment length of polystyrene.[23,24] Since $D = 2R$, where R is the lateral radius of a grafted chain in the brush and is computed directly from the number of chains/nm^2, the value for the reduced grafting density was computed as $\sigma = a^2/(2R)^2$ for each preexisting brush used in our experiments.

While theorists can examine the full range of σ, from 0 to 1, experimentalists working with polymer brushes in solvent are limited to the very low end of this range. The upper limit, $\sigma = 1$, represents a grafting density so high that there is no room for solvent, and the grafted chains are stretched out nearly straight and packed closely as in a crystalline array, a physical state observed only for short alkyl chains in self-assembled monolayers on coinage metals. For polymer brushes in solvent, σ is much closer to zero.[25]

Table 3 presents values for grafting density, and for the corresponding reduced grafting density, of some typical polymer brushes prepared in the present study from end-functionalized polystyrene of $M_n = 90\,000$ g/mol. These values of grafting density span ∼1 order of magnitude. Also shown is the readily visualized quantity, $\pi R_g^2/\pi R^2$, where R_g is the radius of gyration of the relaxed (unstretched) chain in good solvent and R is the lateral radius of the stretched chain in the brush. (The lateral radius is computed from the area per grafted chain.) The ratio $\pi R_g^2/\pi R^2$ is always greater than one in a brush, where the chains avoid overlap by contracting laterally and extending away from the solid surface to which they are grafted. For the preexisting brushes in our work, this ratio ran from 1.61 to 11.0. For brushes constructed from dilute solution by means of the grafting-to approach, this range of values is fairly typical, as noted by Kent and Lee et al.[26] Their values of $\pi R_g^2/\pi R^2$ ranged from approximately 1.5 to 12 for polystyrene brushes attached to the

Table 4. Volume Fraction of Grafted Polystyrene Chains Comprising Preexisting Brushes

σ	Φ_N^0
0.001 32	0.0373
0.002 29	0.0541
0.005 08	0.0917
0.009 00	0.134

surface of ethyl benzoate (liquid−air interface). Their neutron reflectivity studies showed that brushes having values in this range, while not strongly stretched, are moderately stretched.

C. Confirmation That Experimental Systems Fall in Regime I. Before presenting the results of our experiments on the grafting of free chains, we wish to demonstrate that our experimental systems fell in regime I of Figure 1. For a system to fall in regime I, Φ_P^{bulk}, the volume fraction of the free chains in the bulk solution, must be less than Φ_N^0, the volume fraction of the grafted polymer chains in a grafted layer exposed to pure solvent of the same type used for the free chains. According to Gast and Leibler's mean-field calculations,[12] the volume fraction of grafted chains can be given by $\Phi_N^0 = (6/\upsilon)^{1/3}\sigma^{2/3}$, where σ is the reduced grafting density as previously defined and υ is the excluded volume parameter for the polymer in the solvent.[12] In most theoretical studies an athermal solvent is selected, for which the Flory interaction parameter, χ, is zero,[27] leading to an excluded volume parameter of 1.0 (from $\upsilon = 1 - 2\chi$). Toluene is not an athermal solvent for polystyrene, and for a dilute solution, $\chi = 0.40$,[28] leading to $\upsilon = 0.2$. The relation given above can be used to compute Φ_N^0 for the polystyrene preexisting brushes used in our investigation. The computed values of Φ_N^0 for a range of different experimental values of σ are shown in Table 4. The free chains used in our investigation, polystyrene and polyisoprene, are similarly well-solvated in toluene; for polyisoprene in toluene, $\chi = 0.31{-}0.35$,[28−30] which is comparable to the value of $\chi = 0.40$ just cited for polystyrene in toluene.[28] For the systems with polystyrene free chains, the experimental Φ_P^{bulk} values ranged from 1.30×10^{-4} to 5.31×10^{-4}, and for the systems with polyisoprene free chains, the experimental Φ_P^{bulk} values ranged from 2.6×10^{-4} to 1.08×10^{-3}. Since these Φ_P^{bulk} values were all ∼2 orders of magnitude smaller than the Φ_N^0 values shown in Table 4, we can be assured that our experimental systems fell well within regime I.

