

## Producing High-Density High-Molecular-Weight Polymer Brushes by a “Grafting to” Method from a Concentrated Homopolymer Solution

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Here, a new procedure and method are presented for the production of highly grafted polymer brushes. Thiol-terminated polyethylene oxide (PEO-SH) of molecular weight ( $M_w$ ) 20 000 (20k) is grafted to a gold surface from highly concentrated aqueous solutions of nonthiolated polyethylene oxide homopolymer. The  $M_w$  and volume fraction of the homopolymer solution are varied in order to control the grafting density of the resulting PEO-SH brush. As a result, 20k  $M_w$  PEO-SH brushes with grafting densities up to 0.3 chains/nm<sup>2</sup> are achieved, as determined by ellipsometry. Highly concentrated homopolymer solutions of volume fraction greater than ~12% and  $M_w$  greater than ~938 produce near-ideal solvent conditions for the 20k  $M_w$  PEO-SH chains; we have found that this facilitates the achievement of higher grafting densities of end-functionalized polymer brushes than would be possible from simple solutions. We propose this as a suitable method for applications where the grafting density of a brush surface must be accurately varied and controlled consistently. The effect of chemisorption time and cleaning procedure on the resulting brush grafting density are also explored.

### Introduction

Polymer brushes exhibit unique surface properties that are of use and interest in a wide range of disciplines and applications. Brushes consist of a layer of polymers tethered by one end to a solid surface, with the chain extending into the solution. For densely grafted brushes where the mean separation  $D$  between grafting points is small compared to the chain dimensions  $R \approx aN^{3/5}$  of a free chain ( $D < R$ ), the height of the brush  $h$  may be swollen to sizes considerably larger than the free chain radius of gyration. Such a brush has a height  $h \approx aN\sigma_a^{1/3}$ , where  $a$ ,  $N$ , and  $\sigma_a$  are the monomer size, degree of polymerization, and surface grafting density of the chains, respectively.<sup>1,2</sup> Brushes composed of polyethylene oxide (PEO) have attracted particular interest because of their excellent resistance to protein adsorption;<sup>3</sup> this resistance has been found to be dependent upon two variables, the grafting density  $\sigma$  and degree of polymerization  $N$  of the tethered chains.<sup>4,5</sup> Therefore, a method of controlling the grafting density of these brushes is of use to those studying and implementing such systems.

The main factor limiting the achievement of very dense polymer brushes of a high degree of polymerization is the excluded volume interaction, which, once a brush of relatively low grafting density has been created, limits access to the surface for other polymer chains. There are two main strategies that can overcome this limitation and produce polymer brushes of high grafting density, “grafting from” and “grafting to”. Grafting from overcomes the excluded volume interaction by growing the brush chains from a surface initiated radical polymerization.<sup>6</sup> However, due to the nature of free radical polymerization poor control of the chain degree of polymerization is achieved. Grafting to methods involve tethering whole chains to the substrate; therefore, excellent

control of the degree of polymerization can be achieved. However, due to the excluded volume interactions of a chain there is often a much lower grafting density. There are two commonly used “grafting to” procedures which suppress the excluded volume interactions by producing ideal chain conditions, where the ideal chain dimensions  $R_{\text{ideal}}$  of a free polymer chain are given by  $R_{\text{ideal}} \approx aN^{1/2}$ . Polymer melts involve heating an ultrathin layer of the grafting polymer past its melt transition temperature so the chains are mobile but exhibit ideal chain dimensions.<sup>7</sup> A disadvantage of the melt approach is that elevated temperatures are required; for instance, to melt PEO chains with a relatively high degree of polymerization one needs temperatures typically greater than ~70 °C.<sup>8,9</sup> In work by Zdyrko et al., a solvent-assisted melt approach has also been implemented by saturating the grafting polymer films with solvent vapor.<sup>10</sup> In this work, they show by increasing the solvent volume fraction in the PEO film from 0% to 20% the melting temperature could be lowered from ~67 to 20 °C, respectively. This enabled brush layers to be formed at relatively less elevated temperatures of ~40 °C. However, this method still requires the control of elevated temperature and vapor pressure.

Alternatively, brushes can be grown by using polymer solutions at the  $\theta$  temperature, at which excluded volume interactions are suppressed. In the case of PEO,  $\theta$  point aqueous solutions can be produced by control of ionic strength and temperature.<sup>11</sup> A disadvantage of the cloud point method is that it involves accurate control of salt concentration and temperature.

