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## Evidence for Relative Radius of Gyration as the Criterion for Selective Diffusion Behavior of Polymer Brushes

Hyun-Su Lee and Lynn S. Penn\*

Department of Chemistry, Drexel University, 305 Disque Hall, 3141 Chestnut Street, Philadelphia, Pennsylvania 19104

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When exposed to a dilute solution of free species, the polymer brush functions as a selective barrier to diffusion. Experiments with linear polymer chains and dendrimers of various sizes demonstrated that the selection criterion is relative size, i.e., radius of the free species (radius of gyration for linear chains and simple radius for dendrimers) relative to the radius of gyration of the chains composing the brush. This suggests that linear chains do not necessarily assume extended conformations as they diffuse into a brush but have conformations similar to those of nanoscale spherical inclusions.

### Introduction

The behavior and characteristics of polymer brushes have been of interest for 30 years. For many years, descriptions of brush conformation and penetration by free chains were addressed more by theory than experiment. Scaling analyses,<sup>1–3</sup> self-consistent field theory (and lattice versions thereof),<sup>3–9</sup> and, more recently, simulations,<sup>9</sup> have been used to describe systems composed of grafted linear chains and chemically identical free chains in good solvent.

While differing in detail, all of the theoretical treatments concluded that the conformation of the grafted layer (brush) and the penetration of it by free chains depended on: (1) the degree of polymerization of the free chains,  $P$ , with respect to that of the brush chains,  $N$ ; (2) the concentration of the free chains in solution compared with that of the grafted chains in the brush layer,  $\phi_P$  vs  $\phi_N$ ; and (3) the grafting density,  $\sigma$ , of the brush itself. The theoretical papers discuss the three-component system (grafted chains, free chains, and good solvent) in terms of a state diagram composed of at least three regimes. In regime I, where  $\phi_P \ll \phi_N$ , the volume fraction of free chains inside the grafted layer is predicted to be exponentially small and the conformation of the brush to be unperturbed from its conformation in pure solvent. In regime II, where  $\phi_P$  increases to a value close to  $\phi_N$ , the number of free chains penetrating the brush is predicted to remain exponentially small, but the grafted layer is predicted to contract in response to the increased osmotic pressure of the bulk solution. In regime III, where  $\phi_P \gg \phi_N$ , the free chains are predicted to penetrate the grafted layer in large numbers, screening the excluded volume interactions between grafted chains and causing the layer to contract.

Among the few experimental studies of penetration by free chains have been those of Lee, Kent, et al.,<sup>10–12</sup> who studied regime III. Subjecting a system of polystyrene free chains in contact with *semi*-dilute solutions of free polymer chains to neutron reflectivity, they provided direct experimental evidence for the penetration of large numbers of free chains into the brush. For  $P < N$ , they observed complete penetration of free chains into the brush, and for  $P > N$ , they observed partial penetration. These experimental results led to improvement in the theoretical treatments of regime III.<sup>8,9</sup>

Regime I has not received as much attention from theorists as regime III has, probably because free-chain penetration is predicted to be exponentially small. However, our recent experiments on regime I, done on systems composed of polystyrene grafted chains, polystyrene free chains (each with one functional end that could react irreversibly with the grafting surface), and toluene solvent, showed behavior more interesting than that predicted by theory.<sup>13,14</sup> These experiments showed that free chains shorter than the grafted chains ( $P < N$ ) diffused rapidly into the brush and became grafted, occupying volume fractions in the brush more than 2 orders of magnitude higher than in the bulk solution,<sup>15</sup> and well above the “exponentially” small amount predicted by theory for regime I. By contrast, we found that free chains longer than the grafted chains ( $P > N$ ) were prevented from penetrating the brush. These experimental results suggest that the polymer brushes in regime I can be seen as selective barriers to penetration by free species and that the selection criterion is based on size.

\*Corresponding author. Telephone: 215-895-4970. E-mail: lynn.s.penn@drexel.edu.

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(15) Volume fractions of free chains within brushes were computed from previously published experiments.<sup>13,14</sup> For example, the volume fraction of polystyrene in a brush composed of chains of  $M_n = 50\,000$  g/mol in toluene, having a grafting density of 0.107 chains/nm<sup>2</sup> (885 ng/cm<sup>2</sup>) and a brush height of 43 nm, was  $\sim 0.20$ . Free polystyrene chains of  $M_n = 25\,000$  g/mol that penetrated and became grafted at a density of 0.0426 chains/nm<sup>2</sup> (35.4 ng/nm<sup>2</sup>) occupied a volume fraction of  $\sim 0.0078$ . Free polystyrene chains of  $M_n = 5000$  that penetrated and became grafted at a density of 0.0526 chains/nm<sup>2</sup> (43.7 ng/cm<sup>2</sup>) occupied a volume fraction of  $\sim 0.0097$ . The volume fraction of the free polymer in the contacting bulk solution was  $\sim 10^{-5}$ .

