TETHERED POLYMERS: KINETICS AND CONTROL

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ABSTRACT OF DISSERTATION

Heqing Huang

The Graduate School
University of Kentucky
2004
TETHERED POLYMERS: KINETICS AND CONTROL

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Heqing Huang

Lexington, Kentucky
Director: Dr. Lynn S. Penn, Professor of Chemical and Materials Engineering

Lexington, Kentucky
2004

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ABSTRACT OF DISSERTATION

TETHERED POLYMERS: KINETICS AND CONTROL

This dissertation describes a study of the kinetics of formation of tethered polymer layers. Polymer chains diffuse from dilute solution to the surface a solid, to which they become attached by one end. Kinetics profiles composed of three distinct regimes are displayed by all tethering reactions studied in the absence of segmental adsorption, regardless of solvent quality, temperature, chemistry of polymer, architecture of polymer, and type of reactive site on the surface. The first regime, fast and predicted previously by theory, is controlled by diffusion of the polymer chains through solution to the bare surface. The second regime, slow and also predicted by theory, is controlled by diffusion of the polymer chains through the already tethered layer. The third regime, relatively fast and not predicted by theory, appears to be the consequence of cooperative interaction between incoming chains and tethered chains. During the tethering process, each tethered polymer chain changes from a random-coil-like configuration to a vertically stretched configuration. The end of the first regime corresponds to completion of a layer of nonoverlapping, coil-like tethered chains, called a mushroom layer. Cessation of tethering corresponds to a layer of vertically stretched chains, called a polymer brush. Transition from mushroom to brush mainly takes place in the third regime and develops in spatially nonuniform manner. The understanding gained about the kinetics of tethering was used to construct simply tethered layers, bi-component tethered layers, bidisperse (two molecular weights) tethered layers, and tethered layers of mixed architecture (linear and star-branched).
KEYWORDS: Tethered Chain, End-functionalized Polymer, Polymer Brush, Kinetics, Tethered Layer

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June 30, 2004
TETHERED POLYMERS: KINETICS AND CONTROL

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DISSERTATION

Heqing Huang

The Graduate School
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2004
THERED POLYMERS: KINETICS AND CONTROL

DISSERTATION

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For Yichen
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Chapter One
Introduction to Tethered Layers

Since the research in this dissertation is focused on tethered layers, a short introduction to such layers is briefly presented in this chapter.

Definitions

A tethered chain is a polymer chain fixed by one of its ends to the surface of a solid. The remaining length of the chain is not attracted to the surface and is free to interact with another material, usually a solvent. A tethered layer is formed when many tethered chains, side by side, cover the surface of a solid.

Simple Physical Picture

Tethered layers have been the focus of interest to theorists [1] for more than two decades. They were interested in the changes in configuration of the tethered polymer chains as the number of the chains on the surface was increased. Theorists provided the following picture of a tethered layer bathed in good solvent. When tethered chains are widely separated, each one has a configuration identical to that of a polymer chain in solution, i.e., a loose random coil (picture “a” in Figure 1.1) [1-11]. When enough tethered chains are present on the surface to cover the surface well without overlapping each other, the layer is called a mushroom layer [1, 12] (picture “b” in Figure 1.1). The thickness of this layer is approximately equal to the diameter of the loose random coil. When the mushroom layer becomes sufficiently crowded so that the chains are forced to overlap, they stretch away from the surface to minimize or eliminate overlap [13-15]. This layer of stretched chains is called a polymer brush [1, 2, 4-6, 8, 9] (picture “c” in Figure 1.1). The degree of stretching determines the height, \( h \), of the brush layer. Two factors that influence the degree of stretching are surface attachment density and solvent quality. Higher surface attachment density, i.e., more chains tethered per unit area of solid surface, leads to stronger stretching to avoid overlap. Better solvent quality expands the polymer chain in all
directions, an effect that increases overlap and also results in stronger stretching to counteract overlap. According to theory, the segment density as a function of distance from the surface of the solid is a parabolic function \([16]\); the segment density is highest at the surface and diminishes as the bulk solution is approached. The theoretical description of the polymer brush has been validated by numerous experimental studies since the theories were advanced \([17-23]\).

**Different Means to Tether Polymer Chains to Surfaces**

Three means are commonly used to tether a polymer chain on the surface, according to the interaction between the end of the polymer chain and a site on the surface.

The first means is strong physical interaction between the chemical moiety at the end of the chain and an active site on the surface of the solid. The chemical moiety could be a zwitterions \([17, 22, 24]\), a carboxylic acid group \([23, 25]\), a quaternary amine group, or any chemical group that is capable of a strong physical interaction with the appropriate surface. The strength of these physical interactions ranges from 5 to 20 \(kT\). Interactions of this size are weak enough to allow the chemical moieties at the ends of the chains to adjust their positions laterally or even to be completely displaced by another species.

The second means is segmental adsorption of a special polymer block attached to one end of the polymer to be tethered. The segments of this block are chosen specifically to exhibit adsorption to the surface of the solid being used \([26, 27]\). Figure 1.2 illustrates a chain tethered by means of an adsorbed block. The strength of adsorption ranges from 5 to 100 \(kT\), depending on the number of segments in the block. Because the strength of adsorption for each segment is relatively low, the segments can adjust their positions one by one. By this mechanism the adsorbed block can adjust its position laterally on the surface or can even be displaced by a strong solvent.