$\theta$  or poor solutions can also be created by choice of solvent; for instance, work by Huang et al. used a poor solvent, cyclohexane, to graft polystyrene (PS) to epoxy derivatized surfaces.<sup>12</sup> In this

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work, Huang et al. were able to produce brushes with grafting densities ranging up to  $\sim 0.08$  chains/nm<sup>2</sup> for 14.5k  $M_w$  PS, as determined by ellipsometry. A control of grafting density was achieved by varying the volume fraction  $\phi_g$  of the grafting PS polymer up to the semidilute regime.

Here, we present a third way of overcoming the excluded volume barrier that does not suffer from the disadvantages of using melts or  $\theta$  point or poor solvents. Grafting from concentrated homopolymer solutions (CH-solutions) yields a simple, reliable, and highly controllable method for producing PEO brushes with various grafting densities, suitable for industrial and research applications. The additional matrix homopolymer content in the CH-solution enables us to concentrate the solution to the point at which excluded volume interactions become suppressed. A CH-solution consists of a desired grafting polymer  $\phi_g \ll \phi_m$  in a semidilute to highly concentrated matrix of nongrafting homopolymer  $\phi_m^* < \phi_m < \phi_m^{**}$  in a good solvent, where  $\phi_m$  and  $\phi_g$  are the volume fractions of the matrix homopolymer and grafting chains, respectively. These solution conditions are to be contrasted with previous work<sup>12</sup> using brush-forming solutions with grafting polymer volume fractions up to but not exceeding the semidilute regime of  $\leq \phi_g^*$  in poor solvent conditions. In the method presented here, the volume fraction of grafting polymer is kept fixed at  $\phi_g \approx 1.0 \times 10^{-2}$  %, while the volume fraction and degree of polymerization  $P$  of an additional dissolved nongrafting homopolymer is varied in order to produce polymer brushes of a high grafting density.

The grafting chain dimensions  $R_g$  in a CH-solution are governed by the volume fraction of the matrix homopolymer chains  $\phi_m$  and the degree of polymerization of the grafting chain  $N_g$ , as follows:<sup>13</sup>

$$R_g \propto aN_g^{1/2}\phi_m^{-1/8} \quad (1)$$

In this regime, the excluded volume interaction of the chains are dependent on the volume fraction only and not their degree of polymerization. When the volume fraction becomes greater than the critical concentration  $\phi_m^{**}$ , the excluded volume interaction of the matrix homopolymers become screened and the chain dimensions become ideal (the melt). The chain dimensions  $R_{g,melt}$  of a grafting polymer in such conditions is now determined by the degree of polymerization of the matrix homopolymer chains  $P$ ,<sup>1</sup> eq 2:

$$R_{g,melt} \approx aN_g^{1/2} \left( \frac{N_g}{P^2} \right)^{1/10} \quad (2)$$

The excluded volume interactions become screened for the grafting polymer when  $P \leq \sqrt{N_g}$  and the chains assume ideal dimensions, i.e.,  $R_{g,melt} \approx aN_g^{1/2}$ . Therefore, by varying the volume fraction and the degree of polymerization of the homopolymer solution, one should be able to control the degree of excluded volume of the grafting polymer and therefore the chain dimensions and in turn the grafting density of the resulting brush.

It is important to note that one could produce polymer brushes from highly concentrated solutions of the grafting polymer without the additional nongrafting matrix homopolymer. However, end-functionalized polymers suitable for the production of polymer brushes tend to be relatively expensive or difficult to synthesize; therefore, it can be advantageous to use methods which minimize the amount of functionalized polymer used. Another added benefit of using a matrix of homopolymer is that the

grafting chain dimensions can also be varied by changing the degree of polymerization of the homopolymer, as explained above.

## Experimental Section

**Gold-Coated Silicon Wafers.** Silicon wafers were cleaved into strips and cleaned for 15 min in an oxygen plasma chamber: they were then immediately placed in an Edwards Auto 306 Turbo thermal evaporator, Edwards limited 2010. A layer of  $\sim 15$  nm of chrome from chromium chips was thermally evaporated at a slow rate, approximately less than 1 nm/min. This layer was then allowed to cool before a layer of gold with thickness greater than 60 nm was evaporated onto the chrome adherence layer again at rate of less than 1 nm/min. The wafers were then allowed to cool to room temperature before being exposed to the atmosphere as to reduce the risk of surface contamination. These wafers were either immediately used or stored in a freezer and cleaned by sonication in chloroform before use. Chrome chips and gold wire were purchased from Agar Scientific Ltd. Silicon wafers were purchased from Prolog Semi Core, Ukraine.