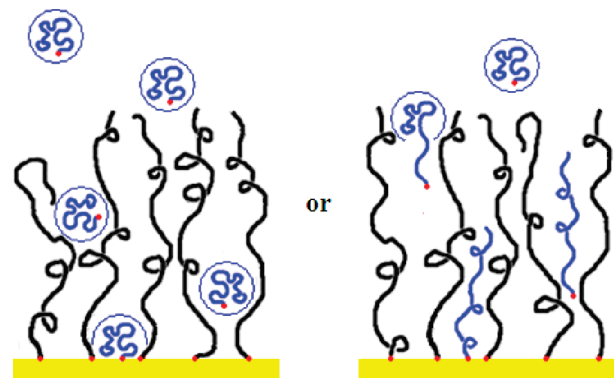
When the free chains in solution are chemically identical to the chains of the brush, size can be expressed as degree of polymerization, and the relative values of  $N$  and  $P$  can be used for prediction of penetration behavior. However, when the free chains and brush are not chemically identical, degree of polymerization as a size criterion makes no sense, because the monomers are of different sizes. For potential practical exploitation of the phenomenon of selective penetration, a measure of size is needed that is physicochemically meaningful and that gives reliable predictions, independent of chemical structure.

Two measures of size or dimension that can be computed and that have physicochemical meaning are the radius of gyration,  $R_g$ , and the contour length,  $l_c$ . When a flexible linear polymer chain diffuses to the grafting surface after having entered the brush from dilute solution, two scenarios can be envisioned, both depicted in Figure 1.

The first scenario is that the randomly coiled flexible chain, which occupies a spherical volume in solution, remains in a spherical geometry not only as it enters the brush but also as it diffuses through the brush to the grafting surface. The chains of the brush, grafted to fixed points on the surface, have limited ability to move aside and make a pathway for incoming coiled free chains. Therefore, large coiled free chains would be expected to have more difficulty reaching the grafting surface than small coiled free chains would. For this scenario,  $R_g$  might be relevant as a measure of size that could be used to predict whether or not the free polymer would fully penetrate the brush. The second scenario is one in which the coiled free chain, upon entry into the brush, would begin to extend its backbone in a direction parallel to the stretched chains of the brush. Because the entropy cost of stretching is higher for longer chains, there could be an entropy barrier to penetration that is insurmountable for free chains over a certain length. For this scenario,  $l_c$  might be relevant as a measure of size that could be used to predict whether or not the free polymer would fully penetrate the brush until one end reached the grafting surface. Because the conformation(s) assumed by a free chain as it diffuses within a brush is not known, the appropriateness of  $R_g$  versus  $l_c$  is not obvious.

The goal of the present study was to identify the measure of size that correctly predicts the penetration of free chains through a brush and to demonstrate that it is appropriate no matter what the chemical identity of the diffusing species. Identifying the relevant measure of size would give insight into the conformation required of free species to diffuse through a brush. To achieve this goal, we conducted penetration studies involving free chains *not* chemically identical to the brush, followed by experiments with dendrimers, which are constrained to an approximately spherical geometry, the size of which is described by a radius.

The quartz crystal microbalance (QCM) technique, which we used to monitor the formation of the brushes and the subsequent penetration of them by free species in solution, warrants some explanation. This technique is based on the change in resonant frequency of a vibrating disk of  $\alpha$  quartz, which is a piezoelectric material, when mass is deposited on or grafted to it.<sup>16–21</sup> The instrument reports not only changes in the frequency of the



**Figure 1.** Illustration of free chains diffusing into brush in the coiled, spherical geometry (left) and in the uncoiled, stretched geometry (right).

fundamental vibrational mode and selected overtones but also reports the dissipation of vibrational energy.

When the deposited layer is elastic, as in an ultrathin and rigid material, dissipation is negligible, and the change in vibrational frequency can be converted directly to mass deposited by means of the Sauerbrey equation<sup>16</sup>

$$\Delta m = -C \frac{\Delta f_n}{n},$$

where  $\Delta m$  is the change in mass,  $C$  is the mass sensitivity constant ( $C = 17.7 \text{ ng} \cdot \text{cm}^{-2} \cdot \text{Hz}^{-1}$  for an AT-cut, 5 MHz crystal), and  $\Delta f_n$  is the change in frequency of the  $n$ th vibrational mode.

When the deposited layer has viscous character, i.e., is viscoelastic, the Sauerbrey equation gives an overestimate of mass deposited,<sup>22–30</sup> because the frequency change is greater than expected for added mass alone. Layers that are thick and highly solvated, such as polymer brushes, are usually viscoelastic. However, some types of polymer brushes can be collapsed by a nonsolvent into a thin, elastic layer.<sup>14</sup> Then the accurate mass of this collapsed layer can be computed from the Sauerbrey equation. Two features of the QCM response indicate that a deposited layer is elastic.<sup>20,21</sup> They are as follows: (a) superposed plots of  $\Delta f_n/n$  versus time for all measurable vibrational modes, and (b) dissipation,  $D$ , that is less than  $2.0 \times 10^{-6}$ .  $D$  is the ratio of energy dissipated to energy stored in a vibration cycle, and thus is a unitless quantity. If the plots of  $\Delta f_n/n$  are not superimposed, and if the  $D$ -values are greater than  $2.0 \times 10^{-6}$ , the layer is viscoelastic. Additional information about the physical characteristics (e.g., thickness, viscosity, shear modulus and density) of any layer, collapsed or not collapsed, can be obtained by means of curve-fitting procedures based on the Voigt mechanical model.<sup>25,26</sup>

