Dense Tethered Layers by the “Grafting-To” Approach

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ABSTRACT: The advantages of the grafting-to approach for the formation of tethered polymer layers, or polymer brushes, include construction under ambient conditions, precise control of polymer molecular weight, and control of dispersity. These advantages are counterbalanced by the relatively low grafting density typically achieved. We developed a method, based on segmental adsorption and high solution concentration, for achieving significant increases in surface attachment density. The method can be used with substrates of any geometry and requires only a minimum of polymer solution. The experimental results revealed that there is a solution concentration, inversely related to molecular weight, above which there is no additional increase in tethered chain density. The surface attachment density was determined by two complementary techniques, solution depletion and ellipsometry, and consistent trends were found.

I. Introduction

Polymer chains attached, or tethered, by one end to the surface of a solid to form a polymer brush are of great interest for a large number of potentially useful applications.[1,2] Polymer brushes can be constructed by either of two overall approaches: grafting-to and grafting-from. The grafting-to approach, alternatively termed “tethering”, consists of exposing the solid to the desired polymer in solution or in the melt. The polymer chains become attached, or tethered, to the substrate by means of strong interaction between one end of each chain and the surface of the solid. Moieties that have been used as chain ends to interact strongly with solid surfaces include highly polar groups,[3−5] charged groups,[6−9] chemically reactive groups,[10−17] and even blocks of segmentally adsorbing polymer different from the rest of the chain.[18−24] The grafting-from approach consists of installing initiator sites onto the surface of the solid and exposing this to a solution of monomers that polymerize from these initiator sites to form chains.[25−31]

The grafting-from approach is able to produce brushes having high values of mass per unit area of substrate and is the suggested approach when a particular application calls for this. The disadvantage associated with most versions of the grafting-from approach is imprecise control of the molecular weight of the brush and also uncontrolled polydispersity.[32−34] The other approach, the grafting-to approach, offers precise control of polymer molecular weight and dispersity because chains with the desired characteristics can be synthesized and purified in advance. Mixed brushes containing different types of chains in controlled ratios also can be constructed by means of the grafting-to approach.[35] Finally, the grafting-to approach can be conducted under ambient conditions, whereas many versions of the grafting-from approach require demanding moisture-free or oxygen-free conditions.

Given the advantages of the grafting-to approach, it would be of obvious benefit if a way could be found to make it yield denser brushes, i.e., more tethered chains per unit area of substrate. We made the hypothesis that two separate aspects of polymer behavior could be combined to produce much denser brushes than usual for the grafting-to approach from solution. One aspect was that denser brushes are constructed when segmental adsorption occurs simultaneously with tethering than when it does not. This behavior has only recently been documented.[36] The other aspect was the well-documented behavior that the amount of polymer adsorbing to a surface increases and approaches an asymptote in response to increases in solution concentration.[37] The experiments described in the present paper uphold our hypothesis and show how these two aspects of polymer behavior can combine to produce much denser brushes.

II. Experimental Section

A. Introduction of Reactive Sites to Surface of the Solid Substrate. The solid substrate selected for the present work was silicate glass in the form of nonporous, spherical beads (Potters Industries, Cleveland, OH), with average diameter of 10 μm and specific surface area equal to 0.24 m^2/g. The spherical geometry and nonporous surface ensured complete accessibility of the surface to polymer in solution and to solvents used during the work. The as-received beads were cleaned with piranha solution and dried before they were derivatized with the epoxide groups that served as reactive sites for subsequent tethering reactions. (The epoxide group was selected for its high reactivity with the primary amine group terminating one end of each polymer chain used in tethering.) For derivatization, the clean, dry beads were exposed to 3-glycidoxypropyltrimethoxysilane (98%, Aldrich, Minneapolis, MN) in toluene at 2 vol % under anhydrous conditions. After derivatization, the beads were subjected to exhaustive extraction in a Soxhlet apparatus to remove any nonchemically bonded silane. As conducted, this derivatization procedure results in 2.71 ± 0.24 epoxide groups/nm^2 of surface, a value well above that needed for tethering of polymer chains at the highest conceivable surface density.[11]