**CH-Solution Preparation.** Thiol–gold chemistry was employed to tether thiol-terminated polyethylene oxide (PEO-SH) chains to the gold surface.<sup>14–16</sup> Thiol groups form a strong coordination bond with gold, supporting the formation of high-density polymer brushes. Polyethylene oxide (PEO-OH) homopolymer of various molecular weights was weighed out into separate glass vials. From here on in the term, matrix homopolymer is used only to refer to the inert-ended PEO-OH polymer. Ultrapure water was then added to these vials at various volume fractions of matrix homopolymer (10–60%). The same concentration of 20k  $M_w$  PEO-SH was added at 0.01 g/mL. These mixtures were allowed to completely dissolve, forming clear, viscous CH-solutions. Gold-coated silicon wafers prepared as described above were then incubated in these solutions at room temperature. The wafers were subsequently removed, rinsed with water, and dried under nitrogen. PEO-SH was purchased from Jenkem Ltd; PEO-OH of various molecular weights was purchased from Sigma Aldrich Ltd.

**Sonication Cleaning Procedure.** Samples removed from CH-solutions were rinsed with water and dried with nitrogen before being immediately placed in chloroform-filled vials (in order to reduce oxidation of the air-sensitive thiol bonds<sup>14–20</sup>). The wafers were sonicated for 5 to 15 min in chloroform to remove any unwanted physically bound PEO. These were then rinsed with ultrapure water and dried under nitrogen. HPLC chloroform and acetonitrile were purchased from Fluka Ltd. All solvents and reagents were used as found.

**Ellipsometry.** A J. A. Woollam Co, Inc., ellipsometer and Jobin Yvon spectroscopic ellipsometer were used to measure the thickness of the dry PEO brush layers adhered to the gold-coated silicon wafer. For work conducted on the Woollam machine, each individual wafer had an initial ellipsometry scan taken to determine the reflectivity profile of the bare gold surface. This reflectivity was then saved as a material file using the B-spline software supplied by Woollam. After the CH-solution chemisorption procedure, a further scan was taken of the dry PEO layer revealing a thickness using a two-layer model using the saved B-spline file for that individual wafer and a Cauchy layer, with parameters

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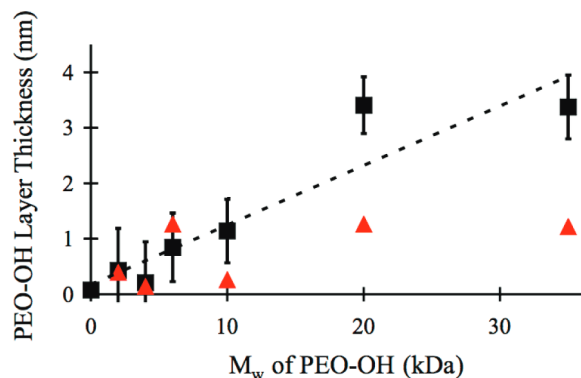
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**Figure 1.** Squares show the dry thickness of physically adsorbed PEO-OH layers after removal from CH-solution (rinsed with water and dried under nitrogen). Triangles show the dry thickness of these same layers after  $\sim 72$  h submerged in water. The dashed line is drawn to guide the eye.

$A_n = 1.45$ ,  $B_n = 0.1$ , and  $C_n = 0$ . (For measurements taken using the Jobin Yvon instrument, a five-layer model was used). This method was found to produce the most consistent and accurate results with  $\chi^2$  typically less than 1. The measured dry thickness was then converted into a mean distance (MD) between chains and grafting density  $\sigma$  using the following expressions:<sup>10</sup>

$$MD = \left( \frac{M_w}{\rho_{\text{PEG}} h_{\text{dry}} N_A} \right)^{1/2} \quad (3)$$

$$\sigma = \left( \frac{1}{MD} \right)^2 \quad (4)$$

where  $\rho_{\text{peo}}$  is the density of PEO at  $1\text{--}1.3 \text{ g cm}^{-3}$ ,  $N_A$  is Avogadro's constant  $\sim 6.023 \times 10^{23}$ , and the molecular weight of the grafting polymer here is 20k.

