Effect of Segmental Adsorption on the Tethering of End-Functionalized Polymer Chains

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ABSTRACT: A comparison study was conducted of tethering in a poor solvent, in which segmental adsorption as well as tethering occurred, and tethering in good solvent, in which, for the conditions used, only tethering, and no adsorption, occurred. Monodisperse, amine end-functionalized polystyrene was tethered to the surface of silicate glass by chemical reaction with epoxide reactive sites thereon. The tethering process was monitored in real time by means of a procedure that enabled differentiation between chains held to the surface of the substrate by segmental adsorption alone and chains tethered to it by chemical bonds. The differences between tethering in the absence and presence of segmental adsorption were striking; not only was the kinetics of tethering changed, but also the number of chains tethered per unit surface area was larger (not smaller) and saturation was reached earlier when segmental adsorption occurred.

I. Introduction

The physical attributes of fully formed polymer brushes have been well studied by others, both experimentally[1−22] and theoretically.[23−40] Therefore, we have focused our efforts on the kinetics of formation of a polymer brush, which has received much less attention. More specifically, we have focused on systems in which tethering is accomplished by formation of a chemical bond between a reactive site on the surface of the solid substrate and the functional group at the end of the chain (Figure 1). Up to now, we have used combinations of polymer, solvent, and substrate for which no segmental adsorption of the polymer to the surface of the substrate occurred.[41,42] In the absence of segmental adsorption, the tethering process exhibited three distinct regimes of kinetics,[41,42] which could be associated with the conformational evolution of the chains in the tethered layer from mushroom to brush as the value of attachment density increased.[42]

Since adsorption of segments along the polymer chain backbone to the substrate would interfere with the ability of the tethered chains to assume traditional mushroom and brush conformations,[43] the hypothesis can be made that segmental adsorption would also change the kinetics of tethering. The present paper describes experiments designed to test this hypothesis. These experiments involved the tethering of monodisperse, end-functionalized polystyrene from a poor solvent to the surface of a solid substrate.

The cornerstone of our studies of kinetics is real-time monitoring of the tethering process, in which the disappearance of the end-functionalized polymer from the solution in contact with the substrate is analyzed quantitatively as a function of time. This quantitative analysis gives a direct measure of the disappearance of polymer from solution. Analysis of the solution can be done in a very precise manner, and if all of the polymer that disappears from solution becomes attached to the surface of the substrate and does not go elsewhere, then the method can be at least as accurate as any method that uses direct observation of the substrate. The details of the monitoring method are provided in the Experimental Section.

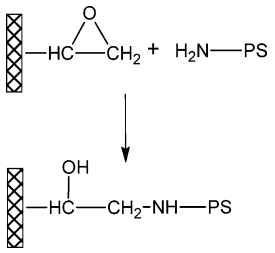

Figure 1. Chemical reaction by which end-functionalized polystyrene ($PS-NH_2$) is tethered to the surface of the substrate.

In the present work, we needed to distinguish between chains attached merely by physical attraction (segmental adsorption) and those attached by chemical bonds. We note that, in the presence of a solvent that allows segmental adsorption, even the chains that are tethered by chemical bonds can have some of their segments adsorbed to the substrate. However, chains that are tethered by chemical bonds cannot be removed by the action of solvent, whereas chains attached by segmental adsorption alone can be removed by the action of the appropriate solvent. We exploited this fact in developing procedures for distinguishing the tethered from the merely adsorbed chains in the systems under investigation. These procedures, used in conjunction with the real-time, quantitative analysis of the solution, are also explained in the Experimental Section.

II. Background

There are three basic ways that have been used by various researchers to attach, or tether, polymer chains

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by one end to the surface of a solid to form a polymer brush. The first way is the use of polymer chains that have at one end a group that experiences a specific attraction to the selected substrate. Examples would be a zwitterion end group attracted to mica[1−3] or a carboxylic acid end group attracted to silica.[4] The second way is the use of a diblock copolymer, where one block in each chain serves as an anchor block by adsorbing segmentally to the surface and the other block does not exhibit segmental adsorption along its backbone and is free to develop the brush conformation.[5−9] The third way is the attachment of polymer chains to the surface by chemical reaction between a reactive functional group on one end of each chain and a complementary reactive site on the surface of the solid.[10−13,41,42] This is the way we use. There are some important differences between these three methods of attachment. In the case of the zwitterion-to-mica or carboxylic acid-to-silica interaction, the bonding energy is less than 10 kcal/mol, or about $6kT$ (far less than a chemical bond). Because they are weaker than chemical bonds, these bonds are reversible, and tethering can involve lateral adjustments of the attachment point of each chain as equilibrium is approached. Furthermore, chains attached in this way can be displaced relatively easily.[1,4] Similarly, when chains are attached to a surface by means of a segmentally adsorbing anchor block, the adsorption of each segment is reversible, and tethering can involve lateral shifting of the anchor block through segment-by-segment desorption and readsorption (to make room for additional copolymers) as equilibrium is approached. It should be recalled that even when the system has reached equilibrium and the mass of polymer adsorbed to the surface has reached a constant value, the adsorbed segments are continuously desorbing and readsorbing.[43] At the other extreme is attachment by chemical bond (several tens of kcal/mol), in which the chain end that undergoes chemical reaction with the surface is irreversibly fixed to a point on the surface. Because there is no measurable back-reaction to undo the forward reaction, tethering by chemical bonding is an irreversible and nonequilibrium process. This makes it unique and, because of its permanence, potentially more useful.

