Solvent Quality Effects on Scaling Behavior of Poly(methyl methacrylate) Brushes in the Moderate- and High-Density Regimes

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ABSTRACT: Herein, we give a detailed experimental analysis for scaling law behavior in the “moderately dense” and “high-density” brush regimes for poly(methyl methacrylate) brushes swollen in a range of solvent conditions. This expansive experimental analysis aims to validate decades of mean field theory predictions on power law scaling behavior of grafted polymer chains. Brushes with grafting densities (σ) ranging from 0.1 to 0.8 nm⁻² are prepared by atom-transfer radical polymerization. The swollen thickness (h) is characterized using liquid cell ellipsometry, and the solvent quality is varied using mixtures of acetone and methanol. In a good solvent, the exponential scaling behavior (h ∝ σⁿ) has the typical n = 1/3 dependency for grafting densities of σ ≤ 0.4 nm⁻². For grafting densities of >0.4 nm⁻², n increases, indicating the transition from the moderately dense to the high-density brush regime. However, in a poor solvent, the scaling behavior is independent of σ and scales as h ∝ σ.80, approaching the theoretical expectations of h ∝ σ. An abrupt transition between these scaling law behaviors occurs at the Θ-solvent condition of ~45% (v/v) methanol in acetone. While our experimental results parallel trends predicted by mean field theory, differences are observed and appear to be attributed to self-solvation of the polymer, polydispersity in the molecular weight, and chain termination.

INTRODUCTION

Polymer chains covalently tethered to a surface can be used to modify the surface properties and engineer a surface’s response to the surrounding environment. Such polymer-grafted surfaces have shown great potential in various applications, including stimulus-responsive smart materials,1,2 protein binding surfaces,1,3–5 stabilized colloidal suspensions,1,2,5 and cell adhesive surfaces.1,3,4 While polymer chemistry plays an important role in determining a grafted layer’s functionality, the spacing between grafted polymer chains is often as important in determining the layer’s properties.

The average spacing between grafted polymer chains scales inversely with the grafting density (σ), the number of chains per area.6 This parameter affects the conformation of the polymer chain in the grafted layer. As σ increases, polymer chains get closer together and begin to overlap, increasing the excluded volume and causing chains to extend farther from the substrate. The behavior of grafted chains as a function of the grafting density (in solvents of various qualities) has been addressed in a number of theoretical studies.7–12 The scaling behavior in solution can generally be described as

\[ h \propto N\sigma^n \]  

where h is the average extended length of the polymer chain (layer thickness), N is the degree of polymerization, and n is an exponent between 0 and 1. Theoretical studies suggest that the exponent n is a function of both the solvent quality7–11 and the grafting density.7–12

Grafted polymer layers swollen in a solvent are generally grouped into two regimes delineated by a critical chain spacing equivalent to the radius of gyration (Rg) for the free polymer in the same solvent. When chains are grafted at distances larger than Rg, the chains do not interact and the layer behaves similarly to a free polymer. The layer thickness is independent of the grafting density (n = 0) and has a constant value of ~2Rg in the swollen state. This has been demonstrated both theoretically and experimentally by a number of groups.7–9,13,14 Grafted chains spaced closer than Rg interact with one another, resulting in conformational extensions greater than 2Rg; this regime is known as a polymer brush. Early calculations and experimental investigations revealed an n = 1/3 scaling law dependence for brushes swollen in a good solvent,7–10,14 but more recent calculations suggest that at higher grafting densities (σ > 0.3 nm⁻²) this increases to as large as n = 1, due to higher order interaction parameters.9,12,15,16 Brushes obeying the σ¹/³ scaling law dependence have been deemed “moderately dense” brushes, while those having a larger power law dependence are deemed “high-density brushes”. Solvent quality is also predicted to influence the scaling behavior between the grafting density and polymer brush

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thickness. As a moderately dense brush is transferred from a good solvent to a Θ-solvent to a poor solvent, the power law exponent is theorized to increase from 1/3 to 1/2 to 1, respectively.9–12

Here, we conduct a detailed experimental study of the scaling behavior for poly(methyl methacrylate) (PMMA) brushes grafted to silicon in the “moderately dense” and “high-density” regimes. Specifically, we aim to determine the exponential dependence (n) of the grafting density over a range of solvent conditions and grafting densities. Despite the large set of theoretical studies, a detailed experimental data set examining these dependencies is not currently available. These results provide important experimental validation for the many theoretical predictions that have been made about the swelling behavior in polymer brushes.