B. Preparation of Stock Solutions for Concentration Series. Monodisperse, primary amine end-functionalized polystyrenes of different molecular weights (M_n = 4000, 15 000, 44 000, and 90 000 g/mol), all with $M_w/M_n \leq 1.04$, were obtained from Prof. Roderic P. Quirk, University of Akron. All polymers had been prepared by means of living anionic polymerization. Two stock solutions of each polymer were prepared at precisely measured concentrations, nominally 4.0 mg/mL, in reagent grade cyclohexane. The stock solutions differed only in the

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identity of the internal standard added to each; one contained the inert-ended polyisoprene (Polysciences, Warrington, PA) as internal standard, while the other contained the inert-ended polystyrene (Polymer Source, Dorval, Quebec) as internal standard. The internal standards were added in carefully measured masses, approximately equal to the mass of the end-functionalized polymer present. In addition, the molecular weight of the internal standard added to each stock solution was selected so its elution band in size exclusion chromatography (SEC) would not overlap that of the end-functionalized polymer. The concentration series needed for the experiments on a given molecular weight of end-functionalized polystyrene was prepared by successive dilutions of both stock solutions.

The purpose of using two stock solutions, each containing a different internal standard, was to be able to make the distinction between polymer *tethered* to the substrate and polymer merely s*egmentally adsorbed* to the substrate. As determined by auxiliary experiments, the polystyrene showed significant segmental adsorption to the epoxide-derivatized substrate from cyclohexane at room temperature, while polyisoprene showed none whatsoever under the same conditions.[36] Obviously, because of their chemically inert ends, the internal standards could not become tethered (by chemical reaction) to the substrate.

C. Tethering Reactions and Preanalysis Preparation. All tethering reactions were carried out by exposing the epoxide-derivatized substrate to the cyclohexane solutions of polymer at selected concentrations at room temperature in stoppered test tubes. In each test tube, 0.400 mL of polymer solution was added to 0.360 g of epoxide-derivatized glass beads, and the mixture was stirred gently for 24 h. As shown in a previous study,[36] segmental adsorption from solution to the substrate reaches equilibrium within 2 h, and also tethering reaches saturation (point at which further tethering ceases) within this time. Thus, the 24 h exposure time was more than ample for reaching the maximum tethering density.

For each concentration in the series, a pair of reactions was run: one with the polymer solution containing the polyisoprene as internal standard and one with the polymer solution containing the polystyrene as internal standard. Running reactions containing different internal standards as pairs provided a way for the quantitative analysis to distinguish between polymer *tethered* to the substrate and polymer merely s*egmentally adsorbed* to the substrate. For added rigor, each member of the pair of reactions at a given concentration was run in triplicate to establish reproducibility.

Once the 24 h exposures were concluded, all unreacted primary amine chain-ends were capped by addition of a 100-fold excess of trichloroacetyl isocyanate. Capping is a common practice, used to eliminate specific interactions between the end group and the column packing in SEC. After that, the two members of each pair of reactions were worked up differently, as follows. The test tube containing the polyisoprene standard was centrifuged to separate the solution from the beads, which held both tethered (attached by chemical bonds) polystyrene chains and segmentally adsorbed polystyrene chains. Then the bead-free supernatant was analyzed quantitatively for end-functionalized polystyrene as described in the next section. The other test tube, containing the polystyrene (inert-ended) standard, had its cyclohexane solvent evaporated completely under flowing nitrogen. The evaporated solvent was replaced with toluene, which is a good solvent for polystyrene ($\chi = 0.40$ at room temperature).[38] This was stirred until all of the nontethered polystyrene was desorbed by the toluene from the epoxide-derivatized substrate.[15,36,39] Then the test tube was centrifuged to separate the solution from the beads, which now contained tethered chains only, and the bead-free supernatant was analyzed quantitatively for end-functionalized polystyrene.