Theoretical papers dealing with the kinetics of tethering of polymers by one end from good solvent (no segmental adsorption),[44−46] although few in number, provide a backdrop against which our experimental data can be discussed. These theoretical works describe a process composed of two distinct regimes of kinetics. A first regime is described that consists of rapid tethering at a rate controlled by center-of-mass diffusion of the chains through the solvent to the bare surface. When the surface of the substrate is covered by a layer of nonoverlapping chains, each in the expanded coil—or mushroom—conformation, a slowdown in rate occurs.[44−46] Theory explains that the source of decrease in rate is the mushroom layer itself; its presence introduces an activation barrier to diffusion of additional free chains to the surface. The predicted second regime is one of slow tethering, at a rate proportional to log(time). According to theory, the proportionality to log(time) is associated with a progressive increase in the activation barrier to diffusion as the surface attachment density of the tethered chains increases progressively with time.[44] The second regime is expected to continue until a constant value of mass tethered is reached, i.e., until tethering of additional chains is no longer favorable from a thermodynamic standpoint. This point is reached when the energy benefit of bond formation with the surface is offset by the various entropy costs of tethering.[44]

As already mentioned, our experimental work has shown a third regime prior to cessation of tethering (saturation) in addition to the two regimes of kinetics described by theory. It is possible that the irreversible nature of tethering (chemical bond formation) underlies the three-regime kinetics we have observed in our systems, and we have speculated that the third regime represents the transition from mushroom to brush conformation.[42] However, the origin of the third regime is not the focus of the present paper. The hypothesis made in the present paper is that all three regimes of kinetics would be changed by the occurrence of segmental adsorption simultaneously with tethering. The details of the experiments designed to test this hypothesis are presented below and are followed by the results of the experiments.

III. Experimental Section

A. Synthesis and Characterization of Amine End-Functionalized Polystyrene. Synthesis of the monodisperse, end-functionalized polymer, ω-(3-aminopropyl)polystyrene, was accomplished by means of anionic living polymerization under standard high-vacuum conditions in sealed, all-glass reactors equipped with break-seals as described in detail previously.[42] Four molecular weights were prepared for this study: M_n = 4000, 15 000, 20 000, and 44 000. In all cases dispersity, M_w/M_n, was <1.04, and the end group was $-(-CH_2-)_3-NH_2$, a primary amine. The fraction of chains containing primary amine end groups was determined by titration in 1/1 (v/v) mixture of chloroform in glacial acetic acid, with perchloric acid (Fisher, 10.1 N in glacial acetic acid) as the titrant and methyl violet 2B (Aldrich, about 75% dye content) as the indicator.[47] Five to seven 0.5 mg samples were analyzed from each batch of polymer, and end-functionalization was found to be >95% for all batches of polymer.

B. Introduction of Reactive Sites to Surface of the Solid Substrate. In order for the amine end-functionalized chains to be tethered, the surface of the substrate must derivatized to contain the appropriate reactive groups. The solid substrate selected for the present work was silicate glass in the form of nonporous, spherical beads (Potters Industries, Cleveland, OH) of specific surface area equal to 0.24 m^2/g. The spherical geometry and nonporous surface ensured complete accessibility of the surface to polymer in solution or to solvents used during the work. The as-received beads were cleaned with piranha solution and dried before derivatization. Epoxide reactive groups were introduced to the surface of the beads by exposing them to 3-glycidoxypropyltrimethoxysilane (98%, Aldrich, Minneapolis, MN) in toluene at 2 vol % under anhydrous conditions. (This group was selected for its reactivity with the primary amine group of the polymer chains to be added subsequently.) After derivatization, the beads were subjected to exhaustive extraction in a Soxhlet apparatus to remove any nonchemically bonded silane. This derivatization procedure results in 2.71 ± 0.24 epoxide groups/nm^2 of glass surface, a surface density value well above that needed for tethering of polymer chains at the highest conceivable surface density.[48]

C. Quantitative Monitoring of Tethering Reactions in Real Time. In our work, tethering is conducted from dilute solution, and the amount of end-functionalized polymer in the solution in contact with the substrate is monitored as it decreases over time. Accurate monitoring of a dilute solution places restrictions on the ratio of substrate to end-functionalized polymer. First, the amount of polymer in solution at the beginning has to be large enough for tethering to proceed to saturation without exhausting the solution. Second, the

initial amount of polymer in solution should not be so high that depletion cannot be measured accurately (i.e., small differences between large numbers must be avoided). We determined by trial-and-error the polymer-to-substrate ratio that fell within these limitations. The particular ratio we have been using (see section IIIE) allows us to see clearly the approximately 10% initial depletion of the solution during the first regime, and leaves a solution that still contains approximately 40−60% of its original polymer (depending on molecular weight) after saturation has been reached.