D. Status of Nongrafted Chains. The suggestion is often made that free chains could become entangled or trapped in the preexisting brush without actually being grafted and thereby could cause errors in the quantitative analysis of the grafted chains. We addressed this issue by conducting a set of experiments in which solutions of *inert-ended* free chains were exposed to preexisting polystyrene brushes ($M_n = 90\,000$ g/mol). Inert-ended chains in solution can exhibit the same diffusional motion as end-functionalized chains, moving through solution and penetrating the brush, but they cannot undergo grafting reactions once they reach the surface of the solid.

The results, presented in Table 5, show that even after 24 h of exposure to the solid substrate, the concentration of free chains in solution is virtually unchanged. This confirms that all chains not chemically grafted to the substrate are detected as part of the solution. The implications of this with regard to the grafting experiments are that the end-functionalized free chains will be detected as part of the solution unless the chemical reaction that grafts them to the surface takes place. As an aside, we note that end-functionalized free chains diffusing *completely* through the thickness of the brush and reaching the solid surface are likely to become grafted. There are two reasons for this. The first is that the ends of a chain explore space rapidly compared with the diffusion rate of the chain's center-of-mass, virtually ensuring that the functional end of a free chain that fully penetrates the brush will come within a bond distance of the solid surface. The second is that the chemical reaction between the amine functional end of the polymer chain and the reactive site (epoxide) on the surface is so facile that it is not rate-determining,[19,21] ensuring that all the functional ends reaching the surface will react immediately with it.

E. Preexisting Brushes and Chemically Identical Free Chains: Influence of Solution Concentration and Brush Density. Theory predicts that penetration by free chains will (a) increase with concentration of free chains in solution and (b) decrease with grafting density of the preexisting brush. An expression developed by Gast and Leibler expresses these predictions mathematically:[12] $\Phi_P^{\text{inlayer}} \cong \Phi_P^{\text{bulk}} \exp(-6^{1/3}\upsilon^{2/3}\sigma^{2/3}P)$, where the symbols on the right-hand side are as defined previously. The quantity Φ_P^{inlayer} is the concentration, expressed as volume fraction, of free chains inside the brush layer. (Φ_P^{inlayer} does not include the grafted chains comprising the brush itself.) To illustrate the predicted behavior, we used the relation above to generate the plots shown in Figure 2, of Φ_P^{inlayer} vs Φ_P^{bulk} for several different σ values of preexisting brushes in our experiments. If, according to the hypothesis stated in the Introduction, grafting behavior parallels the predictions of penetration theory, the experimental grafting data would be expected to form a family of curves qualitatively similar to Figure 2. It should be noted that chains/nm^2, the experimental data related to Φ_P^{inlayer}, cannot be converted directly to Φ_P^{inlayer} because the height of the preexisting brush layer is not known. However, the trends shown by the experimental data should be comparable to those in Figure 2.

The experimental data for grafting of free chains are plotted in Figure 3 as chains/nm^2 vs initial volume fraction of free chains in solution, Φ_P^{bulk}. In Figure 3, the free chains grafted (chains/nm^2) show an obvious rising trend with increasing solution concentration, in qualitative agreement with penetration theory. However, the behavior with respect to σ does not parallel theoretical predictions. The data do not form a *family* of five curves for the five fairly evenly spread values of σ, but fall into an upper and a lower group separated by a gap. Within each group there appears to be no sensitivity to σ.

A possible explanation of the insensitivity to σ might be found in the difference between our systems and systems in which free chains penetrate preexisting brushes attached to a *liquid* surface. Lee and Kent,[32] who used neutron reflectivity to study such systems in regime III, observed progressive reduction in penetration of brushes by free chains as σ was increased, in qualitative agreement with the theoretical predictions shown in Figure 2. An important feature of a preexisting brush attached to a liquid surface is its ability to establish lateral uniformity by adjusting the positions of the anchor blocks that attach the chains of the brush to the liquid surface. Notably, the theories that predict systematic decreases of penetration with increasing σ are all based on the assumption of lateral uniformity in the brush. The actual existence of lateral uniformity in brushes attached to a liquid surface may underlie the qualitative agreement of their behavior with theory. By contrast, a preexisting brush constructed by the grafting-to method, in which the chains are attached by means of irreversible chemical bonds to a solid surface, cannot establish lateral uniformity. The expected effect of nonuniformities, even mild ones, would be to disrupt the systematic effect of σ on penetration of the brush by free