Auxiliary experiments involving inert-ended polystyrene, incapable of undergoing tethering, provided assurance of the ability of toluene to desorb segmentally adsorbed polystyrene. In these experiments, epoxide-derivatized beads containing measured amounts of segmentally adsorbed, inert-ended polystyrene were exposed to fresh toluene containing internal standard. The toluene was monitored quantitatively over time for appearance of polystyrene by means of the SEC-based method described below. The toluene totally desorbed the polystyrene chains from the surface of the beads in a matter of minutes.[36,40]

D. Quantitative Analysis of Tethering Reactions by Solution Depletion. The mass of end-functionalized polymer in solution was quantified by comparison with the mass of the internal standard, whose mass remained constant at its initial value throughout all the steps of the workup prior to quantitative analysis. Solutions were analyzed by means of SEC (Waters LC, Waters Corp., Milford, MA) equipped with a Rheodyne 7725i manual injector, ultraviolet and refractive index detectors, and, for these experiments, two Styragel columns (HR1 and HR3). Although SEC is not typically used for quantitative analysis, careful control over operating conditions, use of the appropriate internal standard, and calibration of the detectors rendered our system quantitative. The signals from the ultraviolet (UV) and the refractive index (RI) detectors attached to the column registered polymer mass in solution. The signals from both detectors were individually calibrated for polymer mass at the beginning of each run. Linearity of both detectors was verified on polymer solutions of six different concentrations that spanned the range used in the tethering reactions. Because the detectors were calibrated with respect to the particular analyte and because the mass of the 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.*

For analysis, a carefully measured volume of bead-free solution from the 24 h exposure was volumetrically diluted to a concentration suitable for quantitative analysis by the UV and RI detectors used. Exactly 50 μL of the diluted solution was injected into the chromatograph, after which a digitized chromatogram was obtained and handled with DAx software (van Mierlo Software, Eindhoven, The Netherlands). The relative area of the elution band of the analyte (end-functionalized polymer) to that of the internal standard, as determined from the digitized chromatogram, was equal to the relative mass of analyte to internal standard. This relative mass of analyte remaining in solution after exposure to the beads was normalized by the relative mass of the analyte in solution initially, i.e., prior to exposure to the beads. Knowledge of the absolute mass of analyte in solution initially allowed direct computation of the absolute mass of analyte in solution at the end of the experiment. The difference in initial and final mass was equivalent to the mass attached to the surface of the beads.

Analysis of the test tubes containing inert-ended polyisoprene as standard yielded the sum of polymer mass attached by tethering (chemical bonds) and polymer mass attached by segmental adsorption to the surface of the epoxide-derivatized silicate glass, while analysis of the test tubes containing inert-ended polystyrene as standard yielded the mass of the tethered polymer only. The difference between the total mass and the tethered-only mass is, of course, the polymer mass merely adsorbed but not tethered. Division of any of these mass values by the M_n of the end-functionalized polystyrene used and multiplication by Avogadro's number yields the number of chains, which, in turn, can be divided by the known surface area of the substrate to yield the 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.[11]

E. Ellipsometry. Measurements of the thickness of the tethered layers were conducted on a manually operated, single wavelength, fixed angle (70°), Stokes ellipsometer (Gaertner Scientific, Skokie, IL). For ellipsometry, which requires a flat, reflective substrate, tethered layers were prepared on silicon wafers by the same procedures and under the same conditions as used to prepare the tethered layers on the silicate glass beads. Large pieces (rectangles measuring 1.5 cm × 4.0 cm) of silicon wafer were oxidized with piranha solution, deriva-

Table 1. Surface Attachment Densities (Avg ± 1 Std Dev) for Polymer Brushes Constructed from Dilute Solution without Segmental Adsorption

M_n (g/mol)	(chains/nm^2)	(mg/m^2)
14 500	0.027 ± 0.002	0.65
44 000	0.0052 ± 0.0002	0.38
90 000	0.0035	0.52

tized with glycidoxysilane (GPS), and then subjected to tethering reactions. Ellipsometry measurements were performed after each treatment step.

At the initial stages of the ellipsometry on the treated silicon, it became clear that the thickness of the initial oxide layer was quite low and was difficult to control precisely. Therefore, auxiliary experiments were conducted to evaluate the extent of uniformity of the oxide coating from piece to piece and within a piece. Results of these experiments showed that the oxide thickness within a piece varied by no more than 10% but that the oxide thickness varied by 22−50% from one piece to another. So that this large piece-to-piece variation would not cause errors in the values determined for subsequent layers (epoxysilane followed by tethered polymer) on each piece of substrate, oxide layer thickness values were determined for each piece and were not averaged.