In our method, the amount of end-functionalized polymer in solution at any given time is quantified by comparison with the mass of an internal standard that neither reacts, evaporates, nor adsorbs from solution. (See results of auxiliary experiments, section IVA, for evidence that the internal standards used do not segmentally adsorb.) The solution is analyzed by means of size exclusion chromatography (SEC) on a Waters LC system (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 usually used for quantitative analysis, careful control over operating conditions, use of an internal standard, and calibration of the detectors, render it quantitative. The signals from the ultraviolet (UV) and the refractive index (RI) detectors attached to the column register polymer mass in solution. The signals from both detectors are 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. The molecular weight of the internal standard is always selected to be significantly different than that of the analyte, i.e., the monodisperse, end-functionalized polystyrene, so that the SEC chromatogram shows two narrow but well-separated elution bands. Since the detector signals are calibrated, and the concentration of the internal standard does not change, *the area ratio of the elution band of the analyte to that of the internal standard in the chromatogram is proportional to the mass ratio of analyte to internal standard*.

For the real-time analysis of a tethering reaction over time, we remove small (about 0.30 mL) aliquots from the stirring reaction mixture at frequent intervals. Not only is each aliquot small, so that very little material is removed from the reaction vessel, but each aliquot contains both solution and beads, so that the balance between substrate surface area and polymer in solution is not upset. Immediately after removal from the reaction vessel, each aliquot is treated with a controlled excess (100-fold) of trichloroacetyl isocyanate to quench the tethering reaction by capping the functional end of each polymer chain. Next, the beads in the aliquot are separated from the solution with a syringe filter and are discarded. The now-bead-free solution contains only the internal standard and the analyte, i.e., the end-functionalized polystyrene. Exactly 50 μL of this solution is injected into the chromatograph, after which a digitized chromatogram is obtained, which is then handled with DAx data acquisition and handling software (vanMierlo Software, Eindhoven, The Netherlands). From the digitized chromatogram, the area of the elution band of the analyte is determined relative to that of the internal standard. This relative area is, of course, equal to the relative mass.

The relative mass of the analyte in the solution at time, t, when the aliquot was taken, is then divided, or normalized, by the relative mass of the analyte in solution at $t = 0$. The absolute mass of end-functionalized polymer (analyte) remaining in solution at time, t, is computed directly from this normalized relative mass. The mass of polymer *tethered* at time, t, is the difference between the mass originally in solution and the mass found remaining in solution at time, t. Division of mass tethered by the known value of M_n yields number of chains tethered. Finally, division of number of chains tethered by the known surface area of the substrate yields surface attachment density, chains/nm^2. It is this last quantity that we use in making plots vs time. We have previously cross-checked surface attachment density values determined by this method with surface attachment density values determined directly by thermogravimetric analysis; agreement was within 3%.[41]

D. Auxiliary Experiments To Prove Absence of Segmental Adsorption. It was necessary to prove that, under the good solvent conditions used by us, neither the end-functionalized polystyrene chains intended for tethering nor the inert-ended chains used as internal standards would exhibit segmental adsorption to the surface of the epoxide-derivatized substrate. Tests for segmental adsorption of polystyrene to the substrate from toluene were made with *inert-ended* polystyrene, obtained from Polymer Standards Service, Silver Spring, MD. Since the inert ends make tethering impossible, the only means of attachment to the substrate would be segmental adsorption, if it occurred. (The surface of all glassware had been rendered inert to adsorption by treatment with *n*-butylsilane.) For the experiment, a toluene solution of carefully weight amounts of monodisperse, inert-ended polystyrene of two molecular weights, $M_n = 4000$ and $M_n = 45\,000$, was exposed to epoxide-derivatized, silicate glass beads under the same conditions used for tethering experiments. The solution was analyzed quantitatively as described in section IIIC before exposure to the beads. Once the beads were added to the solution, aliquots were removed at intervals for quantitative analysis. The beads were separated from the aliquot by syringe filter, and the bead-free solution was subjected to quantitative analysis by the size exclusion chromatography as described in section IIIC. From each digitized chromatogram, the area of each elution band and the area ratio of the two bands were determined. Since the area of each elution band is directly proportional to the mass of polymer in solution, tracking the area of each band over time is a direct measure of the amount of polymer in solution over time. Even more sensitive is tracking the area ratio of the two bands over time. A change in this ratio with time is the most sensitive indicator of segmental adsorption because of the established behavior of the shorter chains (which diffuse faster through solvent) adsorbing first and being displaced at later times by longer chains (which adsorb more strongly due to greater numbers of segments).[49,50] In the absence of segmental adsorption, the area ratio of the two elution bands would be expected to remain constant from beginning to end of exposure to the substrate. The mixture of beads and solution was monitored for a period of time that exceeded the time to saturation of the tethering reactions.