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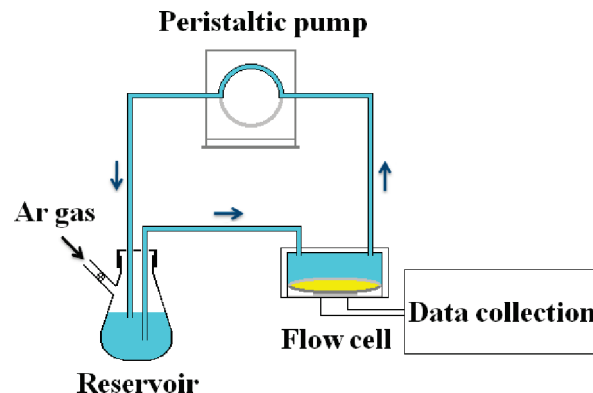
## Experimental Procedures

**Materials.** All linear polymers, which included thiol-ended polystyrene (HS-PS), thiol-ended polyethylene oxide (HS-PEO), methoxy-ended polyethylene oxide (CH<sub>3</sub>O-PEO), and primary amine-ended polyethylene oxide (H<sub>2</sub>N-PEO), were monodisperse ( $M_w/M_n \leq 1.08$ ) and were purchased from Polymer Source, Inc. (Dorval, Quebec). Polyamidoamine (PAMAM) dendrimers (PDI < 1.01) with primary amine terminal groups were obtained from Dendritic Nanotechnologies, Inc., Mount Pleasant, MI. The 11-mercaptodecanoyl-*N*-hydroxysuccinimide ester, used to derivatize the gold surface, was purchased from ProChemia, Gdansk, Poland. HPLC-grade methanol (>99.9%) and HPLC-grade toluene (>99.9%) were purchased from the Aldrich Chemical Co. Anhydrous ethanol (>99.9%) was from Pharmco-Aaper, Shelbyville, KY.

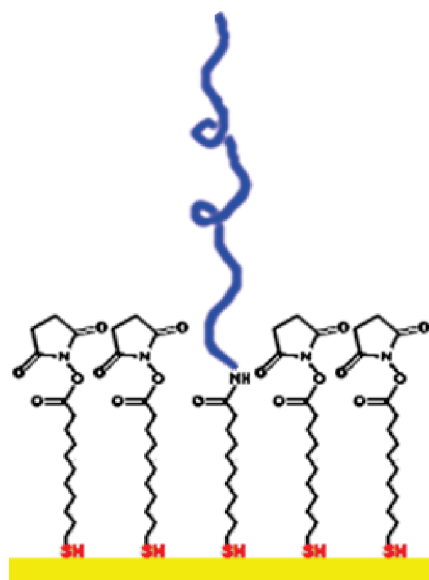
**QCM Operation.** A quartz crystal microbalance (E4 QCM model from Q-Sense Inc., Gothenburg, Sweden) was used to monitor both the formation of polymer brushes and the penetration of them by free chains. Figure 2 shows a diagram of the QCM system. The sensitivity of the instrument was 1.77 ng/cm<sup>2</sup> (0.1 Hz) of mass deposited. A thin gold coating on the quartz provided a surface to which thiol end-functionalized chains or thiol-containing molecules could be attached. The gold-coated, quartz crystal was clamped within a flow cell through which the solvent or solution of interest was forced by means of a peristaltic pump at a rate of 35  $\mu$ L/min. Because of the high sensitivity of the QCM to transient effects, all solvents were freshly distilled, degassed, and filtered under argon to remove moisture, O<sub>2</sub>, and small particles. The temperature of the system was controlled to 21 °C, and the liquid reservoir was protected at all times by a blanket of argon. All polymer solutions were extremely dilute, having concentrations of approximately 1  $\mu$ M. Typically, two replicate experiments were run at the same time in side-by-side flow cells to check for reproducibility.

**Formation of Polymer Brushes.** Polystyrene brushes were formed directly on the gold-coated, quartz crystal in the QCM by exposing it to a dilute toluene solution of the thiol-ended-PS of the desired  $M_n$ . PS brushes formed spontaneously and were monitored continuously with QCM until saturation (no further grafting of chains) was reached. The polyethylene oxide brushes used in experiments involving dendrimers had to be formed on a surface derivatized with a self-assembled monolayer of 11-mercaptodecanoyl-*N*-hydroxysuccinimide ester ( $3.64 \pm 0.32$  alkane thiols/nm<sup>2</sup>), deposited from ethanol solution. This was because primary amine-terminated dendrimers do not attach well to the bare gold surface but do react readily with the succinimide ester group. Because of this derivatization, the PEO chains used to form the brushes also had to be primary amine-ended (see Figure 3). Hence, the PEO brushes were formed by exposing the derivatized surface to a dilute toluene solution of the amine-ended PEO of the desired  $M_n$ . PEO brushes formed spontaneously and were monitored continuously with QCM until they had reached saturation.

**Collapse of Polystyrene Brushes into an Ultrathin, Elastic Layer.** Polystyrene brushes were collapsed *in situ* (in the flow cell) by change of solvent to convert them into ultrathin, elastic layers as described in ref 14. The solvent was switched from toluene, a good solvent for polystyrene, to a 4/3 mixture by volume of methanol/toluene, a nonsolvent for polystyrene. This nonsolvent was discovered by trial and error,<sup>14</sup> and it met the requirement imposed by us of leaving the vibrational frequency of the bare gold-coated crystal unchanged from that in pure toluene. The absence of solvent effect on frequency of the bare crystal meant that any frequency changes observed upon collapse of the brush could be attributed entirely to the change in conformation of the brush and not to change of solvent. Polystyrene brushes collapsed in this manner met the criteria described in the introduction for an elastic layer, so that the Sauerbrey equation could be used to convert frequency change to mass. Values for mass/area were



**Figure 2.** Circulating system of QCM for real-time monitoring of formation and behavior of polymer brush on gold-coated crystal inside the flow cell.