Table 5. Concentration of Inert-Ended Free Chains in Solution[a] Exposed to Brushes

preexisting brush, grafting density, chains/nm^2 (σ)	free chains, type and mol wt, g/mol	initial concn of free chains in solution, normalized to 1.000	concn of free chains after 24 h, relative to initial
0.003 74 (0.001 32)	PS: 20 000	1.000 ± 0.0057[b]	1.001 ± 0.0035[b,c]
0.006 48 (0.002 29)	PS: 20 000	1.000 ± 0.0057[b]	1.002 ± 0.0038[b,c]
0.003 74 (0.001 32)	PS: 45 000	1.000 ± 0.0063[b]	1.016 ± 0.0052[b,c]
0.006 48 (0.002 29)	PS: 45 000	1.000 ± 0.0063[b]	1.012 ± 0.0042[b,c]
0.003 74 (0.001 32)	PI: 75 000[d]	1.000	1.028[c,e]
0.006 48 (0.002 29)	PI: 75 000[d]	1.000	1.026[c,e]

[a] Concentration of free chains in solution = 0.255 mg/mL or a volume fraction of 2.43 × 10^{-4}. [b] Average and standard deviation of three replicate experiments run concurrently. [c] Small increase in apparent concentration of free chains after 24 h is due only to baseline drift of detectors. [d] Although much higher molecular weight than its end-functionalized counterpart, this molecular weight was the only one available at the time of this study. [e] Result from a single experiment.

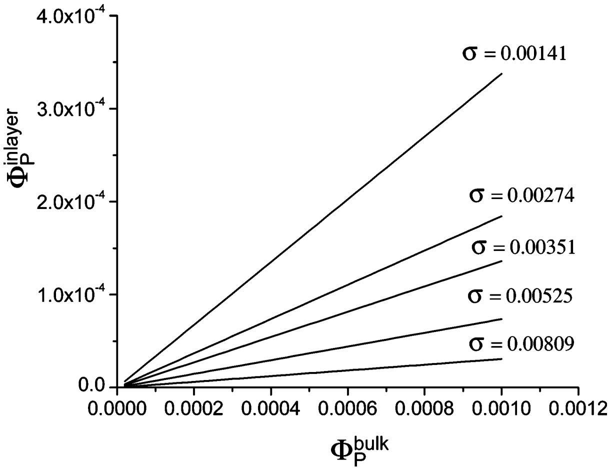

Figure 2. Theoretical plots for $\Phi_P^{inlayer}$ vs Φ_P^{bulk} computed for preexisting brushes of different reduced grafting densities, σ. Values used in computations were $P = 139$ ($M_n = 14\,500$ g/mol) and $\upsilon = 0.20$.

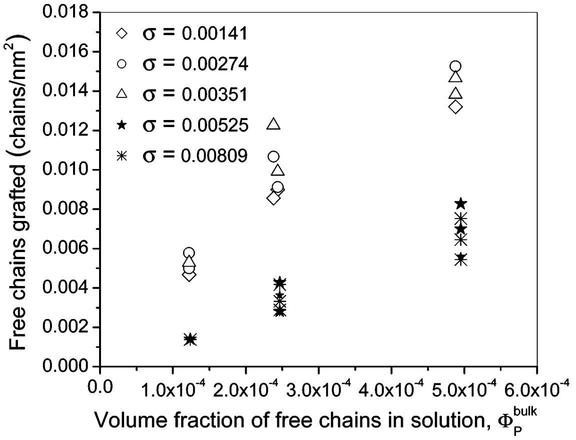

Figure 3. Free chains grafted vs Φ_P^{bulk} in the presence of preexisting polystyrene brushes ($M_n = 90\,000$ g/mol) of several different reduced grafting densities, σ. Free chains were end-functionalized polystyrene of $M_n = 14\,500$ ($P = 139$). Each point in plot represents an individual grafting experiment.

chains, perhaps to the extent that there is no apparent effect for preexisting brushes comprised of moderately stretched, not strongly stretched, chains. It is harder to conceive of an explanation for the gap that separates the data in Figure 3 into upper and lower groups is harder to explain. It is possible that there is a critical value of σ, and therefore of chain stretching in the preexisting brush, above which penetration is somewhat reduced. Obviously, this is an area that requires further investigation.