### Experimental Section

To evaluate the relationship between h and σ, polymer brushes of varying grafting density (σ) are required and compared after the layer thickness (h) is normalized by the molecular weight of the brushes. To achieve a variation in grafting density, “grafted-from” PMMA brushes were prepared on silicon substrates with varying initiator density. The initiator density was controlled by solution deposition of a mixed monolayer of the initiator molecule, [11-[(2-bromo-2-methylpropenyl)oxy]undecyl]trichlorosilane (BMPUS), and an inactive spacer, octadecyltrichlorosilane (OTS). Monolayers were prepared from 1 μL/mL active species in toluene solutions with BMPUS/OTS ratios ranging from 1:1000 to pure BMPUS. Brushes were then synthesized on these substrates using atom-transfer radical polymerization (ATRP) as described by Gorman et al. with CuCl2 as the catalyst.18 A complete description of our synthesis procedures is included in the Supporting Information. Ethyl 2-bromoisobutyrate was added as an unbound initiator molecule (BMPUS) in the preparatory self-assembled monolayer solution (see the text for details).

The molecular weight distribution was characterized using gel permeation chromatography (GPC). The grafting density was then calculated using

\[
\sigma = \frac{\rho N_A h_{\text{dry}}}{M_w}
\]

where ρ is the bulk density of PMMA (1.19 g/cm³), N_A is Avogadro’s number, h_{\text{dry}} is the dry thickness measured by ellipsometry, and M_w is the number average molecular weight measured by GPC.15 Also used to estimate the radius of gyration, R_g of PMMA in acetonitrile.19

This is to ensure that the height measured is greater than 2R_g and that the PMMA brushes synthesized are in the brush regime.

The polymer brush thickness was measured with a fixed-angle, single-wavelength ellipsometer (Gaertner L116C) having a He–Ne laser of wavelength 633 nm at an incident angle of 70°. To measure the swollen polymer thickness, brushes were immersed in solvent inside a custom-made liquid cell with 70° sloped windows. Although relatively straightforward, these measurements do have limitations. Most importantly, the refractive index of the solvent must be appreciably different from that of the polymer layer to distinguish between the layers in the optical model. Good solvents for PMMA such as toluene and chloroform have refractive indexes (n ≈ 1.49) nearly identical to that of PMMA and therefore cannot be used in this measurement design. Instead, acetone (n ≈ 1.36) is selected as the good solvent and methanol (n ≈ 1.33) as the poor solvent. Mixtures of these two solvents are used to vary the solvent quality from good to poor. A second limitation to this setup is in the accuracy of extracting both the thickness and refractive index in the swollen brushes. To obtain reliable results, the ellipsometric functions (ψ and Δ) must be in a region where their values change rapidly with small changes in refractive index or layer thickness. We find for our system that this occurs for PMMA brushes in the thickness range of 40–300 nm. Thus, only “thick” brushes with a dry thickness (h_{\text{dry}}) of more than 40 nm are used in this experiment. The ellipsometric functions reach constant values within ~20 s of brush immersion in solvent, indicating that the equilibrium thickness is being measured (see Figure S1 in the Supporting Information).

### Results and Discussion

To confirm that the BMPUS concentration controls the polymer brush grafting density, σ is plotted against the volume fraction of BMPUS (f_B) in the BMPUS/OTS mixture for the deposition of the surface-bound initiator layer (Figure 1). In Figure 1, σ scales linearly with f_B for volume fractions below 0.7, indicating our ability to methodically control the grafting density. For volume fractions greater than 0.7, the grafting density saturates at ~0.8 nm⁻². Similar saturation in the grafting density was observed by Yamamoto et al., who controlled the initiator density by irradiated deactivation of initiator molecules.15 This saturation is believed to result from either steric hindrance of growing polymer chains obstructing further initiation or nearby reaction sites terminating into loops.

To characterize the power law relationship between the swollen brush thickness (h_s) and σ, h_s is normalized by the polymer’s contour length (l_0, length of a fully extended chain), which is calculated from the molecular weight:

\[
h_0 = \frac{(M_w/M_0)}{l_0}
\]

where M_0 is the molecular weight of the monomer (100 g/mol for MMA) and l_0 is the length of each monomer (0.25 nm for PMMA15). We chose to normalize the height because the molecular weight varies modestly for brushes prepared in different reaction vessels.