Typically, three thickness measurements were taken per sample and averaged. The standard deviation (std) for these measurements was found to be consistently low,  $\sim 7\%$  of the average thickness. The std is therefore much lower than the systematic errors estimated to be at maximum  $\sim 20\%$ . This low statistical spread suggests that the layers produced are homogeneous across the sample and consistent in thickness. Errors for thickness and grafting density are shown as the sum of the estimated systematic error of around  $\pm 0.25 \text{ nm}$  and the std in a sample measurement.

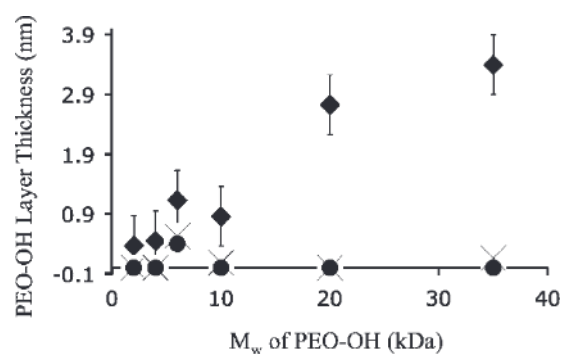
## Results and Discussion

**Physically Bound Polymer Layers.** The thickness of adsorbed matrix homopolymer on gold-coated substrates is shown in Figure 1. The samples were submerged in the CH-solutions of various molecular weight PEO-OH at volume fraction 50% for  $\sim 24$  h, before being removed and rinsed with ultrapure water and dried under nitrogen. It is clear from Figure 1 that physically bound layers of PEO-OH matrix homopolymer have formed with thicknesses ranging from  $\sim 0.4$  to  $3.5 \text{ nm}$ . Figure 1 shows that the layer thickness is proportional to the  $M_w$  of the matrix homopolymer used to make the CH-solution, with higher  $M_w$  polymers producing thicker layers. These ultrathin films are physically bound (as there is no known OH gold chemical bond) and are clearly resistant to rinsing with water. After soaking in water for  $\sim 72$  h, there still persists a layer of material despite being somewhat diminished. This suggests that the PEO-OH chains are experiencing a remarkably strong physical interaction with the gold surface. The affinity of PEO for gold is an important revelation that has consequences for the interpretation of PEO layers

**Table 1.** Thickness of 48.5k  $M_w$  PEO-OH Layers after Various Submersion Time Periods in Acetonitrile or Chloroform<sup>a</sup>

time submersed (min)	thickness of PEO layer (nm)
Chloroform Washing	
0	3.954
2	2.058
7	1.746
50	1.192
770	0.07
Acetonitrile Washing	
0	3.699
1	1.282
6	0.8415
16	0.5285
26	0.455
56	0.257
136	0.093

<sup>a</sup> Thickness measured via ellipsometry with errors of  $\pm 0.25 \text{ nm}$ . Samples were removed after the stated time intervals, measured, and re-submersed.



**Figure 2.** Diamonds show the thickness of dry PEO-OH layers as determined by ellipsometry after removal from CH-solutions of various matrix homopolymer  $M_w$ . Crosses and circles show the thickness of the same PEO-OH layers after 7 and 14 min of sonication in chloroform, respectively.

such as brushes which are adhered upon them. The conventional Alexander brush model of an end-tethered chain extending away from a surface could be somewhat of a simplification for a gold/PEO brush system. There could be multiple physical adsorption sites along a chain, as well as the coordination thiol gold bond, with the brush layers exhibiting Guiselin pseudobrush behavior.<sup>21</sup>

**Sonication Cleaning Procedure.** In order to produce a brush which does not contain the physically bound PEO-OH matrix homopolymer and only the preferred end-tethered PEO-SH chains, a suitable cleaning procedure to remove the unwanted PEO-OH polymer must be found. It is evident from Figure 1 that water is not a suitable solvent for overcoming the PEO-OH/Au affinity. Therefore, initially two solvents were chosen as candidates for removal of the physically bound PEO-OH: acetonitrile and chloroform. Table 1 shows that both solvents are effective at removing the physically bound PEO-OH layers (48.5k  $M_w$ ) of thickness greater than  $3.5 \text{ nm}$ . However, both solvents remove the PEO-OH layers at a slow rate, longer than 60 min. In order to remove the physically bound polymer quickly, the PEO-OH layers were sonicated in chloroform. The effect of sonication in chloroform on physically bound layers of various molecular weights can