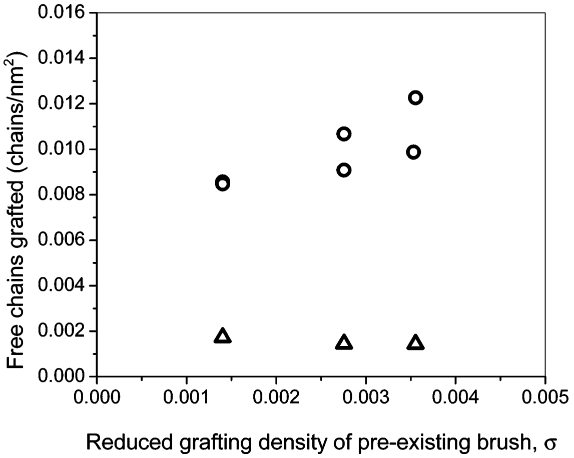

Figure 4. Free chains grafted vs reduced grafting density, σ, of preexisting polystyrene brushes of $M_n = 90\,000$ g/mol. Each point represents an individual grafting experiment. In all cases, $\Phi_P^{bulk} = 2.43 \times 10^{-4}$ (0.255 mg/mL). Open circles indicate free chains of $M_n = 14\,500$ g/mol, and open triangles indicate free chains of $M_n = 44\,000$ g/mol.

F. Preexisting Brushes and Chemically Identical Free Chains: Influence of Free Chain Molecular Weight. The theoretical relation presented previously for penetration of a brush by chemically identical free chains,[12] $\Phi_P^{inlayer} \cong \Phi_P^{bulk} \exp(-6^{1/3}\upsilon^{2/3}\sigma^{2/3}P)$, predicts that the volume fraction of free chains penetrating the brush should decline exponentially with P, the degree of polymerization of the free chains. With the amount of end-functionalized polystyrene that remained, we were able to make a very limited evaluation of the effect of P. We used free chains of two molecular weights: $M_n = 14\,500$ g/mol ($P = 139$) and $M_n = 44\,000$ g/mol ($P = 423$). The results are presented in Figure 4, which shows an average of 0.010 chains/nm^2 grafted for $P = 139$ and an average of 0.0018 chains/nm^2 grafted for $P = 423$. When converted to mass grafted per unit area, which is directly related to $\Phi_P^{inlayer}$, these values are 0.241 and 0.132 mg/m^2 for $P = 139$ and $P = 423$, respectively. This is a reduction of only 45% in mass grafted for the given increase in P, whereas the theoretical relation[12] for $\Phi_P^{inlayer}$ predicts a reduction of nearly 3 orders of magnitude for the same increase in P. These results show that free chain molecular weight plays a les important role in grafting than in penetration theory.

Another significant aspect of Figure 4 is the virtually horizontal pattern of the grafting data, indicating insensitivity of both molecular weights to σ. This was already noted in Figure 3 for $M_n = 14\,500$ g/mol, but now it is shown in Figure 4 for $M_n = 44\,000$ g/mol, as well. This lends credence to the idea that insensitivity of grafting to σ is general for moderately stretched brushes attached irreversibly to a solid surface.

G. Preexisting Brushes and Chemically Different Free Chains: Influence of Solution Concentration and Brush Density. The last item addressed in our investigation was our

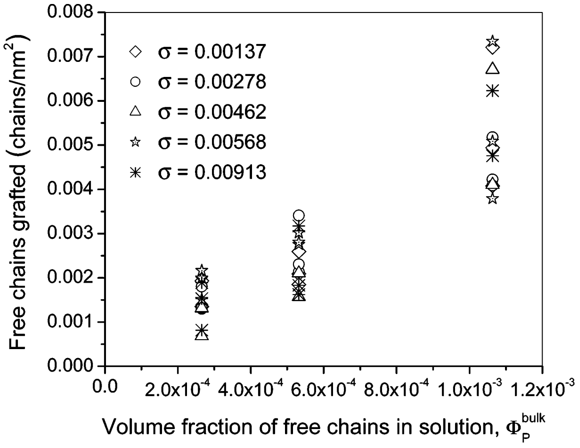

Figure 5. Free chains grafted vs Φ_P^{bulk} in the presence of preexisting polystyrene brushes (M_n = 90 000 g/mol) of different reduced grafting densities, σ. Free chains were end-functionalized polyisoprene of M_n = 45 000 g/mol, about 50% longer than the brush chains. Each point represents an individual grafting experiment.