**Figure 3.** Surface chemistry for grafting amine-ended PEO chains.

converted to chains/area with the aid of the  $M_n$ -values of the various polystyrene brushes. After they were collapsed for mass determination, the polystyrene brushes were restored to their brush-like conformation by a switch of solvent back to toluene. The polyethylene oxide brushes could not be collapsed, because no appropriate nonsolvent could be found.

**Penetration Experiments.** Penetration experiments were done *in situ*, with continuous monitoring of frequency and dissipation and without removing the crystal containing the prepared brushes from the flow cell of the QCM.

**Penetration of Polystyrene Brushes by Free Polyethylene Oxide Chains.** Polystyrene brushes were exposed to dilute ( $\sim 1 \mu$ M) solutions of free chains of polyethylene oxide in toluene. Exposures of several hours allowed ample time for penetration, after which the brushes were rinsed in pure solvent. Some control experiments were conducted in which the PEO free chains were inert-ended rather than thiol-ended.

**Penetration of Polyethylene Oxide Brushes by Dendrimers.** Polyethylene oxide brushes were exposed *in situ* in the QCM to dilute ( $\sim 1 \mu$ M) solutions of dendrimers in ethanol. Although the brushes were prepared in toluene, ethanol was used for the penetration studies because the PAMAM dendrimers are insoluble in toluene. Exposures of several hours were conducted to allow ample time for penetration, after which the brushes were rinsed in pure solvent.



## Results and Discussion

**Characteristics of Brushes.** The characteristics of the polystyrene and polyethylene oxide brushes used in penetration experiments are presented in Table 1. Because we were able to collapse the polystyrene brushes into an ultrathin, elastic layer, as described above in the experimental section, we were able to use the Sauerbrey equation to compute the mass of the collapsed layer. The values computed from this mass are listed in Table 1. Unfortunately, we were not able to collapse the PEO brushes, because we were not able to find an appropriate nonsolvent; as a result, Table 1 reports no values for mass-related quantities of the PEO brushes. The last column in Table 1 is the height of the (noncollapsed) brushes used in this study. Brush height was determined by means of a computational, curve-fitting program included in the QCM instrument. The mathematical description of a viscoelastic layer that has a frequency-dependent response to oscillating vibration is based on the well-known Voigt element, which is composed of a spring and a dashpot in parallel.<sup>25</sup> The spring, with its elastic shear modulus,  $\mu$ , and the dashpot, with its viscosity,  $\eta$ , represent the elastic and viscous character of the layer (subscript  $l$ ) attached to the surface of the vibrating crystal. These values, along with values for  $\rho_l$  (density of the layer) and  $d_l$  (height of the layer) are inserted into the fitting program as initial guesses. Also inserted into the program are the known values of density,  $\rho_b$ , and viscosity,  $\eta_b$ , of the semi-infinite bulk liquid (subscript  $b$ ) in contact with the viscoelastic layer on the vibrating crystal. The last two values can be measured or looked up. Starting with the initial guesses for the unknown values, the program generates simulated curves for  $\Delta f_n/n$  and  $D$  versus time, and performs iterations until a fit with the experimental curves is achieved. Once a fit has been achieved, the physical and geometric parameters, including height, that produced the fitted plots can be taken as the actual layer characteristics. This curve fitting process yields values that compare favorably with values obtained by other means. In one case, curve fitting yielded height values for thick, viscoelastic layers within 13% of those determined directly by means of ellipsometry.<sup>26</sup> In another case, the curve fitting process yielded height values for collapsed brushes (thin and elastic) within 10–15% of those computed directly from mass per unit area and bulk density.<sup>14</sup>

There are several different indications that the grafted layers described in Table 1 are indeed brushes. Most important is the fact that the values for brush height are considerably larger than the radii of gyration,  $R_g$ , of the corresponding chains floating freely in good solvent. This means that the grafted chains are stretched away from the grafting surface, behavior characteristic of a brush. The second indication is that the values of  $R$ , where it was possible to compute them, are less than the corresponding radii of gyration,  $R_g$ .  $R$  is the lateral radius of a grafted chain in the layer, computed from the measured grafting density; when  $R < R_g$ , the grafted chains in the layer are laterally compressed, also the hallmark of a brush. A visualizable quantity is provided by the ratio,  $\pi R_g^2/\pi R^2$ , which represents the number of grafted chains occupying the lateral area normally occupied by a single isolated and nondeformed grafted chain, termed a mushroom. The high values of this ratio indicate considerable crowding, also characteristic of polymer brushes.