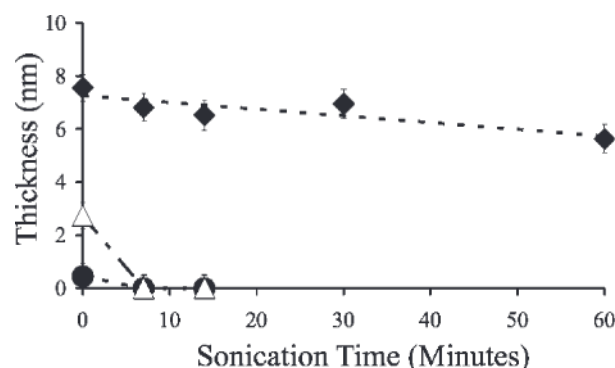
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**Table 2. Thickness of PEO-OH/SH Layers before and after Cleaning<sup>a</sup>**

$M_w$ of matrix polymer	PEO-SH layer thickness (20k $M_w$ )		PEO-OH control layer thickness	
	precleaning (nm)	postcleaning (nm)	precleaning (nm)	postcleaning (nm)
2000	8.74	5.91	0.47	0
4000	5.82	4.18	0.58	0
20000	9.38	7.55	3.99	0
35000	11.09	8.22	3.34	0

<sup>a</sup> Thickness of layers made from CH-solutions of various  $M_w$  matrix homopolymers (PEO-OH) at volume fraction of 50% in water, in the presence and absence of 0.01 g/mL of 20k  $M_w$  PEO-SH, are shown in the pre-cleaning columns. The thicknesses after 5 min of sonication in chloroform are shown in the post-cleaning columns. Layer thickness measured via ellipsometry with errors  $\pm 0.25$  nm.

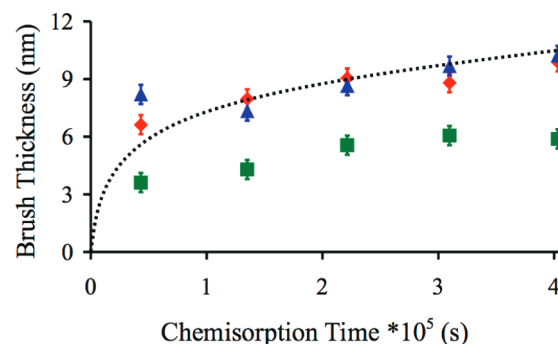


**Figure 3.** Diamonds show the thicknesses of various PEO-SH 20k  $M_w$  brushes after sonication in chloroform for various time periods (made from a CH-solution containing 4k  $M_w$  matrix polymer PEO-OH). Triangles and circles show the thickness of 20k and 4k  $M_w$  PEO-OH control layers after various sonication times in chloroform. Lines are drawn to guide the eye.

be seen in Figure 2. It is evident from Figure 2 that between 7 and 15 min of sonication in chloroform is adequate to remove physically bound layers of PEO-OH of various  $M_w$  (1–35k). As a result, sonication in chloroform was chosen as the standard method for removing the unwanted physically adsorbed PEO-OH from the gold surface.

**End-Tethered Brush Layers.** The effect of adding 0.01 g/mL of PEO-SH to CH-solutions was explored in the data shown in Table 2. The brushes formed from the PEO-SH CH-solutions are much thicker than the PEO-OH control layers (240–1900% enhancement). This suggests that the thiol–gold end-tethering chemistry is enabling thicker layers to form than are possible via physical bonds alone. Table 2 and Figure 2 show that sonication in chloroform for 7 to 15 min is adequate to remove  $\sim 100\%$  of all the different  $M_w$  physically bound PEO-OH layers, whereas the PEO-SH layers postsonication are only partially thinner, typically around 26%. This implies that sonication is removing residual physically bound PEO-OH from the PEO-SH layers leaving a layer of end-tethered chains. Figure 3 shows the effect of sonication time on the thickness of individual samples made from PEO-SH-containing CH-solutions; there appears to be an initial thinning of these layers after which the thinning rate becomes negligible. This further illustrates that such layers are resistant to long periods of sonication of  $\gg 60$  min, which is far in excess of the amount of time needed to remove an equivalent physically bound layer,  $\sim 7$  min.