own postulate that free chains longer but more flexible than the chains in the preexisting brush would be able to penetrate it and become grafted. We chose polyisoprene, whose chemical structure makes it inherently more flexible than polystyrene, as indicated by the fact that polyisoprene is an elastomer and polystyrene is a rigid plastic at room temperature. The polyisoprene free chains used in our investigation were considerably longer than the polystyrene chains comprising the preexisting brushes. An estimate of contour length based on number of C−C bonds in the backbone shows that end-functionalized polyisoprene free chains of M_n = 45 000 g/mol are ~50% longer than the polystyrene chains of M_n = 90 000 g/mol. Penetration theory, built on free chains and brush chains of the same chemistry, is framed in terms of chain length expressed as degree of polymerization. Expressed in terms of polystyrene monomer units, the degree of polymerization of the polyisoprene is P = 1342. We note that the R_g value for polyisoprene of M_n = 45 000 g/mol in good solvent is only 7.10 nm, comparable to polystyrene of similar molecular weight (see Table 2), but this has no bearing on the predictions of penetration theory, which are in terms of P.

The data from the grafting experiments done with polyisoprene free chains are shown in Figure 5. The fact that grafting did occur proves that the polyisoprene free chains completely penetrated the preexisting polystyrene brushes. This confirms our postulate that free chains longer than those comprising the brush will penetrate and become grafted if they are more flexible (and therefore not chemically identical) than those in the brush. Grafting (chains/nm^2) shows a distinct rising trend with solution concentration, in qualitative agreement with the predictions of penetration theory. However, contrary to theory, the 7-fold increase in σ in Figure 5 has no commensurate effect on the grafting of free chains, i.e., no effect larger than the random variation among replicate experiments. This lack of sensitivity of polyisoprene free chains to σ adds strength to the previous suggestion that theory may have failed to recognize some important features of the penetration process when the chains of the preexisting brush are irreversibly attached to a solid surface.

H. Rate of Grafting in the Presence of Preexisting Brushes. All of our experiments on grafting of free chains in the presence of preexisting brushes were conducted in dilute solution, and the grafting reached its final level well within 2 h. This surprisingly short amount of time was barely more than that required for the formation of a mushroom layer from dilute solution, on a *bare* surface.[1,19] Furthermore, the number of free chains grafted in the presence of preexisting brushes in our experiments was nearly equal to the grafting densities of mushroom layers formed on bare surfaces by these chains in previous studies.[1,33,34] Table 6 compares the grafting densities of mushroom layers with the grafting densities of some of the free chains in the present investigation.

Table 6. Grafting Densities of End-Functionalized Polystyrene on Bare Surface and in the Presence of Preexisting Brush

M_n, g/mol	Φ_P^{bulk}	mushroom layer on bare surface, chains/nm^2	in presence of preexisting brush, chains/nm^2
14 500	2.43 × 10^{-4}	0.014 ± 0.001[a]	0.010 ± 0.0015 [b]
44 000	2.43 × 10^{-4}	0.0013 ± 0.0002[a]	0.0019 ± 0.0002 [b]

[a] From refs 1 and 31. [b] For preexisting brushes with σ values from 0.001 41 to 0.003 51, from Figures 3 and 4.

The observation that grafting of free chains to a surface containing a preexisting brush takes approximately the same amount of time as formation of a mushroom layer on a *bare* surface is rather astounding and suggests that the perception of a brush as a barrier to diffusion needs reexamination. What it suggests is a process of facilitated diffusion in a solvated brush, caused by the stretched (even if only moderately stretched) nature of the chains already grafted.