The third means is chemical bonding between the reactive functional end of the chain and a reactive site on the surface of the solid \([28]\). The strength of the chemical bonding is 300 \(kT\) and above. This high strength makes tethering by chemical bonding irreversible. Chains
tethered by chemical bonding cannot adjust their positions laterally on the surface and cannot be displaced.

**Applications**

Tethered polymer layers have been used for some time to stabilize colloidal particles; for this, the repulsion between tethered layers on each particle prevents agglomeration [24, 29-31]. It is now known that tethered layers can be used to enhance adhesion between two different materials [32-36] to reduce friction[27, 34, 37-39], and to prevent adsorption of protein to surfaces [40-44], to name just a few examples.

**Predicted Tethering Kinetics**

Compared with the great attention given to completely formed tethered layers, relatively little attention has been focused on the kinetics of the tethering process, either hypothetically [45, 46] or experimentally [47-51]. The few theoretical studies that have considered the kinetics [45, 46] have predicted that the tethering process would exhibit *two* distinct regimes, as shown in Figure 1.3. In the first predicted regime, during which chains were tethered to the bare, solid surface, tethering would proceed rapidly, and the tethering rate would be controlled by center-of-mass diffusion of the chains through the solution to the bare surface. Liguore predicted that the length of the first regime would be inversely proportional to the diffusion coefficient of polymer chains at the same concentration [46]. The second regime is predicted to begin as soon as the surface is covered with a layer of nonoverlapping chains. This tethered layer would present an energy barrier to the diffusion of subsequent chains to the surface. With passing time, incoming chains would overcome the energy barrier, become tethered to the surface, and increase the energy barrier to diffusion even more. The progressively increasing energy barrier is predicted to cause the tethering rate to diminish logarithmically with time. The second regime is predicted to end when the chains become so stretched due to crowding that further tethering would be energetically unfavorable, i.e., when the entropy cost associated with chain stretching balances the energy benefit associated with formation of the chemical bond between the chain-end and the
solid surface. The cessation of tethering is called saturation. Ligoure predicted that the time to saturation could be as long as 100 days [46].

According to theory, tethered chains would change their configurations as tethering proceeds. Each tethered chain would be in a mushroom configuration during the first regime. During the second regime, tethered chains gradually would stretch away from the surface to avoid each other as the surface attachment density increased. The smooth progress of tethering with the logarithm of time predicted for the second regime implies that the transition from the mushroom to brush would be a random process and would develop uniformly over the surface. At saturation, all chains would be in a stretched configuration, forming a polymer brush on the surface.

Up to now, experimental studies focused on the tethering kinetics have been relatively rare [47-51]. Most of them were not long-term and were stopped at the first appearance of a slowdown in rate. These studies were typically less than two days and therefore showed only two regimes [18, 28, 47, 49, 51-53]. Thus, we were motivated to conduct more comprehensive and long-term studies of the tethering process to understand the tethering kinetics in depth.
Figure 1.1. Picture (a) depicts the configuration of a polymer chain in good solvent; picture (b) depicts a mushroom layer on the surface; picture (c) depicts a brush layer on the surface.
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Chapter Two
Goal, Hypothesis, and Approach

The overall goal of this research was to understand the process by which a tethered layer is formed. We wanted to know what the general features of the tethering process were, especially how the mushroom configuration made the transformation to the brush configuration. We also wanted to learn how experimental variables, such as temperature, molecular weight of the end-functionalized polymer, type of reactive site on surface, etc., affected the process. Our subordinate goal was to learn to control the tethering process to construct specific tethered layers.

These goals reflect that the primary hypothesis of this research was that formation of a tethered layer would occur by an understandable and reproducible natural process. Our subordinate hypothesis was that the tethering process could be manipulated to achieve specific tethered layers.

We applied the following experimental approach, consisting of five distinct tasks, to accomplish the goals of this research.

First, we conducted tethering reactions by using well-controlled materials. We used monodispersed, end-functionalized polymers. We also used solid substrates with well-defined surface areas as well as accurately known densities of reactive sites.

Second, we monitored the kinetics of the process from the beginning to the end, until the tethering reaction stopped naturally. We developed a real-time method for quantitative analysis; and followed the disappearance of end-functionalized polymer chains from solution for many different tethering reactions.

Third, we characterized the tethered layers by means of atomic force microscopy at all stages of tethering process.
Fourth, we correlated experimental findings with the results of a computer simulation. The tethering process was simulated by a Monte Carlo simulation based on a random sequential deposition model. We compared experimental kinetics with simulated kinetics. Likewise, we compared experimental surface texture with simulated surface texture.

Lastly, we manipulated the tethering process to construct specific tethered layers of mixed molecular weights, mixed types of polymers, or containing different chain architectures.
Chapter Three
Overview to Experiments

In this chapter, the experimental procedures used in this work are described in detail.

Materials

Substrates

Three forms of silicate were chosen to serve as a nonporous, impenetrable substrate to which end-functionalized polymer chains were tethered. They were: silicate glass beads, silica powder, and silicate discs.

Silicate glass beads of spherical geometry were obtained from Potters Industries, Cleveland, OH (Grade 500 UNC, Lot #0600R1948). According to the manufacturer, the silicate glass beads had a mean diameter of 10 µm, a specific surface area of 0.24 m²/g, and no surface treatment. Figure 3.1 shows a scanning electron micrograph (700X magnification) of beads after they had been cleaned with piranha solution. The figure shows that they are spherical and nonporous. The diameters of 200 beads selected at random were measured and the specific surface area was computed for each. The mean specific surface area was 0.24 m²/g, which agrees with the value provided by the manufacturer.