Tests for segmental adsorption of (inert-ended) polyisoprene from cyclohexane to the substrate were conducted in a similar fashion. For this, cyclohexane containing monodisperse, inert-ended polyisoprene of two molecular weights, $M_n = 3000$ and $M_n = 60\,000$, was exposed to epoxide-derivatized beads under the same conditions used for tethering experiments. Since polyisoprene cannot be detected by UV spectroscopy, the refractive index detector on the SEC was used for the quantitative analysis in this case. The mixture of beads and solution was monitored over a period of time that exceeded the time to saturation of the tethering reactions.

E. Tethering Reactions in the Absence of Segmental Adsorption (Good Solvent). The χ-parameter for polystyrene in toluene at room temperature is 0.40, indicative of a good solvent.[51] All tethering reactions in toluene were run at room temperature, under an argon atmosphere, in glassware that had been previously treated with *n*-butyltrichlorosilane (an effective surface energy reducer) to prevent segmental adsorption of polystyrene to the glassware. The end-functionalized polystyrene of the desired M_n was dissolved ahead of time in dried, reagent grade toluene at a concentration of 0.225 mg/mL. A carefully weighed amount of internal standard, about equal to the mass of the end-functionalized polymer, was added to this solution. Monodisperse, inert-ended polystyrene, purchased as a molecular weight standard from Polymer Standards Service, Silver Spring, MD, was used as the internal standard. This polymer was a suitable internal standard because it did not exhibit segmental adsorption from toluene (see section IVA) and did not become tethered to the substrate (chemically inert chain ends). The molecular weight of the internal standard was selected so its elution band in SEC did

not overlap that of the analyte (the end-functionalized polystyrene). This solution was quantitatively analyzed (see section IIIC) to establish the area ratio for end-functionalized polymer to internal standard at zero time. (The mass ratio was known from the initial weighing operation.) Then, 20 mL of the polymer solution was added all at once to 18.1 g of surface-derivatized glass beads stirring in the reaction flask, and the tethering process began immediately. Monitoring was conducted as described in section IIIC. It was our usual practice to run each tethering reaction in duplicate, i.e., two separate but identical reactions run simultaneously in separate flasks, to confirm reaction-to-reaction reproducibility.

F. Tethering Reactions in the Presence of Segmental Adsorption (Poor Solvent). When it was desired that the end-functionalized polystyrene exhibit segmental adsorption as well as tethering to the epoxide-derivatized substrate, dried, reagent grade cyclohexane was used as the solvent. The χ parameter for polystyrene in cyclohexane at room temperature is 0.52, indicative of a poor solvent.[52] The details of the twin tethering reactions run in poor solvent were the same as in good solvent. However, instead of only one set of twin reactions being run, two sets were run, so that the procedure described in the next section could be used to distinguish between chains attached to the surface by chemical bonds (tethered) and those attached solely by segmental adsorption. One set of twins contained monodisperse, inert-ended polystyrene as the internal standard, while the other set contained monodisperse, inert-ended polyisoprene as the internal standard. As shown in auxiliary experiments (section IVA), polyisoprene shows no segmental adsorption whatsoever from cyclohexane, which is good solvent for it.

G. Procedure for Distinguishing Tethered Chains from Those Held Solely by Segmental Adsorption for Reactions Run in Poor Solvent. The two sets of twins described immediately above, with two different internal standards, were subjected to the slightly different analysis procedures below, so that the chains that were actually tethered to the substrate could be distinguished from those attached to the surface of the substrate by segmental adsorption alone. For the monitoring of the twin reactions containing polyisoprene as the internal standard, the cyclohexane solutions in which the tethering runs were conducted was monitored by means of quantitative analysis of frequently taken aliquots, as described in detail in section IIIC. (The internal standard, polyisoprene, remained completely in solution for the duration of the run.) Quantitative analysis yielded, after reduction of the data, the total amount of end-functionalized polystyrene attached to the surface of the beads, whether by chemical bonding and/or segmental adsorption.