In previous work,[19,21] we have observed evidence of a similar facilitated diffusion in the last stage of construction of simple polymer brushes. The first stage of construction was rapid formation of the mushroom layer on a bare surface. The second stage was one in which the mushroom layer acted as a sever diffusion barrier, and additional chains were grafted at an exceedingly low rate. In the third and last stage, grafting resumed speed and continued to saturation. The increased rate in the third stage was explained in terms of a facilitated diffusion associated with mutual and cooperative stretching of the free chain diffusing to the surface and the grafted chains immediately surrounding it.[19,21] Similarly, in the investigation described in the present paper, it is reasonable to think that the diffusion of the free chains through the preexisting brush to the grafting surface would be facilitated by the stretching of the free chains as they enter the moderately stretched chains of the brush.

Finally, we note that the ease of penetration of a preexisting brush by free chains is not in conflict with the well-known mutual repulsion of brushes attached to opposing surfaces. Penetration of one brush by another requires simultaneous diffusion of all of the chains of one brush into the other, an event that will not occur due to the huge entropy cost associated with it.

IV. Conclusions

We conducted experiments on the grafting of end-functionalized free chains from dilute solution to a solid surface bearing a preexisting polymer brush. The purpose was to determine the validity of our hypothesis that grafting behavior would parallel the theoretical predictions made for penetration of free chains into a preexisting brush. Control experiments showed that free chains are removed from the bulk solution only by being grafted to the solid surface and not by entanglement with the chains of the brush.

We found that some aspects of grafting behavior were consistent with the theoretical predictions of penetration theory. Specifically, the number of free chains grafted increased with increasing concentration of the bulk solution. This was true for free chains both chemically identical to and chemically different from the chains in the preexisting brush. We also showed that, in qualitative agreement with theory, the number of chains grafted per unit area of surface decreased with an increase in the molecular weight of the free chains, although the decrease was less pronounced than predicted by penetration theory.

We also found that free chains longer but more flexible (and therefore of different chemical structure) than the chains in the preexisting brush did become grafted, whereas chemically identical chains longer than the chains in the brush did not. In our case, the chemically different chains were polyisoprene, about 50% longer than the polystyrene chains comprising the brush. For these flexible free chains, grafting also increased with solution concentration, as observed for chains chemically identical to the brush.

Unexpectedly, and contrary to our hypothesis, the effect of the reduced grafting density, σ, of the preexisting brush did not parallel penetration theory. Instead of decreasing exponentially with σ, grafting of the free chains appeared to have little to no sensitivity to σ. The reason for this was not clear, but it was notable that the insensitivity was observed for free chains of three different molecular weights and two different chemical structures. This unexplained behavior suggests that there are aspects of penetration that have not been identified by theory and also suggests a direction for future experiments. The preexisting brushes we prepared were neither strongly stretched nor laterally perfectly uniform, attributes that might contribute to the absence of a strong effect of σ on the grafting behavior of free chains.

One of the most surprising findings of our investigation was that the free chains penetrated the preexisting brush and became grafted so rapidly—almost as rapidly as free chains become grafted to a bare surface to form a mushroom layer. Such rapid grafting indicates that the preexisting brush does *not* constitute a strong barrier to diffusion of free chains through it. This apparent facilitated diffusion might be explained by the anisotropic nature of the preexisting brush, which might offer a more channel-like pathway, normal to the surface, for free chains to use in diffusing through the brush to the solid surface.

In sum, our experiments on grafting of end-functionalized chains from solution to a solid bearing a preexisting polymer brush have elucidated some of the behavior previously only addressed by theoretical predictions of penetration of brushes by free chains.

Acknowledgment. This work was supported in part by a grant (CTS0218977) from the National Science Foundation.

References and Notes

(1) Huang, H.; Penn, L. S.; Quirk, R. P.; Cheong, T. H. *Macromolecules* **2004**, *37*, 5807−5813.

(2) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983−987.

(3) Zhulina, E. B.; Semenov, A. N. *Polym. Sci. USSR* **1989**, *31*, 196−204.

(4) Wijmans, C. M.; Factor, B. J. *Macromolecules* **1996**, *29*, 4406−4411.

(5) DeGennes, P. G. *Macromolecules* **1980**, *13*, 1069−1075.

(6) Aubouy, M.; Frederickson, G. H.; Pincus, P.; Raphael, E. *Macromolecules* **1995**, *28*, 2979−2981.