**Penetration Experiments with Polyethylene Oxide Free Chains.** Table 2 presents the measures of size for the brush chains and the free chains used in the penetration studies. When the values of  $R_g$  and  $l_c$  for the free chains are smaller than those of the brush chains, penetration is predicted, whereas for larger relative values no penetration is predicted.<sup>14</sup> The particular case in

**Table 1. Characteristics of Polymer Brushes Used in Penetration Studies**

polymer	mass grafted (ng/cm <sup>2</sup> ) <sup>a</sup>	grafting density (chains/nm <sup>2</sup> ) <sup>a</sup>	$R_g$ in toluene <sup>31</sup> (nm)	$R$ in toluene <sup>32</sup> (nm)	$\pi R_g^2/\pi R^2$	brush height (nm)
HS-PS-25K	729 ± 52	0.176 ± 0.012	5.7	1.3	18	16
HS-PS-50K	912 ± 33	0.111 ± 0.0040	8.4	1.7	24	43
H <sub>2</sub> N-PEO-5K			2.6			7.6
H <sub>2</sub> N-PEO-19K			5.4			10

<sup>a</sup> Average ± 1 std dev, for six replicate brushes prepared at different times.

**Table 2. Measures of Size for Experimental Systems**

polymer	$R_g$ , nm	$R_g^{\text{free}}/R_g^{\text{brush}}$	$l_c$ , nm	$l_c^{\text{free}}/l_c^{\text{brush}}$
<b>HS-PS-50K (brush)</b>	<b>8.4</b>		<b>148</b>	
CH <sub>3</sub> O-PEO-10K (free)	3.8	0.45	102	0.69
HS-PEO-10K (free)	3.8	0.45	102	0.69
HS-PEO-49K (free)	9.1	1.1	496	3.4
<b>HS-PS-25K (brush)</b>	<b>5.7</b>		<b>74</b>	
HS-PEO-10K (free)	3.8	0.67	102	1.4
HS-PEO-49K (free)	9.1	1.6	496	6.7
CH <sub>3</sub> O-PEO-51K (free)	9.3	1.6	519	7.0

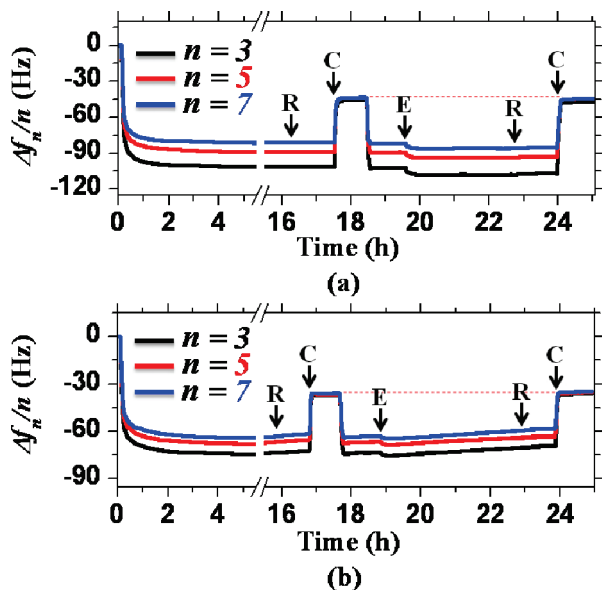
Table 2 that can differentiate  $R_g$  from  $l_c$  as a predictive measure is the case of HS-PS-25K brush exposed to HS-PEO-10 K free chains. For this case,  $R_g$  of the free chains is smaller than the  $R_g$  of the brush, but  $l_c$  of the free chains is larger than  $l_c$  of the brush, leading to a conflicting prediction. Thus, experiment must be relied upon to decide between these two quantities as predictive measures.

Figure 4 presents results of control experiments, in which the free chains were inert-ended and could not possibly become grafted. Data are presented in the form of continuous plots of  $\Delta f_n/n$  versus time, and in these and all subsequent experiments, the exposure to free chains was only one step of the complete time history of these systems. The features of the plots prior to the introduction of free chains are similar, and are described now. Starting at zero time, the rapid decrease in frequency depicts the formation of the brush on the bare gold surface. This was followed several hours later by rinsing (indicated by R), which caused no frequency change, thereby signifying that the chains of the brush were firmly attached to the grafting surface. Next was the introduction of nonsolvent (at C) to collapse the brush into a thin, elastic layer, so that the Sauerbrey equation could be used in the computation of mass. (The frequency of the collapsed brush with respect to zero was used in the Sauerbrey equation.) After an hour, the collapsed brush was restored to its stretched form by a switch back to good solvent, pure toluene. The results of exposures of the brushes to free chains are discussed separately, below, for each control experiment.

In Figure 4a, the letter E marks the introduction of a solution of CH<sub>3</sub>O-PEO-10K free chains to the flow cell containing a HS-PS-50K brush. These free chains were predicted to be small enough to penetrate (see Table 2) but, because of their inert ends,

(31)  $R_g$  is the radius of gyration in good solvent, computed from  $R_g = \alpha \sqrt{C_\infty/6(n^{1/2}l)}$ , where  $\alpha$  is the expansion factor of a polymer coil in good solvent,  $C_\infty$  is the characteristic ratio (10.8 for polystyrene and 4.25 for poly(ethylene oxide),  $n$  is the number of single bonds in the polymer backbone, and  $l$  is the length in nm of a single bond.

(32)  $R$  is the lateral radius of a circular cross-section of the stretched chain, computed from  $[(\text{chains/nm}^2)^{-1} \div \pi]^{1/2}$ .