For the monitoring of the twin reactions containing polystyrene as the internal standard, an additional procedural step was inserted into the analysis of each aliquot taken during the course of the reaction. As soon as the aliquot was taken and quenched, the cyclohexane was evaporated from it and was replaced with an equal amount of toluene. This accomplished the desorption of the inert-ended polystyrene internal standard as well as the end-functionalized polystyrene held to the surface of the beads by segmental adsorption alone. Desorption was complete within 10 min. (Note that desorption cannot detach tethered chains from the surface, and even though it might desorb adsorbed segments of these chains, it cannot release the chains into the solution.) The beads, now containing only tethered chains, i.e., attached by chemical bonds, were removed from the aliquot by means of a syringe filter and discarded. The clear toluene solution was quantitatively analyzed by size exclusion chromatography as described in section IIIC. This analysis yielded, after reduction of the data, the amount of end-functionalized polystyrene actually tethered (chemically bonded) to the surface of the beads.

IV. Results and Discussion

A. Auxiliary Experiments To Prove Absence of Segmental Adsorption. The auxiliary experiments probing the possibility of segmental adsorption from good solvent confirmed the absence of segmental adsorption. The areas of the elution bands in SEC remained constant over time within 3%. As mentioned before, the most sensitive measure of adsorption is the mass ratio of two different molecular weights of polymer in solution over time. The mass ratio is the same as the area ratio of the elution bands of the two molecular weights as measured by SEC. The results for polystyrene in toluene are shown in Table 1, and the results for polyisoprene in cyclohexane are presented in Table 2. The variation of the area ratio over the exposure time of many days was less than the 3% random variation obtained for replicate injections of a single polymer solution. Additional experiments showing similar results for inert-ended polystyrene are described in refs 41 and 42. These references also describe contact angle measurements of epoxide-derivatized surfaces of silicate glass exposed for long times to solutions of inert-ended polystyrene; the contact angle studies corroborated the absence of segmentally adsorbed polystyrene.[42]

Table 1. Relative Masses in Solution of Inert-Ended Polystyrene of Two Molecular Weights Exposed to Derivatized Silicate Glass Beads

exposure time (min)	mass ratio of $M_n = 45\,000$ to $M_n = 4000$	deviation from initial, %
0	0.944	0.00
2	0.948	+0.42
5	0.961	+1.80
13	0.960	+1.69
40	0.955	+1.17
90	0.968	+2.54
1140	0.953	+0.95
2700	0.930	−1.48
7200	0.950	+0.64
12960	0.929	−1.59
31680	0.970	+2.75

Table 2. Relative Masses in Solution of Inert-Ended Polyisoprene of Two Molecular Weights Exposed to Derivatized Silicate Glass Beads

exposure time (min)	mass ratio of $M_n = 60\,000$ to $M_n = 3000$	deviation from initial, %
0	1.006	0.00
2	0.977	−2.88
5	0.997	−0.89
13	0.992	−1.39
40	1.017	+1.19
90	0.988	−1.79
1500	0.984	−2.19
2880	0.978	−2.78

B. Tethering in the Absence of Segmental Adsorption. Since tethering conducted in good solvent (no segmental adsorption) serves as the reference process for tethering in poor solvent, we present the results of tethering in good solvent first. Figures 2 and 3 show typical experimental results for the tethering of monodisperse, amine end-functionalized polystyrene of $M_n = 4000$ and $M_n = 44\,000$, respectively, allowed to run to saturation. *Each point in the plots is the quantitative analysis value for one aliquot*. Error bars do not appear in the figures because the scatter for replicate analyses of a single aliquot is smaller than the size of each symbol. Results are expressed as surface attachment density vs time; after 60 min, the horizontal axis switches from linear time to log(time) to accommodate the long time to saturation for each reaction. The vertical lines in the plots were added to separate the three distinct regimes of kinetics from one another. Saturation, indicated by the constancy of the last several data points, is not regarded as a regime of kinetics. Note

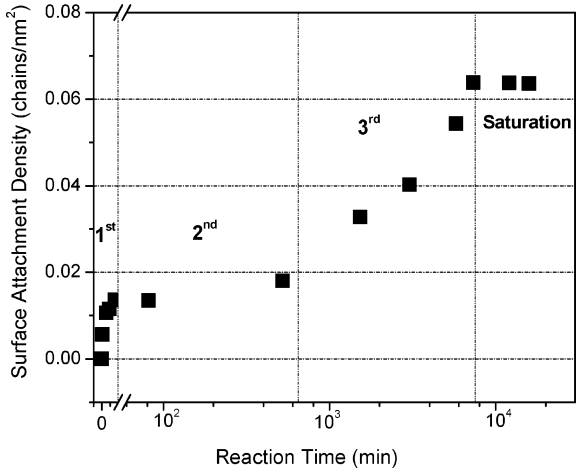

Figure 2. Typical plot of surface attachment density vs time for tethering of monodisperse, end-functionalized polystyrene, $M_n = 4000$, in good solvent showing three distinct regimes prior to saturation. The *x*-axis is linear up to 60 min and is logarithmic thereafter. Each data point represents one aliquot removed from the reaction mixture for analysis. Error bars for multiple analyses of single aliquot are smaller than the symbol.