After each large rectangular piece of oxidized silicon was derivatized with 3-glycidoxypropyl trimethoxysilane to introduce epoxide groups to the surface, it was cut into 10 small pieces, and the thickness of the epoxysilane layer on each small piece was individually determined. Then each small piece was exposed, in its own test tube, to a solution of primary amine end-functionalized polystyrene in cyclohexane at the desired concentration for 24 h. Then, polymer layer thickness was determined elliptometrically for each small piece. The polymer layer at this point was composed of both tethered and adsorbed chains. Next, each small piece was subjected to extraction in a Soxhlet with toluene to remove nontethered chains, after which it was subjected to ellipsometry to determine the thickness of the remaining polymer layer, comprised of tethered chains only. Thickness values obtained were converted to chains/nm^2 with the aid of the standard value for bulk density of polystyrene, the molecular weight of the end-functionalized polymer chains, and Avogadro's number.

For ultrathin layers, the refractive index and the layer thickness are highly correlated and are both unknown. The values we report for layer thickness were determined with the assumption of the bulk value for refractive index, which is an upper limit. The overestimate in refractive index automatically leads to an underestimate in the layer thickness.[41,42]

III. Results and Discussion

A. Previous Preparation of Low-Density Brushes by Grafting-to Approach. In the past, many our tethering reactions were conducted in dilute polymer solution (0.255 mg/mL) and in a solvent (toluene) that did not allow segmental adsorption of the polymer chains to the surface of the substrate.[15,35,40,43] Under these conditions, the tethered polymer layers formed at saturation (the natural cessation of tethering) were not dense, but they did qualify as brushes according to the criterion that the distance between tethering points be less than twice the radius of gyration. The densities of polymer brushes of M_n = 14 500, 44 000, and 90 000 g/mol are presented in Table 1 in terms of chains/nm^2 and mg/m^2. As stated in the Introduction, the purpose of the studies reported in the present paper was to change to conditions that would produce denser polymer brushes by the grafting-to approach. The remainder of this paper describes the results of these efforts and compares them with the low-density brushes that are described in Table 1.

B. Current Preparation of Higher Density Brushes by the Grafting-To Approach. The results obtained when tethering reactions were conducted under conditions of high solution concentration and in the presence of segmental adsorption are presented in this section. Two methods, solution depletion and ellipsometry, were used to analyze the surface attachment density at saturation. The results obtained by each method are presented below.