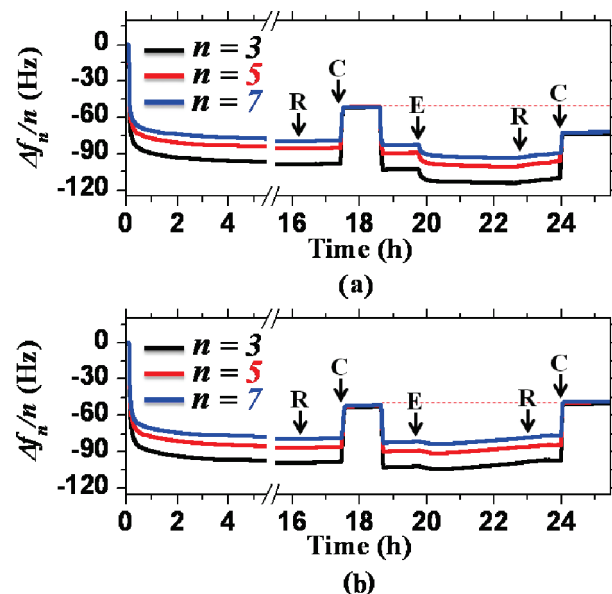


**Figure 4.** Plots of  $\Delta f_n/n$  versus time for control systems of inert-ended free chains. (a) HS-PS-50K brush and inert-PEO-10K free chains, (b) HS-PS-25K brush and inert-PEO-51K free chains. Start of exposure to free chains is marked by E at  $\sim 19$  h.

not to become grafted. A distinct decrease in frequency occurred at E, reflecting the presence of these nongrafted free chains within the layer. (Additional mass anywhere in the grafted layer will cause a change in frequency.) Subsequent collapse of the brush in nonsolvent, at about 24 h in Figure 4a, showed the same frequency as the first collapse, revealing that the grafting surface contained only the grafted chains of the brush and no additional chains. This is exactly what was expected for inert-ended free chains small enough to penetrate the brush but having no ability to become grafted.

The other control experiment, shown in Figure 4b, involved the introduction, at E, of CH<sub>3</sub>O-PEO-51K free chains to a HS-PS-25K brush. In addition to the inability of these inert-ended free chains to become grafted, they are predicted to be too large to penetrate the brush. The most important feature of Figure 4b is the second collapse of the brush, for which the frequency is the same as the first collapse, indicating that, as expected, the grafting surface contained only the grafted chains of the brush and no additional chains. A more subtle feature of Figure 4b is the faint decrease in frequency observed at E, which was unexpected for chains that were predicted to be too large to penetrate the brush. This could be an indication of partial penetration of the brush by the free chains. Partial penetration, not observed in our previous studies of polystyrene brushes exposed to polystyrene free chains,<sup>14</sup> might be enhanced by a weak but attractive interaction between the PEO free chains and the PS brush, possibly between the oxygen lone pairs on PEO and the aryl rings on the PS.<sup>33</sup> Nevertheless, these inert-ended free chains were not able to become grafted and were rinsed away by the mixed solvent used to collapse the brush.

Figure 5 presents results for exposure of brushes,  $M_n = 50\,000$  g/mol to thiol-ended free chains, which do have the capability to become grafted if they reach the grafting surface. The features of the time history of each system are the same as described for the control experiments. Exposure to free chains was started at E in the plots. In Figure 5a, which depicts exposure to thiol-ended free chains smaller (in terms of both  $R_g$  and  $l_c$ ) than the brush chains, there is



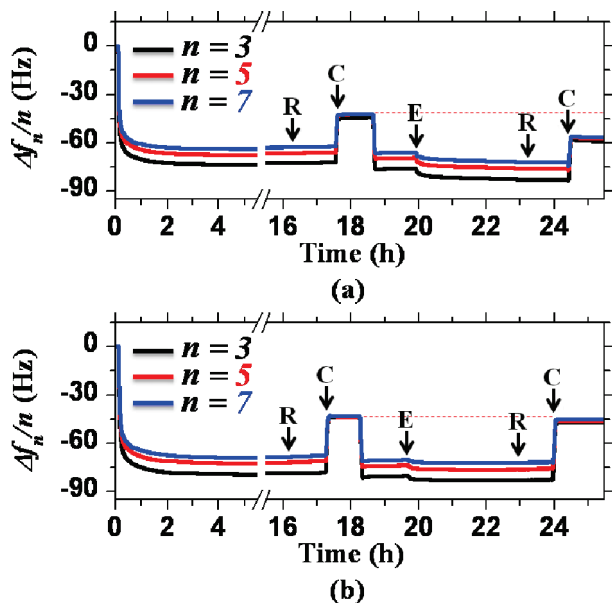
**Figure 5.** Plots of  $\Delta f_n/n$  versus time for polystyrene brushes of  $M_n = 50\,000$  g/mol exposed to thiol-ended chains. (a) HS-PS-50K brush and HS-PEO-10K free chains and (b) HS-PS-50K brush and HS-PEO-49K free chains. Start of exposure to free chains is marked by E at  $\sim 19.5$  h.

a large difference between the collapsed brush before and after exposure. This difference indicates that these free chains were able to penetrate the brush, reach the surface, and become grafted, as predicted from their size. In Figure 5b, which depicts exposure to thiol-ended free chains larger (in terms of both  $R_g$  and  $l_c$ ) than the brush chains, there is no difference between the collapsed brush before and after exposure. The absence of difference means that the large free chains were not able to reach the grafting surface and therefore were not able to become grafted, even though they had functional ends. This was the expected result for chains larger than the chains of the brush.