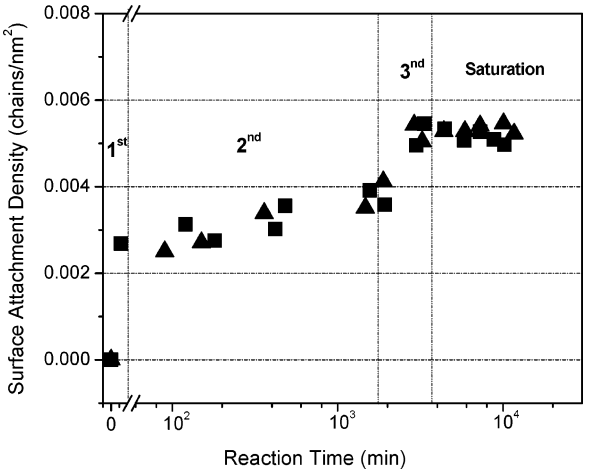

Figure 3. Typical plot of surface attachment density vs time for tethering of monodisperse, end-functionalized polystyrene, $M_n = 44\,000$, in good solvent showing three distinct regimes prior to saturation. The *x*-axis is linear up to 60 min and is logarithmic thereafter. Each data point represents one aliquot removed from the reaction mixture for analysis. The two different symbols represent data from identical twin reactions, run side by side at the same time, to show the reaction-to-reaction reproducibility.

the excellent reaction-to-reaction reproducibility shown in Figure 2 by the twin tethering reactions. (Examples of first regime behavior are shown in greater detail in Figures 4 and 5, which present data obtained by taking aliquots as fast as possible from specially run reactions set up for the purpose.) In both Figures 2 and 3, the data points in the slow second regime make a straight line, indicating that tethering is proportional to log(time). According to theory, the second regime would be expected to continue—proportional to log(time)—to saturation, i.e., until further tethering ceases. In the experimental systems, however, the second regime is interrupted by an unexpected acceleration in tethering rate. The accelerated tethering is also proportional to log(time), but its slope is much greater than the slope of the second regime. This change in slope makes the accelerated tethering a third regime of kinetics, distinct

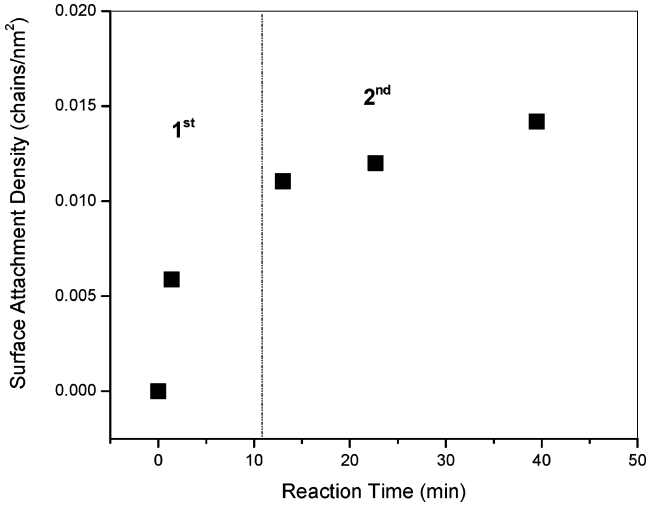

Figure 4. Surface attachment density vs time for tethering of monodisperse, end-functionalized polystyrene, $M_n = 4000$, in good solvent, showing first regime and beginning of second in more detail. Each data point represents one aliquot removed from reaction mixture for analysis.

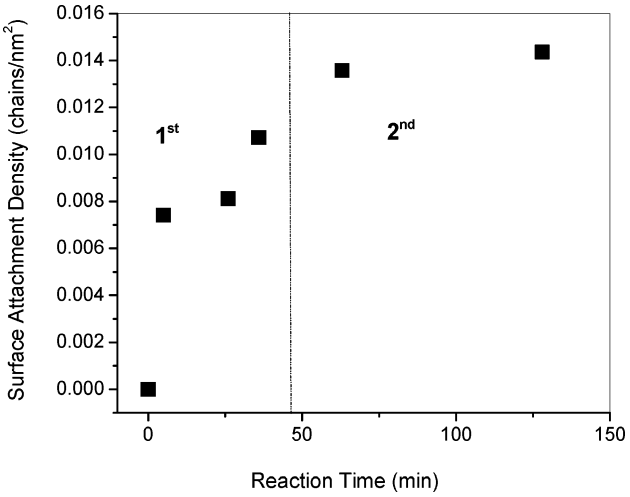

Figure 5. Surface attachment density vs time for tethering of monodisperse, end-functionalized polystyrene, $M_n = 15\,000$, in good solvent, showing first regime and beginning of second in more detail. Each data point represents one aliquot removed from reaction mixture for analysis.

from the second. It is the third regime, not the second, that leads to saturation. Figures 2 and 3 show that the third regime accounts for a large percent of the increase in tethered chain density prior to saturation, while the second regime, although lengthy, accounts for only a small percent of the increase. The three-regime kinetics has been observed for a variety of temperatures and molecular weights.[41,42] As mentioned in the Background section, a definitive understanding of the mechanism of the acceleration behavior and what triggers it is lacking at present.