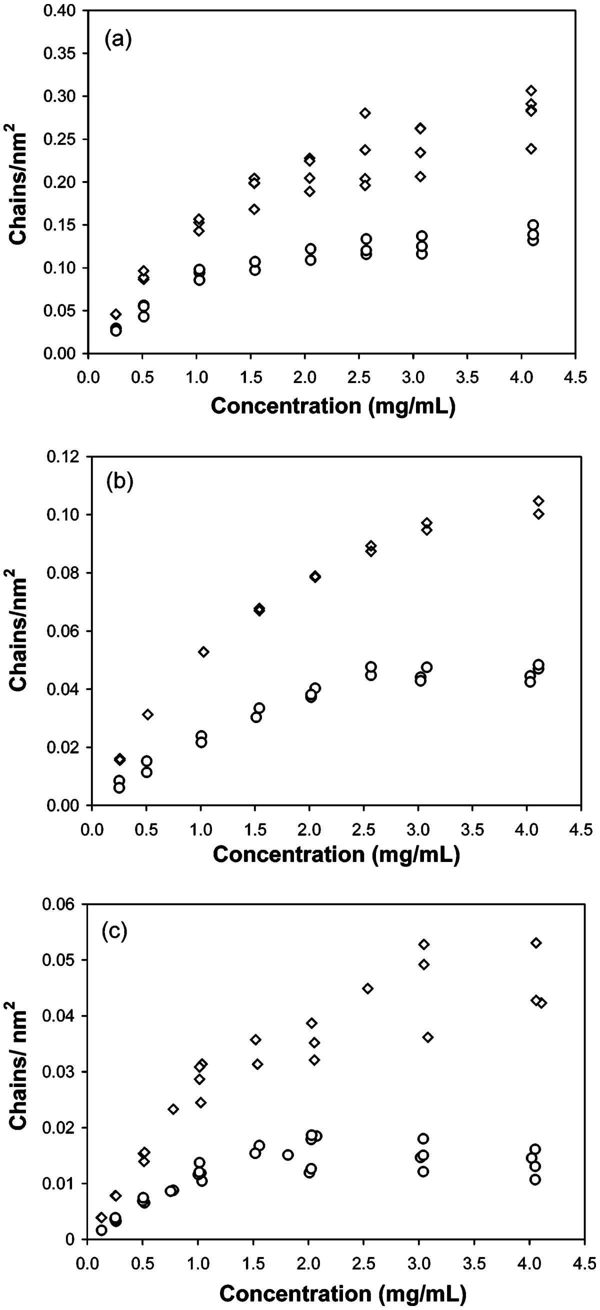

Figure 1. Surface density of polystyrene chains, as measured by solution depletion. Each data point shown represents an individual reaction. Diamonds report adsorbed plus tethered chains and circles report tethered chains only. (a) M_n = 14 500 g/mol, (b) M_n = 44 000 g/mol, and (c) M_n = 90 000 g/mol.

Figure 1 shows polymer per unit surface area vs solution concentration for three different molecular weights (14 500, 44 000, and 90 000 g/mol) of amine-ended polystyrene as determined by means of solution depletion measurements. The top curve for each molecular weight, represented by diamonds, reports a sum: the number of chains tethered plus the number segmentally adsorbed but not tethered. The bottom curve,

Table 2. Surface Attachment Densities (Avg ± 1 Std Dev) for Polymer Brushes Constructed from Concentrated Solution with Segmental Adsorption

M_n (g/mol)	(chains/nm^2)	(mg/m^2)
14 500	0.140 ± 0.009	3.4
44 000	0.045 ± 0.002	3.3
90 000	0.017 ± 0.002	2.6

formed by the circles, reports only the number of chains tethered (adsorbed chains having been desorbed by good solvent).

At all concentrations in Figure 1, for each molecular weight, the values in the top curve are approximately twice those in the bottom curve, indicating that about half of the chains adsorbed to the surface become tethered. Figure 1 also shows that the amount of polymer tethered appears to reach a true limit, or plateau, even though the amount of polymer adsorbed continues to slowly approach an asymptote. This reveals that continued increases in solution concentration beyond a certain point are ineffective in increasing the tethered chain density. In addition, the lowest solution concentration at which the tethered chains density reached a maximum is different for each molecular weight and decreases with molecular weight.

We focused on the lowest solution concentration at which the tethered chain density reached a maximum for each molecular weight. This was 4 mg/mL for M_n = 14 500 g/mol, 3 mg/mL for M_n = 44 000 g/mol, and 2 mg/mL for M_n = 90 000 g/mol. (Interestingly, these concentrations correspond to the changeover from dilute to semidilute solution for each molecular weight, respectively.) The densities of the polymer brushes formed from these concentrations are listed in Table 2 in terms of chains/nm^2 and mg/m^2. Comparison of the values in Table 2 with those in Table 1 shows that the number of chains tethered per unit area of substrate was enhanced significantly by the use of concentrated solution with segmental adsorption vs dilute solution without segmental adsorption. A reasonable explanation is that, when an increase in the solution concentration brings about an increase in the number of adsorbed polymer chains, there is a commensurate increase in the number of reactive chain ends in the vicinity of the surface, ready to undergo chemical reaction with the active sites there. Tables 1 and 2 also show that, while the number of tethered chains per nm^2 is inversely related to molecular weight, the *mass* tethered is fairly constant and independent of molecular weight.

Figure 2 summarizes the data, obtained from solution depletion measurements, as a function of molecular weight. The top curve reports the sum of adsorbed and tethered polystyrene chains, while the middle curve reports only the polystyrene chains actually tethered (from Table 2) for conditions of high concentration with segmental adsorption. The bottom curve reports the data shown in Table 1 for polystyrene chains tethered from dilute solution (0.255 mg/mL) and in the absence of segmental adsorption.[40,43] The figure reveals the inverse dependence on molecular weight of number of chains adsorbed as well as tethered.