Figure 6 depicts results for brushes of  $M_n = 25\,000$  g/mol. As before, exposure to free chains was started at E in the time history of each experiment. The results shown in Figure 6 are qualitatively similar to those in Figure 5. The thiol-ended free chains in Figure 6(a) penetrated the brush, reached the surface, and were grafted, becoming a permanent part of the brush. This was the expected result from  $R_g$  but not from  $l_c$ , and this will be discussed below. By contrast, the thiol-ended free chains in Figure 6b, larger in terms of both  $R_g$  and  $l_c$  than the brush chains, did not diffuse through the brush to become grafted, which was the expected result.

It is the results in Figure 6a that answer the question of which measure of size is the relevant predictor of diffusion through a polymer brush. Recall that there were conflicting predictions from  $R_g$  and  $l_c$  for whether the HS-PEO-10K free chains would penetrate the HS-PS-25K brush.  $R_g$  predicted penetration and  $l_c$  predicted no penetration. Since penetration was observed experimentally, it can be concluded that  $R_g$  of the free chains relative to the  $R_g$  of the brush chains is the relevant measure of size to be used in predicting penetration. A previously studied experimental system in which conflicting predictions were given by  $R_g$  and  $l_c$  provides a supporting example, although at the time we did not realize its significance.<sup>13</sup> In this example, polystyrene brushes of  $M_n = 90\,000$  g/mol ( $R_g = 12$  nm,  $l_c = 267$  nm) were exposed to free isoprene chains of  $M_n = 45\,000$  g/mol ( $R_g = 7.1$  nm,  $l_c = 400$  nm). For this system,  $R_g$  predicts penetration and  $l_c$  predicts no penetration. Penetration was

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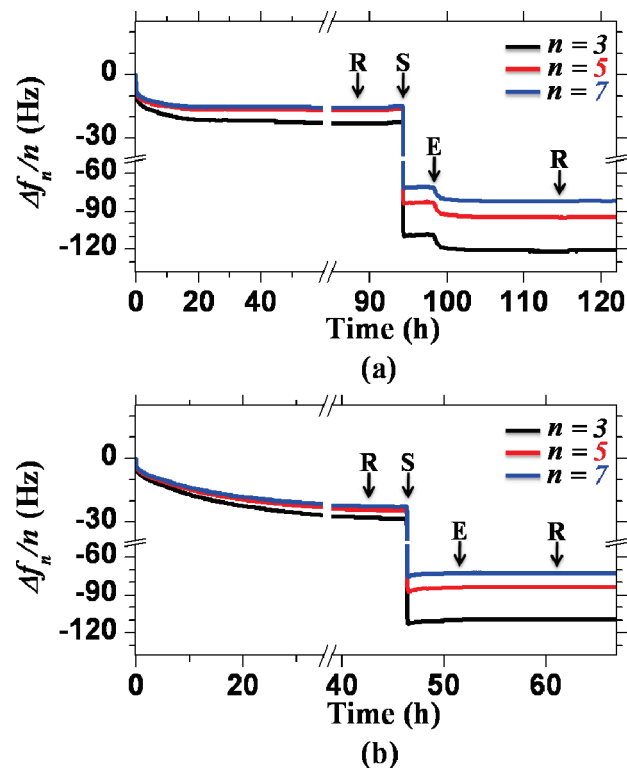
**Figure 6.** Plots of  $\Delta f_n/n$  versus time for polystyrene brushes of  $M_n = 25,000$  g/mol exposed to thiol-ended free chains. (a) HS-PS-25K brush and HS-PEO-10K free chains and (b) HS-PS-25K brush and HS-PEO-49K free chains. Start of exposure to free chains is marked by E at  $\sim 20$  h.

observed experimentally, again showing that  $R_g$  is the appropriate measure of size and not  $l_c$ .

To sum up, results obtained in our lab with polystyrene brushes exposed to polyethylene oxide free chains, polyisoprene free chains, and polystyrene free chains all showed that only free chains having  $R_g$  less than the  $R_g$  of the brush chains were able to penetrate the brush completely and reach the grafting surface. The consistency of these results with chemically different free chains suggests that the selective diffusion behavior is general. Limited availability of the kinds of well-controlled materials (end-functionalized, monodisperse, and pairwise-soluble) needed for penetration experiments makes it impossible to generate a wider database at the present time. However, we were able to extend our work to one more materials system — of somewhat different composition from the previous ones. In this system polyethylene oxide served as the brush, ethanol as solvent, and poly(amidoamine) (PAMAM) dendrimers as the free species.

**Penetration Experiments with PAMAM Dendrimers.** To corroborate the correctness of  $R_g$  as the measure of size for predicting penetration of a polymer brush, and also to demonstrate its universality, we exposed polymer brushes to large and small dendrimers. Being approximately spherical, dendrimers are typically characterized by a radius. The PAMAM dendrimer, in particular, is limited in its ability to assume conformations other than *approximately* spherical. Even when solvent conditions are changed, this dendrimer remains approximately spherical.<sup>34</sup> As Table 3 shows, dendrimers with radius ( $R_d$ ) values both smaller and larger than the  $R_g$  of the brush were used.

Typical results are shown in Figure 7, where the left-hand half of each plot shows formation of the original brush from toluene on the succinimide ester-derivatized surface (see Experimental Procedures) of the gold-coated crystal. Rinsing in pure toluene, indicated by R, produced no change in frequency, confirming that the chains of the brush were firmly attached. At S, the pure toluene was switched to pure ethanol, in preparation for exposure



**Figure 7.** Plots of  $\Delta f_n/n$  versus time for brushes exposed to dendrimers. (a)  $H_2N$ -PEO-19K brush exposed to a 6-generation dendrimer, and (b)  $H_2N$ -PEO-5K brush and 6-generation dendrimer.