C. Tethering in the Presence of Segmental Adsorption. Now we come to tethering in poor solvent, from which segmental adsorption of polystyrene does occur. It is to be emphasized that the term "tethering" in this paper refers exclusively to irreversible attachment of a polymer chain to the substrate by chemical bonding between the chain end and a reactive site on the surface of the substrate. Figures 6 and 7 show the results for monodisperse, end-functionalized polystyrene of $M_n = 4000$ and $M_n = 44\,000$, respectively. Each data

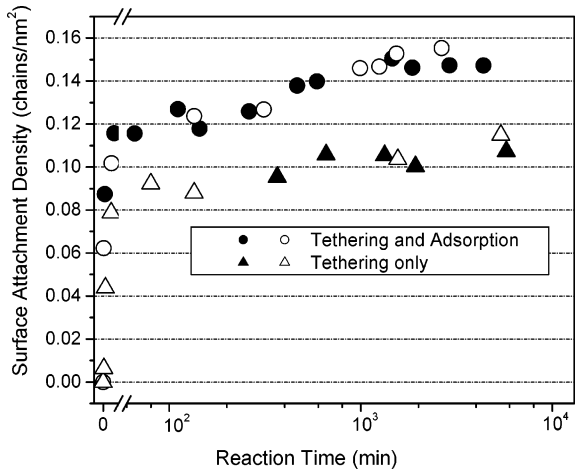

Figure 6. Surface attachment density vs time for tethering of monodisperse, end-functionalized polystyrene, $M_n = 4000$, in poor solvent. The circles represent the sum of tethered and segmentally adsorbed chains for twin reactions; open symbols are for one twin while closed symbols are for the other twin. The triangles represent the tethered chains; open symbols are for one twin while closed symbols are for the other.

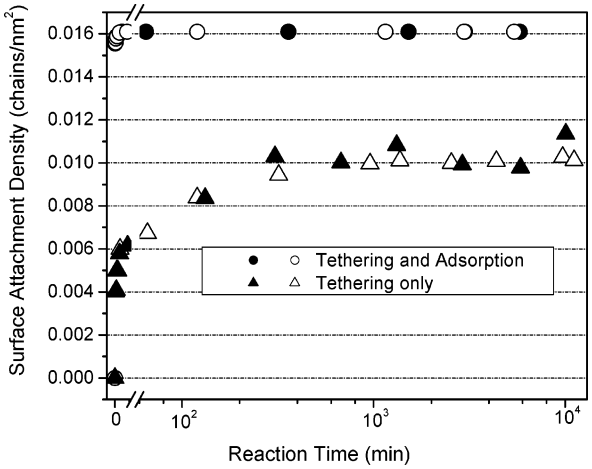

Figure 7. Surface attachment density vs time for tethering of monodisperse, end-functionalized polystyrene, $M_n = 44\,000$, in poor solvent. The circles represent the sum of tethered and segmentally adsorbed chains for twin reactions; open symbols are for one twin while closed symbols are for the other twin. The triangles represent the tethered chains; open symbols are for one twin while closed symbols are for the other.

point in the plots represents the quantitative analysis value for one aliquot. Scatter among replicate analyses of a single aliquot is smaller than the size of the symbol. These figures provide the evidence that segmental adsorption and tethering occur simultaneously in the poor solvent used in these experiments. The upper curve in each figure, composed of open and closed circles for one and the other twin in the set, reports the polymer chains attached to the surface by any means, i.e., by segmental adsorption or by tethering. We recognize that the tethered chains could also have segments along their backbones adsorbed to the substrate. However, desorption would not be able to detach these chains from the substrate. The lower curve in each figure, composed of open and closed triangles, reports the polymer chains that remain attached to the surface after the desorption operation. In other words, the lower curve reports the chains that are tethered. The difference between the upper and lower curves represents the number of chains held to the surface by segmental adsorption alone.

The upper curves in Figures 6 and 7 are similar in shape and time scale to those found in studies of polymer adsorption,[53−57] where the kinetics was dominated by the diffusion of the polymer chains through the solvent to the surface. The lower curves show no evidence of the three distinct regimes of kinetics associated with the development of the mushroom layer and brush layer in good solvent. This is in accordance with our hypothesis that the kinetics of tethering would be altered by segmental adsorption.