Silica powder in the form of irregular particles (Figure 3.2), processed from crystalline quartz, was obtained from Sigma, St. Louis, MO (S-5631, Lot 122K0117). The specific surface area of silica powder was measured by means of BET gas adsorption. These measurements were conducted separately on the as-received silica powder, the cleaned silica powder, the epoxide-derivatized silica powder, and the silica powder to which PEO-NH₂ was tethered. The measured value of specific area for each version of the silica powder is listed in Table 3.1. The differences among them deserve comment. The cleaning procedure removed impurities on the surface. The successive treatments, derivatization and tethering, probably filled the fissures (so small they were not visible at 8000X magnification by an SEM) on the surface and reduced the surface area.
of the substrate. Since the BET method presents the surface area accessible to small molecules of inert gas, the value we used in our subsequent computation was that of the substrate containing tethered polymer chains. This value of 4.84 m$^2$/g is the closest to the actual surface area that was accessible to the polymer chains themselves.

Silicate discs with a diameter of 15 mm were obtained from Ted Pella, Inc., Redding, CA. The silicate discs were manufactured especially for use in atomic force microscopy.

**Polymer chains for tethering**

Amine-ended polystyrene, designated PS-NH$_2$, was provided by Prof. Roderic P. Quirk at the University of Akron, and had been prepared by anionic polymerization. The molecular weight and the molecular weight distribution of the polymers were determined by size exclusion chromatography (SEC). The end-functionalization of the chains was found to be over 97% of theoretical, determined by titration. The end-functionalized polymers were stored in a vacuum desiccator and placed in a refrigerator. Molecular weight data for all amine-ended polystyrene chains are given in Table 3.2.

Amine-ended poly(ethylene oxide), designated PEO-NH$_2$, was purchased from Polymer Source, Inc.(Quebec, Canada), and had been prepared by anionic polymerization. Molecular weight data for both linear and four-arm PEO-NH$_2$ are listed in Table 3.2. Their structures are shown in Figure 3.3.

**Polymers used as internal standards**

Monodispersed, inert-ended polymers were used as internal standards. The characteristics and sources of polymers used are listed in Table 3.3.
**Solvents**

Four hydrocarbon liquids were used as solvents for the polymers: toluene (Mallinckrodt Baker, Inc., Paris, KY), cyclohexane (Mallinckrodt Baker, Inc., Paris, KY), p-xylene (EMD Chemicals, Inc., Gibbstown, NJ), and ethylbenzene (EMD Chemicals, Inc., Gibbstown, NJ). HPLC-grade tetrahydrofuran (EMD Chemicals, Inc., Gibbstown, NJ) was used as the eluent in size exclusion chromatography.

**Organosilanes**

Four organofunctional silanes were used to derivatize the surface of the silicate solids. They were 3-glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltri-methoxysilane, aminopropyl-trimethoxysilane, and n-butyltrichlorosilane (all from Aldrich, Milwaukee, WI). Their chemical structures are shown in Figure 3.4.

**Procedures**

**Scanning electron microscopy**

Scanning electron microscopy (SEM) was applied to determine the size of the silicate glass beads and to evaluate the geometry of the silica powder. To prepare a sample, about 0.02 g of silicate glass beads or silica powder, cleaned by piranha solution, was glued on the SEM stub and coated with gold. The images of the silicate glass beads were obtained on a Hitachi S3600 (Naperville, IL) scanning electron microscope at 700X magnification. Then, the average surface area of about 200 individual silicate glass beads was computed from the diameters exhibited on the image. These values were averaged to yield the specific surface area of the silicate glass beads. The images of the silica powder were obtained on a Hitachi S900 (Naperville, IL) scanning electron microscope at 8000X magnification.
**Gas adsorption analysis**

Gas adsorption analyses by the BET method were performed to determine the specific surface area of the silica powder in a Tristar 300 gas adsorption analyzer (Micrometritics, Norcross, GA). Nitrogen was used as the adsorptive. Before analysis, about 2 grams of sample was weighed into a tubular glass cuvette and was degassed at 150 °C for one hour in a FlowPrep 600 degas apparatus (Micrometritics, Norcross, GA). Then, the sample weight was measured on a balance with 0.001-gram accuracy. Gas adsorption analyses were conducted at 77 K, under liquid nitrogen. The equilibration interval was 10 seconds. The surface area was calculated by means of the BET method. Pore volume evaluation was derived by the instrument software, which indicated that the silica powder was non-porous. BET measurements were carried out on the as-received silica powder, the piranha-solution-washed silica powder, the organosilane-derivatized silica powder, and the silica powder containing tethered linear PEO-NH₂-10K.

**Atomic force microscopy**

Silicate discs interrupted at different stages of tethering were imaged by using the tapping mode of atomic force microscopy (AFM) in air to characterize their surface topography. The tips used in our application were Olympus TappingMode etched silicon probes, obtained from Veeco Instruments, Inc., Santa Barbara, CA. The backs of the probes were aluminized on the back for better reflection during alignment. The single-beam cantilever on the probe had a length of 160 µm and a typical spring constant of 42 N/m. The resonant frequency of the cantilever ranged from 200-400 kHz. Alignment of the laser was performed by applying the vertical digital magnifier method described in the user’s manual.