**Kinetics of Brush Formation.** In order to quickly investigate the effect CH-solution conditions have on the kinetics of brush

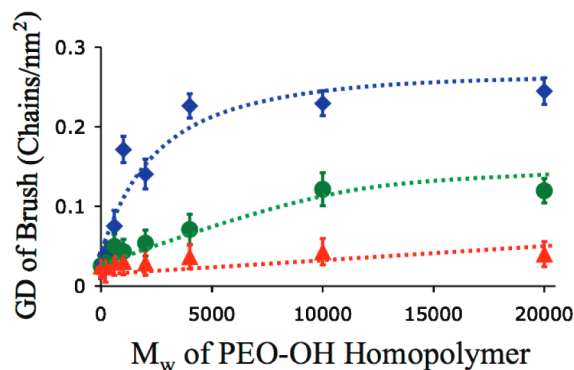


**Figure 4.** Kinetics of brush layer formation. Diamonds and triangles show the dry thickness of 20k PEO-SH layers after various chemisorption times in 35k and 2k  $M_w$  PEO-OH matrix homopolymer CH-solutions at volume fractions 50% and 66%, respectively. Squares show the thicknesses of 35k PEO-OH layers after various chemisorption times in a 35k PEO-OH control matrix homopolymer CH-solution at 50% volume fraction. Diamonds and triangles were sonicated in chloroform for  $\sim 7$  min and rinsed and dried under nitrogen. Line is drawn to guide the eye.

formation, two contrasting CH-solutions were chosen with matrix homopolymer  $M_w$  2k and 35k and volume fractions 66% and 50%, respectively, mixed with 0.01 mg/mL of 20k  $M_w$  PEO-SH. Samples were incubated at room temperature and removed from these CH-solutions every 24 h for five days (see Figure 4). It is evident that for both CH-solutions the majority of brush formation occurs within the first 12 h, after which the rate of layer thickening appears to continue at a slow rate, with layer thickness increasing on the order of 0.4 nm every 24 h. The 35k  $M_w$  PEO-OH control matrix homopolymer series also shows similar kinetics for the physically bound layers. From these results, it was decided that a suitable chemisorption time to achieve approximate maximal thickness is  $\sim 24$  h.

The kinetics of PEO brush formation from a polymer melt at elevated temperatures without solvent and homopolymer have been studied by Zdyrko et al.<sup>8,9</sup> In this work, it was found that the kinetics of brush formation were faster at higher temperatures (110 °C), leveling off after  $\sim 8$  h with marginal thickening over a 24 h period.<sup>8</sup> The thickness achieved for 24k  $M_w$  PEO polymer after approximately 24 h was around  $\sim 6$  nm and equivalent to the thickness achieved through the CH-solution procedure presented here for a 20k  $M_w$  PEO grafting polymer of  $\sim 7$  nm. The kinetics of brush formation for both procedures are roughly equivalent; however, the CH-solution method here is conducted at room temperature and therefore does not require elevated temperatures to achieve similar brush thicknesses.

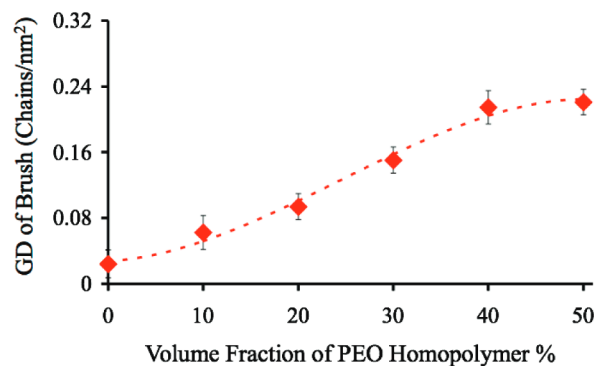
**Control of Grafting Density via Homopolymer Volume Fraction and  $M_w$ .** Having determined an adequate cleaning procedure and chemisorption time, the effect of matrix homopolymer  $M_w$  and volume fraction on the PEO-SH brush grafting density was investigated. According to eqs 3 and 4, the excluded volume interactions of the grafting PEO-SH chains can be controlled by varying the  $M_w$  (i.e., the degree of polymerization) and volume fraction of the CH-solution. The excluded volume interactions of the grafting chain should become ideal when the volume fraction of matrix polymer is  $> 10\%$  and their degree of polymerization is  $P \geq N_g^{1/2}$ . Figure 5 shows the resulting grafting densities (GD) of brushes made from three matrix homopolymer volume fractions 5%, 25%, and 50%, over a range of molecular weights from 100 to 35k. The 5% volume fraction series only appears to have a very weak dependence on the  $M_w$  of the matrix homopolymer; this indicates that these solutions are below the critical concentration  $\phi^{**}$ . Interestingly, however, layers satisfying brush