The remainder of this paper presents results for surface attachment density obtained by means of ellipsometry. Ellipsometry was performed on silicon wafers containing tethered layers analogous to those prepared on the silicate glass beads. Values for layer thickness obtained with the ellipsometer were converted to polymer per unit surface area, as explained in the Experimental Section. These values are shown in Figure 3, where chains/nm^2 is plotted against solution concentration for the three molecular weights used. For expediency, the concentration series for each molecular weight was composed of only three concentrations, the highest of which was identified from Figure 1 as the lowest concentration that gave the plateau, or maximum, value of tethered chain density for each molecular weight. In Figure 3, the diamonds report a sum: the number of chains tethered plus the number segmentally adsorbed but not tethered. The circles report only the number of chains tethered (after desorption of the adsorbed chains).

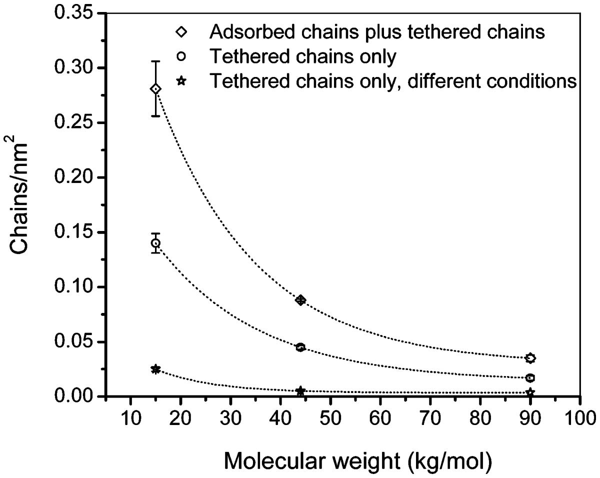

Figure 2. Maximum values for surface density of polystyrene (by solution depletion) vs molecular weight. Diamonds (top curve) report adsorbed plus tethered chains, circles (middle curve) report tethered chains only, and stars (bottom curve) report prior results obtained in tethering from dilute solution without segmental adsorption. Some error bars are within the symbol.

It is very noticeable in Figure 3 that the data for adsorbed plus tethered chains, indicated by diamonds, do not show the trendlike behavior. This can be explained by procedural differences between ellipsometry and solution depletion methods. The solution depletion measurements are made in situ, i.e., without removal of the solid substrate from the solution, whereas the ellipsometry measurements are made ex situ, i.e., in air after the substrate has been removed from the solution and drained. In the latter case, as the substrate is removed from the reaction solution and drained, it drags along some of the solution, which contains free chains. For a volatile solvent such as that used here (cyclohexane), removal from solution and draining is tantamount to a dip-coating step that deposits an imprecisely controlled amount of additional chains onto a substrate. Hence, the values indicated by the diamonds in Figure 3 include uncontrolled amounts of extra chains, which obscure any underlying trends with concentration. On the other hand, the circles, which report only tethered chains (all nontethered chains having been desorbed by good solvent), show the expected increasing trends with solution concentration.

Figure 4 plots the maximum value of surface attachment density for tethered chains of each molecular weight from the concentration series presented in Figure 3. In theory, the curve in Figure 4 and the middle curve in Figure 2 should be in fairly good agreement, since both represent tethered layers that were prepared under the same conditions and from identical materials, except for the primary substrate. However, comparison