The AFM images were taken of a surface area of 1.0 µm x 1.0 µm. The instrument settings were a scan rate of 0.50 Hertz, an integral gain and proportional gain of approximately 0.50, a set-point of 1.0 volt, and a driving frequency of approximately 300 KHz. At least four images were taken from separate locations on each silicate disc to ensure that they were representative.
**Colorimetric analysis for amine**

The density of free amine groups on the surface of silica powder was determined by using a colorimetric analysis method. The analysis was based on the reaction scheme shown in Figure 3.5. The amino groups were first protonated to form ammonium ions, which then was coupled with a chromophore, Ponceau 3R to form a complex. This complex was rinsed and isolated; then the chromophore was decoupled and collected for analysis. The concentration of decoupled Ponceau 3R was determined by using a UV-detector.

The detailed experimental procedure was as follows. A mixture of 1.0 g of silica powder and 10 mL of 1.0 M HCl was placed in a 50-mL-centrifuge tube and agitated on a vortex until a fine dispersion formed. After the dispersion was stored overnight to allow all the amine groups to become protonated, the powder was spun down in a centrifuge and the supernatant (HCl solution) was decanted and discarded. Then, 10 mL of 0.01 M Ponceau 3R was added to the protonated silica powder and the mixture was stirred for one hour to achieve coupling of the dye to the protonated amine group. The excess dye, not coupled to the amine groups, was removed by thoroughly rinsing the silica powder with 0.1 M CH₃COOH until no trace of Ponceau 3R could be detected in the rinse solution by UV. Complete removal of excess, noncoupled dye required five rinse cycles. The silica powder was dried in the vacuum at room temperature for 4 hours and weighed on a balance to an accuracy of ± 0.0001 g. Then 10.0 mL of 0.1 M NaOH was added to the rinsed silica powder of known mass \( M \), and the mixture was agitated on the vortex until the silicate powder was well dispersed in the liquid. The dispersion was allowed to sit for 1 hour to fully decouple Ponceau 3R. The mixture was then centrifuged and the supernatant containing decoupled Ponceau 3R was filtered through a 0.2-µm membrane on a filtration apparatus and collected in a 25-mL volumetric flask. The collected solution of decoupled Ponceau 3R was diluted to the 25-mL mark, and its absorbance was measured at a wavelength of 510 nm in the UV detector. The concentration of the solution, \( C \) (mol/L), was obtained according to the absorption coefficient of the Ponceau 3R solution, which was predetermined by a calibration curve made from a series of Ponceau 3R solutions of different concentrations spanning the entire UV linear range. Consequently, the density, \( \sigma \), of the amino group on the surface was computed from the following expression:
\[ \sigma = \frac{CVA}{MS} \] (Equation 3.1)

where: \( C \) is the concentration of solution of the decoupled Ponceau 3R; \( V \) is the volume of this solution; \( A \) is Avogadro’s number (6.02 \times 10^{23} \) groups per mole); \( M \) is the mass of the silicate measured before decoupling; and \( S \) is the specific surface area of the silica powder, obtained by means of BET.

**Cleaning silicate substrates**

Before use, the silicate substrate was cleaned as described below to remove contamination and expose the native hydroxyl groups. It was critical to remove any residue of organic contaminant on the surface; otherwise it would inhibit the grafting of the organosilane to the surface. In addition, the organic contaminant would result in formation of an uneven layer of organosilane on the surface [54, 55]. Both of these results would adversely affect the subsequent quantitative study on the tethering kinetics. To completely remove the organic contaminant on the surface of the silicate substrate, the voracious piranha solution, a mixture of H\(_2\)SO\(_4\) (sulfuric acid) and 30\% H\(_2\)O\(_2\) (hydrogen peroxide) in volume ratios of 7:3, was used to clean the substrate.

**Silicate glass beads**

To clean silicate glass beads, one hundred grams of as-received silicate glass beads were placed in a beaker and were covered with piranha solution (70 mL of H\(_2\)SO\(_4\) and 30 mL of 30\% aqueous H\(_2\)O\(_2\)). This slurry was heated for 2 hours at 90 °C with vigorous stirring. After heating and stirring, 500 mL of deionized water was gently added to the beaker to dilute the mixture. The diluted mixture was allowed to settle at room temperature for overnight. The supernatant acidic liquid and the remaining slurry was decanted into a Fisherbrand\textsuperscript{®} glass microanalysis vacuum filtration apparatus and filtered with the aid of a vacuum through an alumina filter membrane containing 0.2-\( \mu \)m pores (Anodisc 47, Whatman Int., Maidstone, England). The beaker was rinsed with 50 mL of deionized water, and this water plus the remaining silicate glass beads was poured into the filtration funnel. The filter cake of the silicate glass beads was washed
repeatedly with water until the filtered water reached a pH of 7.0. On the filter membrane, the beads were washed with 10 mL of HPLC-grade acetone three times to remove water and were dried in a vacuum oven at 110 °C for 24 hours. One batch of cleaned beads was subjected to scanning electron microscopy for verification of the diameter and surface area values provided by the manufacturer.

Silica powder

As-received silica powder was subjected to the same cleaning procedure described above. One batch of cleaned silica powder was subjected to BET gas adsorption analysis to determine the specific surface area.

Silicate discs

Handling of the flat silicate discs during cleaning was different from that of round silicate glass beads or silica powder. To avoid the problem of discs in the vessel sticking to each other face-to-face, each disc was handled individually in a test tube. The tube containing a single disc and 5 mL of piranha solution was heated at 90 °C for 30 minutes. It was then rinsed with copious amounts of deionized water until neutral and finally was rinsed with HPLC-grade acetone. The moisture was removed in a convection oven at 120 °C. The cleaned silicate disc sitting in that test tube then was dried at 110 °C in a vacuum oven. The as-received and cleaned silicate discs were subjected to AFM and contact angle measurement to determine the consequence of the cleaning procedure.