(7) Shull, K. R. *J. Chem. Phys.* **1991**, *94*, 5723−5738.

(8) Shull, K. R. *Macromolecules* **1996**, *29*, 2659−2666.

(9) Lecourtier, J.; Audebert, R.; Quivoron, C. *Macromolecules* **1979**, *12*, 141−146.

(10) Aubouy, M.; Raphael, E. *Macromolecules* **1994**, *27*, 5182−5186.

(11) Gast, A. P.; Leibler, L. *J. Phys. Chem.* **1985**, *89*, 3947−3949.

(12) Gast, A. P.; Leibler, L. *Macromolecules* **1986**, *9*, 686−691.

(13) Zhulina, E. B.; Borisov, O. V.; Brombacher, L. *Macromolecules* **1991**, *24*, 4679−4690.

(14) Wijmans, C. M.; Zhulina, E. B.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3238−3248.

(15) Martin, J. I.; Wang, Z. G. *J. Phys. Chem.* **1995**, *99*, 2833−2844.

(16) Grest, G. S. *J. Chem. Phys.* **1996**, *105*, 5532−5541.

(17) Pepin, M. P.; Whitmore, M. D. *J. Chem. Phys.* **2001**, *114*, 8181−8195.

(18) Huang, H.; Penn, L. S.; Quirk, R. P.; Cheong, T. H. *Macromolecules* **2004**, *37*, 516−523.

(19) Huang, H.; Rankin, S. E.; Penn, L. S.; Quirk, R. P.; Cheong, T. H. *Langmuir* **2004**, *27*, 5770−5775.

(20) Lin, R.; Wang, H.; Kalika, D. S.; Penn, L. S. *J. Adhes. Sci. Technol.* **1996**, *10*, 327−339.

(21) Penn, L. S.; Huang, H.; Sindkhedkar, M.; Rankin, S. E.; Chittenden, K.; Quirk, R. P.; Mathers, R. T.; Lee, Y. *Macromolecules* **2002**, *35*, 7054−7066.

(22) Huang, H.; Penn, L. S. *Macromolecules* **2005**, *38*, 4837−4843.

(23) Fetter, L. J.; Lohse, D. J.; Witten, T. A.; Zirkel, A. D. *Macromolecules* **1994**, *27*, 4639−4647.

(24) Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*; CRC Press: Boca Raton, FL, 2007; Chapter 6.

(25) For polystyrene of $M_n = 90\,000$ g/mol in good solvent, $R_g = 11.7$ nm. Therefore, the lateral surface area occupied by one relaxed (mushroom) chain is $\pi R_g^2 = 430$ nm^2. A mushroom layer, i.e., a surface filled with relaxed chains, corresponds to $\sigma = 0.000\,819$. This can be compared with $\sigma = 0.010$, a value that seems small but actually represents an extremely dense brush, with each chain occupying 8.76 nm^2 of surface area. Thus, ~50 highly stretched chains would be squeezed into the surface area normally occupied by a single mushroom.

(26) Kent, M. S.; Lee, L. T.; Factor, B. J.; Rondelez, F.; Smith, G. S. *J. Chem. Phys.* **1995**, *193*, 2320−2324.

(27) Chanda, M. *Advanced Polymer Chemistry, A Problem Solving Guide*; Marcel Dekker: New York, 2000; Chapter 3, pp 174−175.

(28) Duda, J. L.; Vrentas, J. S.; Ju, T. S.; Liu, H. T. *AIChE J.* **1982**, *28*, 279−285.

(29) Tewari, Y. B.; Schreiber, H. P. *Macromolecules* **1972**, *5*, 329−331.

(30) Tseng, H. S.; Lloyd, D. R.; Ward, T. C. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 161−170.

(31) Romdhane, I. H.; Danner, R. P. *J. Chem. Eng. Data* **1991**, *36*, 15−20.

(32) Lee, L. T.; Kent, M. S. *Phys. Rev. Lett.* **1997**, *79*, 2899−2902.

(33) Huang, H. Dissertation for the Ph.D., University of Kentucky, Lexington, KY, 2004.

(34) Penn, L. S.; Hunter, T. F.; Lee, Y.; Quirk, R. P. *Macromolecules* **2000**, *33*, 1105−1107.

MA060623I