**Table 3. Measures of Size for Experimental Systems with Dendrimers**

polymer	$R_g$ or $R_d$ , nm	$R_d/R_g$
<b><math>H_2N</math>-PEO-19K (brush)</b>	<b>5.4</b>	
3-generation dendrimer	1.8	0.19
6-generation dendrimer	3.6	0.67
<b><math>H_2N</math>-PEO-5K (brush)</b>	<b>2.6</b>	
3-generation dendrimer	1.8	0.69
6-generation dendrimer	3.6	1.38

to PAMAM dendrimers, which are insoluble in toluene. The switch from one pure solvent to the other was made prior to the introduction of the dendrimers in order to isolate the effect of change of solvent on frequency from the effect of penetration and grafting on frequency. At E, the dilute solution of dendrimer in ethanol was introduced.

In the experiment depicted in Figure 7a, the radius,  $R_d$ , of the 6-generation dendrimer was smaller than the  $R_g$  of the chains of the brush, leading to a prediction that penetration would occur. The obvious frequency change at E confirms that the dendrimers penetrated the brush and became grafted to the underlying surface. Subsequent rinsing in pure ethanol (R) without effect on frequency verified that the dendrimers were permanently affixed to the surface. Additional experiments (results not shown) were conducted with 3-generation dendrimers, which are even smaller than the 6-generation dendrimers of Figure 7(a). The 3-generation dendrimers, as predicted from Table 3, penetrated both  $H_2N$ -PEO-19K and  $H_2N$ -PEO-5K brushes.

The situation was different for the experiment depicted in Figure 7b, where the radius of the dendrimer was *larger* than the  $R_g$  of the polymer chains composing the brush. For this case, there is no change in frequency observable at E, meaning that the dendrimer molecules did not penetrate the brush and therefore could not become grafted to the underlying surface. This was the

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expected result for dendrimers having large  $R_d$  relative to the  $R_g$  of the brush chains.

The dendrimer experiments show that a species of roughly spherical geometry can penetrate completely through the brush to reach the underlying surface, as long as its radius is smaller than the  $R_g$  of the brush chains. These experiments also show that the brush excludes spherical species having larger radii than the  $R_g$  of the brush chains. The observation that spherical species can penetrate the brush completely to reach the grafting surface suggests that polymer chains in solution might not have to undergo a drastic change in conformation from a roughly spherical coil to an extended chain to penetrate a brush.

An explanation of why the brush is sensitive to radius may come from theoretical work by the O'Shaughnessy group at Columbia explaining what governs penetration of solid inclusions in dry brushes.<sup>35</sup> This theoretical work describes that each chain in a brush seeks to minimize its stretching energy, and when the trajectory of the chain must make a large lateral displacement to circumvent a solid object, the energy of the chain increases dramatically. When the lateral displacement of the brush chain is too large, i.e., on the order of its own radius of gyration, the inclusion will remain outside the brush. Our data support this, and so do experimental observations involving solid inclusions. In one case a dry brush was observed to exclude solid aggregates having overall radii greater than the  $R_g$  of the brush chains,<sup>36</sup> and in a separate case a solvated brush was observed to exclude solid particles having individual radii larger than the  $R_g$  of the brush chains.<sup>37</sup>

The question remains as to exactly how sharp is the dividing line between penetration and no penetration of a given brush. The sizes of the free species used in our experiments approached the  $R_g$  of the brush as close as 30% below and 10% above. Because it was not possible, with the currently available materials, to approach the size of the brush infinitely closely, we cannot define

the size criterion with perfect precision at this time. Even though the transition from penetration to no penetration is not sharply defined, the selective barrier behavior observed for a polymer brush is potentially very useful. For example, a brush of the right size can protect surface-immobilized dendrimers used as reservoirs for drugs from being blocked by larger species, thus allowing the egress of the therapeutic contents of the dendrimer. More generally, a polymer brush of the appropriate  $R_g$  grafted to a derivatized surface can be used to select and capture target species in a wide variety of applications.

## Conclusion

Experiments with linear polymer chains of various sizes were conducted to investigate which exact measure of size led to consistently correct predictions of penetration of the brush. The results showed that radius of gyration of linear free chains relative to the radius of gyration of the chains composing the brush led to consistently correct predictions of free chain penetration of brushes. When  $R_g$  of the free chains was larger than  $R_g$  of the chains composing the brush, penetration through the brush to the grafting surface was not observed, but when  $R_g$  of the free chains was smaller, penetration all the way to the grafting surface was observed. By contrast, comparison of the contour length of the free chains relative to that of the chains composing the brush failed to provide consistent predictions of whether or not penetration would occur. Additional experiments with dendrimers, for which radius is the characteristic measure of size, showed that dendrimers having radii larger than  $R_g$  of the chains composing the brush did not penetrate the brush. However, dendrimers having radii smaller than the  $R_g$  of the brush chains penetrated all the way to the grafting surface was observed. These experiments provide evidence that the radius of the free species with respect to the radius of gyration of the brush chains is the most important measure of size governing whether penetration will or will not occur. The importance of radius also suggests that linear chains do not need to assume an extended conformation in order to penetrate the brush.

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