Introduction of reactive sites to substrate (derivatization)

Epoxide or amine groups were introduced to the surface of the substrate (silicate in the form of bead, powder, or disc) according to a scheme shown in Figure 3.6 [56]. The native hydroxyl groups on the silicate surface reacted with the organosilane to leave reactive groups on the surface of the substrate. The density of hydroxyl groups was taken to be about 5~8 sites/nm² regardless of the geometry of the substrate [57]. It was assumed that one molecule of organosilane reacts with three hydroxyl groups on the silicate surface. Typically, approximately
20-fold excess of organosilane molecules over the total number of the surface hydroxyl groups present in the substrate was used to prepare the organosilane-derivatized surface. The concentration of organosilane in solution was controlled to 2 vol%. Detailed procedures for each derivatization are given below.

**Glycidoxypropyl groups**

The detailed procedure for introducing glycidoxypropyl groups (hereafter termed simply epoxide groups) to the silicate glass beads is as follows. After being dried with calcium hydride, 100 mL of toluene was transferred by means of a cannula into a 250-mL, 3-necked, round-bottomed flask, which was fitted with a reflux condenser and a Teflon-stopcock. The flask contained 100 g of dried silicate glass beads. Then, 50 µL of triethylamine was injected into the flask containing the stirred slurry of beads and solvent [58]. After 30 minutes of stirring at room temperature, 2 mL of 3-glycidoxypropyltrimethoxy silane was added to the flask with an air-tight syringe. The mixture was heated to reflux under argon for 16 hours. The derivatized silicate glass beads were filtered through a 0.2-µm alumina membrane (25 mm in diameter) by force of vacuum. The unreacted organosilane on the surface of the silicate glass beads was removed by means of two days of Soxhlet extraction with toluene under argon protection. After Soxhlet extraction, the beads were dried in a vacuum oven at 60 °C. The dried beads were kept in a desiccator ready for the tethering reaction.

The procedure of introducing the epoxide groups to the surface of silica powder was the same as that which was used on the surface of silicate glass beads, because the chemistry of the surface of silica powder is identical to that of silicate glass beads. However, because of the large specific surface area of the silica powder, only 10 g was derivatized at one time.

Introduction of the epoxide groups to the silicate discs followed basically the same procedure as described above, except for some special handling. Since two or more silicate discs in one reaction vessel would stick together, each disc had to be handled separately. A test tube containing one cleaned silicate disc was removed from the vacuum oven and the top of the test
tube was sealed with a rubber septum, through which argon was passed to fill the test tube. Just before derivatization, fresh silane solution was prepared by mixing 2 vol % of distilled 3-glycidoxypropyltrimethoxy silane and 98 vol% of anhydrous toluene in a sealed volumetric flask under argon. Four milliliters of the silane solution were pumped under pressure of argon into the test tube, which contained one cleaned silicate disc. The silane solution was covered with argon and the test tube was placed in a sand bath at 105 ºC for 16 hours. The silicate disc was removed from the test tube and was extracted with toluene in a Soxhlet apparatus for 16 hours to remove nonchemically bonded silane from the surface. The derivatized silicate disc was placed in a clean test tube and was dried in the vacuum oven at 60 ºC overnight prior to the subsequent tethering reaction.

**Cyclohexyl-epoxide groups**

Cyclohexyl-epoxide groups were introduced to the surface of the silicate glass beads following the same procedure described above for introduction of epoxide groups to silicate glass beads, except that 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane was used instead of 3-glycidoxypropyltrimethoxy silane.

**Amine groups**

Primary amino groups were introduced to the surface of the silica powder by means of the same procedure described above for introduction of epoxide groups to silica powder, except that triethylamine was eliminated. It was not necessary because the aminosilane could serve as a self-catalyst in the derivatization reaction between organosilane molecule and hydroxyl group on the surface [59, 60].

**Real-time monitoring of kinetics**

To study the development of a tethered layer on the surface of the substrate, we monitored the disappearance of polymers from the solution. During the tethering process, small representative aliquots were removed from the mixture of the tethering reaction at frequent intervals. The solid substrate was separated from each aliquot, and the solution portion was
quantitatively analyzed. Accurate quantitative analysis was achieved by the use of an internal standard, a material that does not change in nature or amount through the whole duration of the tethering reaction. The end-functionalized polymer emerged separately from the internal standard on a size exclusion chromatograph and was quantitatively analyzed by the UV and/or reflective index (RI) detectors attached to the chromatograph. The ratio of the end-functionalized polymer to the internal standard at the time each aliquot was taken was normalized to the ratio at zero time. This was converted into the number of polymer chains remaining in the solution. The number of chains tethered (removed from solution) was determined by difference and was used, along with the surface area of the substrate, to compute the surface attachment density at the time aliquot was taken. A plot of values for surface attachment density with respect to time was made; this represented the kinetics profile of the tethering process. The details of the real-time monitoring method are given below.