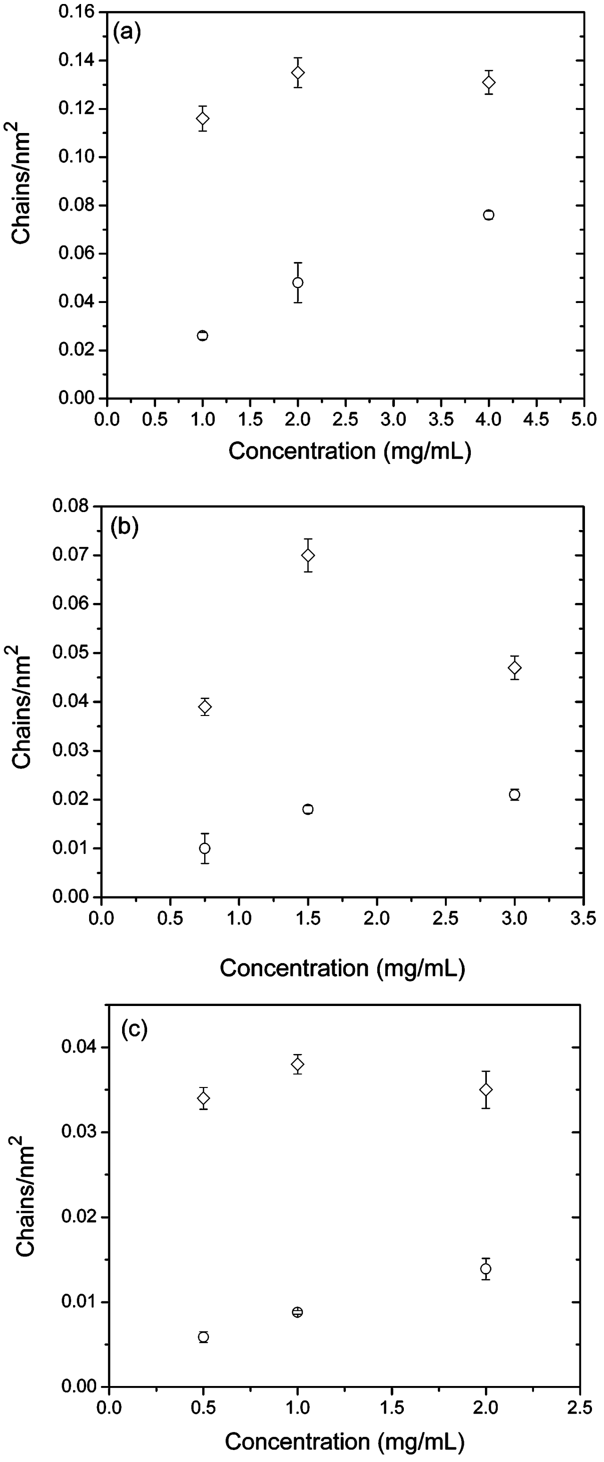

Figure 3. Surface density of polystyrene chains, as measured by ellipsometry. Each data point shown is an average of six measurements. Diamonds report adsorbed plus tethered chains, and circles report tethered chains only. Some error bars are inside the symbol. (a) M_n = 14 500 g/mol, (b) M_n = 44 000 g/mol, and (c) M_n = 90 000 g/mol.

of these two curves shows that the values from ellipsometry are consistently lower than those obtained from solution depletion methods. Previous comparison of the solution depletion method with thermogravimetric analysis for identically prepared tethered layers on identical substrates yielded agreement within 3%.[11] This good agreement suggests that the solution depletion method is reliable and accurate. On the other hand, the values obtained from our ellipsometry method are undoubtedly

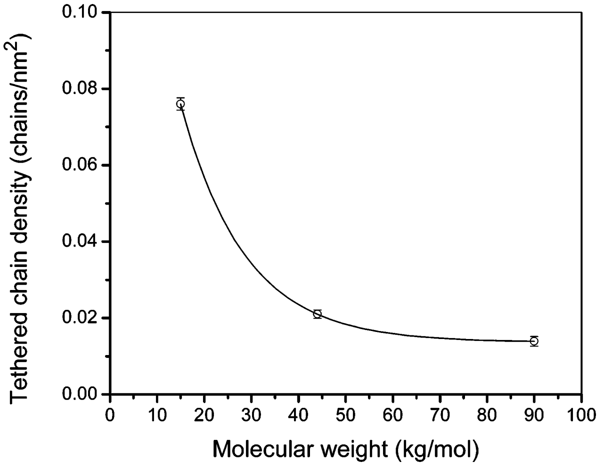

Figure 4. Maximum values for tethered polystyrene chains (by ellipsometry) vs molecular weight. Each point is an average of six measurements.

underestimates resulting from overestimates of the refractive indices of the ultrathin layers (see Experimental Section). It is less likely, but not impossible, that the tethered layers on the flat substrate were actually less dense than those on the beads. In either case, the trends obtained from the ellipsometry measurements made on the substrate from which all nontethered polystyrene had been desorbed can be regarded as reliable and as supplementary to the data obtained from solution depletion measurements.