Figure 2 plots the normalized thickness versus the grafting density for brushes swollen in pure acetone, a good solvent for PMMA. Note that the limitations imposed on our swollen brush thickness due to the reliability of the ellipsometric model restricts our analysis to brushes with σ > 0.06 nm⁻². This restriction is not a serious detriment to our study as the n = 0 scaling behavior for the mushroom regime (σ < 0.05 nm⁻²) has already been experimentally demonstrated.13,14 We are more interested in elucidating the scaling behavior in the so-called moderately dense and high-density brush regimes. The apparent superlinear behavior in the log–log plot of Figure 2 implies that the power law dependence of the brush thickness on the grafting density changes as...
the grafting density increases. For grafting densities of $0.05 \, \text{nm}^{-2} < \sigma < 0.4 \, \text{nm}^{-2}$, the familiar scaling behavior ($h \propto \sigma^{1/3}$) for a moderately dense brush in a good solvent is observed. At grafting densities of $0.4 \, \text{nm}^{-2} < \sigma < 0.7 \, \text{nm}^{-2}$, the scaling exponent ($n$) increases from $1/3$ to $\sim 3/5$. The exponent appears to increase further for grafting densities greater than $0.7 \, \text{nm}^{-2}$. Although a reliable fit cannot be made to the available data, we can conclude that, for $\sigma > 0.7 \, \text{nm}^{-2}$, $n$ is between 0.8 and 1.3. This change in the scaling behavior with grafting density was previously predicted in theory and suggested in limited experimental work by Yamamoto et al. Specifically, theoretical calculations predict that as the grafting density and chain overlap become greater, higher order interactions become important. The calculations of Lai and Halperin suggest that chains near full extension ($h/h_0 > 0.7$) show a linear scaling behavior between the thickness and grafting density ($h \propto \sigma^1$). This prediction is consistent with our experimental observations of $0.8 < n < 1.3$ at the highest grafting densities.

We next examine this series of PMMA brushes swollen in a poor solvent. Figure 3 plots the PMMA brush thickness versus grafting density when swollen in methanol. We note that the log-log plot appears linear, indicating a single power law dependency in the poor solvent conditions over the investigated range of grafting densities. A regression line fit to this data gives a scaling law dependency of $h \propto \sigma^{0.80}$. Previous mean field theory evaluations of polymer brushes have predicted $h \propto \sigma^{1/2}$ for swelling in poor solvent and $h \propto \sigma^{1/2}$ for $\Theta$-solvent conditions. Thus, our value of $n = 0.80$ appears to fit within these predictions. This intermediate behavior between poor and $\Theta$-solvent conditions may result from the high polymer concentration in these dense brushes. Since the polymer is a $\Theta$-solvent for itself, it may skew the behavior toward $\Theta$-solvent conditions. We also note that mean field theory calculations often assume no polymer–substrate attraction and no polydispersity, both of which occur in and contribute to the behavior of our experimental system.

In Figure 4 we present the same set of brushes swollen in mixtures of acetone and methanol (MeOH). $h/h_0$ is observed to decrease with the increasing concentration of MeOH, indicating brush collapse due to a decrease in solvent quality. (b) Scaling law exponent ($n$) plotted against the volume percentage of methanol in the solvent mixture for the moderate-density brush regime ($\sigma < 0.4 \, \text{nm}^{-2}$).
condition, we find that Θ-solvent behavior occurs between 40% and 50% methanol concentrations. This is somewhat larger than the value reported (22% methanol) for bulk PMMA dissolved in methanol/acetone solutions at room temperature.20,21 This shift in the Θ-solvent condition again suggests that the high polymer concentration in these dense brushes creates self-solvent conditions, giving a better effective solvent than in a dilute system. The observed Θ-solvent transition at ∼45% methanol also demarcates a transition in brush swelling behavior. For solvent mixtures better than this “Θ-solvent” condition, the log–log plots in Figure 4a are clearly superlinear, while mixtures poorer than this condition fit a single power law behavior.