First, to take each aliquot, a polypropylene transfer pipette (Cat. No. 232 Samco Scientific Corporation, San Fernando, CA) was threaded through the Teflon stopcock on one of the necks of the reaction flask to draw off about 0.30 mL of the reaction mixture. This was done under positive argon pressure. Not only was each aliquot small, so that the scale of the reaction was not perturbed, but also each aliquot contained both solution and beads, so that the balance between the substrate surface area and polymer in the solution was not upset. As soon as the drawn aliquot was released into a polypropylene 0.65-mL micro-vial topped with a lid, the tethering reaction in the aliquot was immediately quenched by the addition of excess trichloroacetyl isocyanate. This reagent, which instantly caps any unreacted primary amine, as shown in Figure 3.7, was delivered to the aliquot as 20 µL of 1% solution in anhydrous toluene by means of an air-tight microsyringe.

Next, the micro-vial containing the quenched reaction mixture was centrifuged to separate the solid substrate from the polymer solution. The solution was drawn off with a polypropylene transfer pipette and was deposited into the barrel of a polypropylene syringe (Norm-Ject®, Tuttlingen, Germany). The tip of this syringe was fitted with a syringe filter (Millex®-FG 0.2-µm pore size, 4-mm diameter PTFE membrane filter). Any remaining particles of solid substrate were removed from the solution by forcing the solution through the syringe
The filtered polymer solution was collected in a polypropylene micro-vial until ready for quantitative analysis.

The polymer solution of each aliquot was analyzed on a size exclusion chromatography (SEC) system, which consisted of a Waters 515 HPLC Pump (Waters Corp., Milford, MA), a Rheodyne 7725i manual injector, a series of StyrageL columns (Waters Corp., Milford, MA), an ultraviolet detector (Waters 2487 Dual λ Absorbance Detector) and a refractive index detector (Waters 2414 Refractive Index Detector) in sequence. The mobile phase in the SEC system was tetrahydrofuran (THF). More than 100 µL of this solution was brought into the Rheodyne injector, which was equipped with a 50-µL loop to ensure that the exact amount of 50 µL of aliquot would enter the SEC columns. A UV detector has a better linearity and a wider linear range than a RI detector, so a UV detector was chosen for quantitative analysis when the polymer of interest showed enough UV absorbance. The UV detector was used to study all tethering reactions that involved polystyrene, while the RI detector was used to study tethering reactions that involved PEO and polyisoprene, both of which have a low response factor in the UV detector. Before they were used for analysis, the linearity of both detectors was experimentally verified on polymer solutions of six different concentrations.

Injecting an aliquot initiated the acquisition of the digitized chromatogram by an on-line computer. The chromatogram was analyzed with DAx data acquisition and handling software (vanMierlo Software, Eindhoven, Netherlands), which provides the area of the eluted peak of the end-functionalized polymer relative to that of the internal standard. This relative area is, of course, equal to the relative mass.

Next, the surface attachment density ($\Sigma_t$) of tethered chains at a given time, $t$, during tethering was computed from the following expression:

$$\Sigma_t (\text{chains} / \text{nm}^2) = \frac{(R_0 - R_t) m_0 A}{R_0 M_n S} \quad \text{(Equation 3.2)}$$

where $R_0$ is the relative mass of the end-functionalized polymer with respect to the internal standard for the original solution at $t = 0$; $R_t$ is the relative mass of the end-functionalized polymer with respect to the internal standard for the aliquot at taken time, $t$; $m_0$ is the mass of the
end-functionalized polymer dissolved in the original solution at $t = 0$; $A$ is Avogadro’s number; $M_n$ is the molecular weight of the end-functionalized polymer; and $S$ is the total surface area of the substrate (the product of the mass of the substrate used and the specific surface area of the substrate). The computed surface attachment density is the quantity to be used eventually in making the kinetics plot versus time for each tethering reaction.

Several key practices in the method described above deserve additional comment, since they bolstered the accuracy and precision of the real-time, off-line quantitative monitoring method.

The internal standard used in each tethering reaction was an inert-ended polymer similar to the end-functionalized polymer being tethered. However, the molecular weight of the internal standard was always selected to be significantly different than that of the monodispersed, end-functionalized polymer, so that the internal standard could be eluted in a position on the SEC chromatogram where it would not interfere or overlap with the peak of the polymer of interest. In addition, caution was taken to avoid segmental adsorption of polymers while the aliquot was handled. The aliquots were always exposed to containers (syringe, pipette, and micro-vial) made of pure polypropylene, the surface energy of which is so low that no segmental adsorption can occur.

Another key practice was the use of trichloroacetyl isocyanate to quench the tethering reaction in each aliquot by instantaneously converting active amine groups at the ends of polymer chains to nonreactive amide groups. This end-capping also eliminated any possible interaction between the amine-ends of the polymer chains and the packing material in the SEC column during elution of each aliquot [61, 62]. However, trichloroacetyl isocyanate is extremely moisture-sensitive, so that strict handling was required to retain its freshness and to ensure that all the free amine groups were capped instantly. To prepare a trichloroacetyl isocyanate solution, a sealed amber vial containing one gram of trichloroacetyl isocyanate (Aldrich, Milwaukee, WI) was broken at its neck and the fresh compound was transferred to 100 mL of anhydrous toluene in a dried, air-tight, 250-mL-flat-bottomed flask fitted with a three-way, Teflon stopcock. All of this was done under a blanket of argon. The flask containing the solution was blanketed with
argon and stored in a refrigerator. When aliquots were to be taken, 0.5 mL of this trichloracetyl isocyanate solution was transferred from the flask by means of an air-tight syringe to a dried amber glass vial capped with a tri-ply lid (National Scientific Company, Gultuth, GA). The tri-ply lid on the vial consisted of three layers: Teflon, silicon rubber, and Teflon. This unique sandwich structure made it possible to keep the solution from exposure to air even after the lid had been pierced by a needle several times. The amber vial was also blanketed with argon and wrapped with parafilm after each use. Even with the careful handlings described above, the solution in each vial had to be discarded within one day after it was used.