The present study did not include examination of the effect of temperature on the tethered layer density. Elevating the temperature of the reaction solution in an attempt to increase tethering density is not necessarily wise because the extent of segmental adsorption will vary (and may go down) with temperature. However, a preliminary experiment in which we annealed a specimen at elevated temperature after it was removed from the polymer solution but before the nontethered chains were desorbed by extraction suggested that annealing can double the number of chains actually tethered.[44]

Our approach of using poor solvent and high solution concentration to achieve higher grafting density can be compared to the results of spin-casting methods used recently by others to achieve higher grafting density. Jones et al.[13] and Luzinov et al.[14] both report spin-casting monodisperse, functional-ended polystyrene from solution onto prepared silicon, allowing the solvent to evaporate, and conducting an elevated temperature annealing step prior to extracting the nontethered chains and evaluating the layer thickness by means of ellipsometry. Jones et al. obtained a tethered layer of 1.68 mg/m^2 for polystyrene of M_n = 107 000 g/mol, slightly lower than the value of 2.6 mg/m^2 obtained by us for a similar molecular weight (see Table 2). Luzinov et al. obtained tethered layers of 8.5 mg/m^2 for M_n = 45 900 g/mol and 5.0 mg/m^2 for M_n = 16 900 g/mol, both of which are higher than the values of 3.3 and 3.4 mg/m^2 obtained by us for comparable molecular weights (see Table 2). The differences between our results and the spin-casting results might be due to the differences in substrate or end-functional groups or could be due to effects of elevated temperature annealing. If, as indicated by the preliminary experiment mentioned in the previous paragraph, we could double the grafting density by elevated temperature annealing, our results would agree fairly well with those of Luzinov et al. for tethered chains of similar molecular weight.

Finally, we attempt to compare our results to those obtained by means of the grafting-from approach. In fact, the comparison is not at all straightforward because the surface attachment density (chains/nm^2) depends on the surface density of the initiator and the efficiency of the initiator, both of which can vary widely. Furthermore, at any given surface attachment density, very long polymer chains, corresponding to very high values of surface mass (mg/m^2), can be obtained by allowing the surface-initiated polymerization to proceed for long times. Wide-ranging surface attachment density values have been obtained with this approach: from 0.0068 chains/nm^2 for polystyrene of $M_n = 42\,000$ g/mol[26] to 0.13 chains/nm^2 for polystyrene of $M_n = 505\,000$ g/mol[31] to 0.94 chains/nm^2 for a mixed poly(methyl methacrylate)/polystyrene layer of mixed molecular weight.[25] Clearly, in the grafting-from approach, surface attachment density and chain molecular weight are independent variables, whereas in the grafting-to approach they are interdependent and have an inverse relationship (see Figure 2). Because of these fundamental differences between the grafting-to and grafting-from approaches, they cannot be compared on a fair basis.

A major practical advantage of our method, in which the substrate is exposed to a polymer solution (not melt), is that it is not restricted to flat substrates. Another practical advantage is that the excellent predictability and control of the grafting-to approach is preserved, while enhancements in surface attachment density are achieved through segmental adsorption and higher solution concentration. Overall, access to a very wide range of surface attachment densities is provided by the method described in the present paper combined with the method (dilute solution, no segmental adsorption) described previously.[39,43]

IV. Conclusion

A method has been described for obtaining fairly dense tethered layers, or brushes, by means of the grafting-to approach. The method is based on a combination of high solution concentration and solvent quality that permits segmental adsorption. The method can be used with substrates of any geometry and requires only a minimum of polymer solution. The experimental results revealed that there is a solution concentration above which there is no additional increase in tethered chain density. This concentration is inversely related to the molecular weight of the dissolved polymer chains. A comparison was made between quantitative analysis for tethered chain density by means of solution depletion and by means of ellipsometry of dry layers, and consistent trends were found.

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(44) We used a flat silicon substrate that had been oxidized, derivatized, and exposed for 24 h to end-functionalized polystyrene (M_n = 90 000 g/mol) in cyclohexane solution (2 mg/mL). Instead of subjecting this substrate to the usual extraction procedure to remove nontethered chains, we annealed it for 24 h at 110 °C in a vacuum, after which we extracted it exhaustively with good solvent (toluene) in a Soxhlet. Subsequent examination with ellipsometry gave a layer thickness corresponding to 0.0256 ± 0.0009 chains/nm^2. This value is nearly twice that achieved on comparable specimens not subjected to annealing (0.0139 ± 0.0013 chains/nm^2). Although investigation of the effects of annealing was not the purpose of the work reported in this paper, this limited experiment did show that annealing can drive the surface attachment density up even higher.

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