Next we consider the change in refractive index measured for the swollen brushes as a function of the grafting density and solvent quality. These results are presented in Figure 5a. As the grafting density increases, the refractive index approaches that of pure PMMA (1.49), indicating less solvent can penetrate these denser brushes. In Figure 5b we approximate the amount of solvent in the swollen brushes by assuming the refractive index scales linearly with the solvent-to-polymer concentration. In good solvent conditions, the lowest density brushes contain ∼80% solvent, but this solvent incorporation drops to ∼50% for the densest brushes. In poor solvent, the concentration drops from 50% to 20% with increasing brush density. For the highest brush densities (0.7 nm−2 < σ < 0.8 nm−2), the solvent concentration anomalously increases with σ when swollen in good solvent. We speculate that this change in solvent concentration reflects a change in the uniformity of the brush density with thickness. This range corresponds to an increase in the initiator density with nearly invariant grafting density (as demonstrated in Figure 1). Thus, during polymerization it is likely that some chains are either terminating into loops or becoming inaccessible due to steric hindrance from surrounding chains. These terminated polymer chains effectively create a gradient in brush density with higher brush density near the substrate/brush interface and lower brush density at the brush surface. We speculate that this variation in brush density permits increased solvent incorporation near the surface, resulting in the anomalous decrease observed in the refractive index for brushes swollen in good solvent at high grafting densities.

Finally, we consider the amount of collapse caused by varying the solvent quality. In Figure 6 we replot the data from Figure 4 to show the fractional brush collapse as the solvent is changed from pure acetone to pure methanol. Mean field analysis predicts that brushes with lower grafting density will experience strong collapse similar to free polymer chains while high-density brushes will have a “weaker” collapse.12 To investigate this prediction, Figure 6 plots the fractional height of brushes swollen in methanol relative to acetone (h_{methanol}/h_{acetone}) as a function of the grafting density. At low grafting densities, brushes in methanol collapse to ∼40% of their height in acetone. As the grafting density increases, the collapse becomes less severe, which is consistent with mean field theory. For σ > 0.6 nm−2, the fractional thickness in methanol reaches a constant value that is ∼70% of the acetone-swollen thickness. In this regime, the difference in the swollen brush thickness for good and poor solvents is only 30%. Thus, this previously predicted “weak” collapse regime appears to occur for brushes with grafting densities greater than 0.6 nm−2.

**CONCLUSIONS**

In conclusion, we have systematically varied the surface concentration of initiator molecules to allow methodical control of the grafting density of PMMA polymer brushes. Using these brushes of different σ values, we have observed the scaling law behavior (h ∝ σ^n) at different grafting densities and solvent conditions.

In good solvent (acetone), we find that a grafting density of ∼0.4 nm−2 delineates the moderate-density regime (where n = 1/3) from the high-density regime (where n > 1/3).
swollen in good solvent in the high-density regime appear to have two scaling law behaviors, \( n = 3/5 \) for 0.4 nm\(^{-2} \) < \( \sigma \) < 0.7 nm\(^{-2} \) and \( n \approx 1 \) for \( \sigma > 0.7 \) nm\(^{-2} \). In poor solvent (methanol), the scaling relation has a single dependency in both the moderate- and high-density regimes \((n = 0.8)\). This value falls between the mean field theory predictions of 0.5 and 1 for \( \Theta \)-solvent and poor solvent, respectively. This behavior is attributed to the self-solvation of the PMMA brushes, which are \( \Theta \)-solvents for themselves. The transition between multiple scaling laws and a single scaling law behavior appears to occur at the \( \Theta \)-solvent condition. Finally, we observe the effects of steric hindrance on chain collapse in poor solvent and identify \( \sigma > 0.6 \) nm\(^{-2} \) as the transition point for weak collapse. Polymer brushes prepared with grafting densities of >0.6 nm\(^{-2} \) exhibit only a 30% collapse in thickness when changed from good to poor solvent conditions.

In summary, we have presented experimental results for swollen polymer brushes that are consistent with many of the previous predictions made by mean field theory calculations. Several new experimental quantities are reported for the poor solvent collapse of physical models for polymer brush systems. These experimental results will help in the further refinement of physical models for polymer brush systems.

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**ASSOCIATED CONTENT**

Supporting Information. Additional experimental details and characterization of the brushes in the dry state. This material is available free of charge via the Internet at http://pubs.acs.org/.

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