**Segmental adsorption studies**

In most work of this dissertation, we sought to conduct tethering experiments in which segmental adsorption of either functional-ended polymer or the inert-ended internal standard to the epoxide-derivatized substrate was completely absent. The possibility of segmental adsorption was evaluated by means of auxiliary experiments with inert-ended polymer, for which tethering was not possible.

The first type of auxiliary experiment was based on the well-known competitive segmental adsorption between two different chain lengths [63-66]. When segmental adsorption of a polymer does occur, the short chains adsorb first and then are displaced by the long chains later. In this case, a change in ratio of short-to-long chains in the solution occurs over time, and this change is one of the most sensitive indicators of the occurrence of segmental adsorption. If no segmental adsorption occurs, the ratio of short-to-long chains in solution remains constant from the beginning to the end of exposure to the substrate [66].

Tests for segmental adsorption of the polymer to the derivatized substrate from the solvent of interest were made with the inert-ended counterparts of the polymers used for tethering. Since the inert ends made 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-butyl silane.) For the experiment, a solution of carefully weighed amounts of monodispersed, inert-ended polymer of two molecular weights,
close to those of the end-functionalized polymer and internal standard, was exposed to epoxide-derivatized substrate under the same conditions used for tethering experiments. The solution was analyzed quantitatively before it was exposed to the substrate. Once the substrate was added to the solution, aliquots were removed at intervals for quantitative analysis. The substrate was separated from the aliquot by a syringe filter, and the substrate-free solution was injected into the size exclusion chromatography. 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 was directly proportional to the mass of the polymer in the solution, tracking the area of each band over time was a direct measure of the amount of the polymer in the solution over time. The solution was monitored over a period that exceeded the whole duration of the tethering reactions. Table 3.4 lists several pairs of inert-ended polymer chains used to test for segmental adsorption of polymers used in various tethering reactions.

The second type of auxiliary experiment used to test for segmental adsorption was contact angle measurement. Epoxide-derivatized silicate discs were exposed to the solution of inert-ended PS-40K. After many hours of exposure, the disc was removed from the solution and the contact angle made of water was measured. The value of the contact angle was compared with that of a non-exposed epoxide-derivatized disc.

**Tethering reactions**

Since tethering reactions were done with many different end-functionalized polymers, the experimental details of each type of tethering reaction are described as needed in the chapters that follow.
**Tables**

Table 3.1. Specific surface area acquired by means of BET

<table>
<thead>
<tr>
<th>Silica powder</th>
<th>As-received (m²/g)</th>
<th>Cleaned (m²/g)</th>
<th>Epoxide-derivatized treated (m²/g)</th>
<th>Containing tethered PEO (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>5.849 ± 0.026</td>
<td>6.591 ± 0.050</td>
<td>5.803 ± 0.015</td>
<td>4.836 ± 0.168</td>
</tr>
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Table 3.2. Characteristics of end-functionalized polymer

<table>
<thead>
<tr>
<th>Designation of amine-ended polymer</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-NH$_2$-4K</td>
<td>4,000</td>
<td>&lt; 1.04</td>
</tr>
<tr>
<td>PS-NH$_2$-15K</td>
<td>15,000</td>
<td>1.02</td>
</tr>
<tr>
<td>PS-NH$_2$-44K</td>
<td>44,000</td>
<td>&lt; 1.04</td>
</tr>
<tr>
<td>Linear PEO-NH$_2$-10K</td>
<td>10,000</td>
<td>1.08</td>
</tr>
<tr>
<td>Four-arm PEO-NH$_2$-10K</td>
<td>10,000</td>
<td>1.08</td>
</tr>
</tbody>
</table>

*The molecular weight values are abbreviated in $XK$ in the designation of the polymer.*
Table 3.3. Characteristics of internal standards

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-40K</td>
<td>40,000</td>
<td>1.06</td>
<td>Aldrich (Milwaukee, WI)</td>
</tr>
<tr>
<td>PS-13K</td>
<td>13,200</td>
<td>1.06</td>
<td>Aldrich (Milwaukee, WI)</td>
</tr>
<tr>
<td>PS-4K</td>
<td>4,000</td>
<td>1.04</td>
<td>Aldrich (Milwaukee, WI)</td>
</tr>
<tr>
<td>PS-2K</td>
<td>1,940</td>
<td>1.04</td>
<td>Polymer Laboratories, Inc. (Amherst, MA)</td>
</tr>
<tr>
<td>PEO-2K</td>
<td>2,000</td>
<td>1.05</td>
<td>Polymer Source, Inc. (Dorval, Quebec)</td>
</tr>
<tr>
<td>PI-60K</td>
<td>60,000</td>
<td>&lt;1.04</td>
<td>Polysciences, Inc. (Warrington, PA)</td>
</tr>
<tr>
<td>PI-3K</td>
<td>3,000</td>
<td>1.08</td>
<td>Polysciences, Inc. (Warrington, PA)</td>
</tr>
</tbody>
</table>
Table 3.4. Pairs of inert-ended polymers used for testing the segmental adsorption