**Figure 5.** Effect of homopolymer molecular weight on thickness of 20k  $M_w$  PEG-SH layers made from CH-solutions of three different PEO-OH matrix homopolymer volume fractions: 5%, triangles; 25%, circles; and 50%, diamonds. Samples were removed from CH-solutions after 20 h and sonicated in chloroform for  $\sim 7$  min, rinsed, and dried under nitrogen. Thickness determined by ellipsometry and converted into number of chains/ $\text{nm}^2$ . Lines are drawn to guide the eye.

criteria are achieved under these conditions ( $\sigma > 0.0087$  chains/ $\text{nm}^2$ ). Upon increasing the volume fraction to 25%, a  $M_w$  dependence becomes apparent with grafting density. The grafting density increases from  $\sim 0.025$  to  $0.125$  chains/ $\text{nm}^2$ . The 50% volume fraction shows the strongest molecular weight dependence of the three series. There is a rapid increase in grafting density from  $\sim 0.025$  to  $0.22$  chains/ $\text{nm}^2$  after which the increase in grafting density plateaus with increasing molecular weight (degree of polymerization) of the matrix homopolymer chains. This indicates that the 50% solutions are well over the critical concentration  $\phi^{**}$  of  $\sim 12\%$  and are experiencing an increased excluded volume interaction screening as the degree of polymerization of the matrix homopolymer chains increases past  $P = N_g^{1/2}$  ( $P \sim 21$ ,  $M_w \sim 938$ ).

The effect of homopolymer volume fraction on brush layer thickness was investigated in more detail for a  $0.01$  g/mL 20k  $M_w$  PEO-SH CH-solution with 20k  $M_w$  PEO-OH matrix homopolymer (Figure 6). The matrix homopolymer volume fraction was increased from 0% to 50% producing an increase in the grafting density of the resulting PEO-SH brush layers. The increase in brush grafting density appears to flatten off after  $\sim 40\%$  volume fraction indicating that the CH-solution has passed the critical concentration ( $\phi^{**} \sim 12\%$ ) and the excluded volume interactions of the chain monomers cannot be suppressed further. Figure 6 shows that by varying the volume fraction of the matrix homo-



**Figure 6.** Diamond series shows the grafting density of 20k  $M_w$  PEO-SH brush made from CH-solutions of 20k  $M_w$  PEO-OH matrix homopolymer of increasing volume fraction. Samples were left in CH-solution for  $\sim 24$  h before being removed, sonicated in chloroform for  $\sim 14$  min, rinsed with water, and dried under nitrogen. Line is drawn to guide the eye.

polymer an accurate control of brush layer grafting density can be achieved.

## Conclusion

A novel “grafting to” procedure for producing highly grafted polymer brushes from an aqueous concentrated homopolymer solution has been formulated and characterized. A suitable cleaning procedure has been devised for the removal of physically bound PEO-OH matrix homopolymer, which takes into account sonication time and choice of solvent. We have shown that highly grafted polymer brushes of a high molecular weight, 20k, can be formed from these CH-solutions with grafting densities up to  $0.3$  chains/ $\text{nm}^2$ . By varying the molecular weight and volume fraction of the matrix homopolymer content in the CH-solutions, we have been able to control the grafting densities of the resulting PEO-SH brushes.

The brush-forming procedure presented here has some advantages over current methods that require the control of elevated temperatures to achieve equivalent brush thicknesses. Like other procedures such as cloud point and the work of Huang et al.,<sup>12</sup> this method can theoretically be used to coat any surface geometry with a polymer brush.

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