One key effect of segmental adsorption on tethering is that the tethering occurs faster. This faster tethering, plus the early leveling-off of the surface attachment density, provides assurance that saturation is indeed reached not only without a third regime but also earlier. Specifically, without segmental adsorption, $M_n = 4000$ reaches saturation in about 6000 min (Figure 2), whereas it takes only 400 min when segmental adsorption occurs (Figure 6). Similarly, without segmental adsorption, $M_n = 44\,000$ reaches saturation in 4000 min (Figure 3), whereas it takes only 600 min when segmental adsorption occurs (Figure 7). We speculate that segmental absorption is responsible for the "capture" of many free chains that might otherwise diffuse away without chemical reaction between the functional end of the polymer and a reactive site on the substrate. Even the adsorption of only a few segments of a freely diffusing chain would prevent its immediate diffusion away from the surface. Cumulatively, such captures would have the effect of increasing the tethering rate.

Another effect is that tethering in the presence of segmental adsorption yields higher values of surface attachment density for the tethered chains not only throughout the tethering process but also at saturation. Surface attachment density at saturation was 64% and 78% higher for $M_n = 4000$ and $M_n = 44\,000$, respectively. It has been suggested by some that adsorbed segments would be expected to reduce the rate of tethering by covering and rendering inaccessible some of the reactive sites on the surface. However, the observed increase in number of tethering reactions per unit area of surface belies this expectation. The observed increase can perhaps be better understood if it is remembered that polymer adsorption is a dynamic phenomenon, in which individual segments of an adsorbed polymer chain are reversibly and repeatedly adsorbing and desorbing to cover and uncover active sites, while the tethering reaction is permanent and irreversible.

The higher surface attachment density achieved by constructing the tethered layers in the presence of segmental adsorption is pertinent to practical application. If denser brushes are desired, chains could be tethered in poor solvent and then developed into a brush by replacement of the poor solvent with good solvent. An easily visualized quantity for comparing a brush made in this way with a brush originally constructed in good solvent is d, the average distance between tethering sites on the substrate. The value of d is computed from the experimental value for surface attachment density: $d = [(\text{chains/nm}^2)]^{-1/2}$. The values shown in Tables 3 and 4 for $M_n = 4000$ and $M_n = 44\,000$, respectively, show that each chain in a layer constructed originally in poor solvent and then transferred to good solvent would have much less room on the surface than each chain in a layer originally formed in good solvent. Tethered layers prepared in these two alternate ways

Table 3. Distance Apart of Tethered Chains, $M_n = 4000$ ($2R_g = 4.14$ nm)

original construction solvent	chains/nm^2 at saturation	d, nm, at saturation
good	0.066	3.9
poor	0.11	3.0

Table 4. Distance Apart of Tethered Chains, $M_n = 44\,000$ ($2R_g = 15.6$ nm)

original construction solvent	chains/nm^2 at saturation	d, nm, at saturation
good	0.0056	13
poor	0.010	10

also can be subjected to a commonly used criterion for evaluating whether they qualify as brushes. This criterion is the comparison of d with $2R_g$, twice the radius of gyration for a chain of the same molecular weight floating freely in a solvent.[43] According to this criterion, when $d > 2R_g$, the tethered polymer chains have sufficient lateral space on the surface of the substrate to be in the mushroom conformation, i.e., a relaxed conformation analogous to their conformations as free chains in good solvent. On the other hand, when $d < 2R_g$, the chains are compressed laterally and must stretch away from the surface to avoid overlap, so that the brush conformation is indicated.[43,46,58,59] R_g is computed from theory,[60,61] $R_g = \alpha\sqrt{C_\infty/6}(n^{1/2}l)$, where n is the number of C−C bonds in the backbone, l is the C−C bond length (0.154 nm), C_∞ is the characteristic ratio, which is 10.8 for polystyrene at room temperature,[62] and α is expansion factor of the polymer coil in good solvent.[61] The value of α was determined analytically[61,62] to be 1.14 and 1.30 for $M_n = 4000$ and $M_n = 44\,000$, respectively. When carried out, the computations yield $2R_g = 4.14$ nm for $M_n = 4000$ and $2R_g = 15.6$ nm for $M_n = 44\,000$. Since $d < 2R_g$ for all the tethered layers in Tables 3 and 4, they all qualify as brushes.

V. Conclusion

A comparison study was made of the kinetics of tethering from dilute solution in the presence and in the absence of segmental adsorption by the polymer chains. In this study, tethering refers specifically to the irreversible chemical bonding between end-functionalized polymer chains and reactive sites on the surface of the substrate. The kinetics of tethering was altered significantly when segmental adsorption occurred simultaneously. The kinetics went from a distinct, three-regime profile to a profile more like those observed in polymer adsorption studies. Another consequence of segmental adsorption simultaneous with tethering was that the surface attachment density of the tethered chains at saturation was significantly higher than without segmental adsorption. This has potential applications as a means to construct denser polymer brushes by switching from poor solvent to good solvent after tethering is complete.

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