<table>
<thead>
<tr>
<th>Tested polymer</th>
<th>Solvent of interest</th>
<th>Long Chain</th>
<th>Short Chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Toluene</td>
<td>PS-40K</td>
<td>PS-4K</td>
</tr>
<tr>
<td>Polystrene</td>
<td>Cyclohexane</td>
<td>PS-40K</td>
<td>PS-4K</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>Cyclohexane</td>
<td>PI-60K</td>
<td>PI-3K</td>
</tr>
<tr>
<td>PEO</td>
<td>Toluene</td>
<td>PEO-8K</td>
<td>PEO-2K</td>
</tr>
<tr>
<td>PEO</td>
<td>Ethylbenzene</td>
<td>PEO-8K</td>
<td>PEO-2K</td>
</tr>
<tr>
<td>PEO</td>
<td>p-xylene</td>
<td>PEO-8K</td>
<td>PEO-2K</td>
</tr>
</tbody>
</table>


Figures

Figure 3.1. SEM image of silicate glass beads
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Chapter Four
Kinetics of Formation of a Simple Tethered Layer

Introduction

In this chapter, the tethering kinetics of a monodispersed, end-functionalized polymer to the surface of a solid substrate was systematically investigated by monitoring a series of tethering reactions under various conditions. A kinetics profile of three distinct regimes rather than the two predicted by theory was evident for each tethering process studied. The first regime was fast and appeared to be controlled by diffusion through the solvent, as predicted by theory. The second regime was slow and appeared to be linear in logarithm of time, as predicted by theory. The third regime observed was not predicted by theory. It was also proportional to log(time), but with a steeper slope than that in the second regime. The distinct three-regime kinetics was observed for different molecular weights, temperatures, and reactive sites on the surface of the substrate.

This chapter describes the experiments in which monodispersed, amine-ended polystyrene (PS-NH$_2$) was tethered to the surface of a silicate substrate. The kinetics was monitored throughout the length of each reaction by means of the quantitative analysis method described in Chapter 3. The details of these reactions are described first and are followed by the results, which revealed the three-regime kinetics.

Experimental

To evaluate the reaction-to-reaction reproducibility, tethering reactions were always done as twins, i.e., as duplicate reactions run at the same time with epoxide-derivatized beads from the same batch and with a polymer solution that had been freshly made up in a larger quantity and divided in half. The amounts and procedures given below pertain to a single typical reaction. All glassware used in tethering reactions was exposed to an $n$-butyl-trichlorosilane reagent to prevent segmental adsorption of polystyrene to the glassware. The amine-ended 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 amine-ended polystyrene, was added to this solution. The molecular weight of the internal standard was always chosen so that its elution peak in size exclusion chromatography would not overlap that of the end-functionalized polymer. This solution was analyzed before use by the quantitative analysis method described in Chapter 3. The reaction vessel was a customized 100-mL, three-necked, round-bottomed flask. The three necks were each fitted with a glass stopper, a condenser topped with an inlet for a gas line, and a 6-mm-bore Teflon stopcock, respectively. The reaction vessel containing 18.1 g of epoxide-derivatized silicate glass beads and a 1-inch, egg-shaped stirring bar was dried in a vacuum oven at room temperature overnight. Once the flask was taken out of the vacuum oven, all ground glass joints of the reaction vessel were sealed with Teflon grease, and the gas line was connected through the inlet at the top of the condenser to maintain a slight positive pressure of argon inside the vessel. The tethering process began as soon as 20.0 mL of polymer solution was added to the silicate glass beads being stirred at 300 rpm. The solution was added by means of a 20-mL volumetric pipette through the bore of the Teflon stopcock in one neck. Monitoring was conducted as described in Chapter 3 (quantitative analysis by means of SEC). The temperature of the reaction was controlled by immersing the reaction vessel in a sand bath at a desired temperature. All reactions conducted to form simple (not mixed) tethered layers were conducted in the manner just described.

**Results and Discussion**

*Verification of the absence of segmental adsorption*

Auxiliary experiments were performed to verify that there was no segmental adsorption to interfere with the tethering process. As mentioned in the experimental section, the most sensitive indicator of segmental adsorption is a change in the mass ratio of two different molecular weights of polymer in solution over time [63, 64]. Table 4.1 shows no change in the mass ratio of monodispersed, inert-ended polystyrene of two molecular weights (M_n = 4,000 and M_n = 45,000), exposed for more than three weeks to epoxide-derivatized silicate glass beads. The random experimental variation in their ratio was less than 3%. The constancy of the ratio
confirms the absence of segmental adsorption of polystyrene to the substrate from toluene (good solvent).

Contact angles were also used to verify the absence of segmental adsorption. Contact angles are not only very surface-sensitive (sensing only the top 0.5 nm) but are also very sensitive to changes in surface chemistry. Table 4.2 lists contact angles of water on several relevant surfaces. The data show that the low contact angle of pristine glass was increased considerably by exposure to laboratory air, which is known to contain adventitious hydrocarbons. The silicate surface to which polystyrene chains were tethered gave a high contact angle, typical of commercial polystyrene, while the epoxide-derivatized surface gave a significantly lower contact angle due to the polar nature of the epoxide group. The contact angle of water on the epoxide-derivatized surface that had been exposed to inert-ended polystyrene remained statistically indistinguishable from the surface before exposure, again verifying the total absence of any polymer adsorbed to the surface.

**Results of tethering kinetics**

To investigate the kinetics of the tethering process, the reactions were conducted for long periods (several weeks) to approach the saturation suggested by theory. Numerous practical difficulties associated with lengthy experimental times were encountered. These included instrument instabilities and overnight equipment failures during the reaction, resulting in numerous invalidations or total losses of experiments.

Figure 4.1, Figure 4.2, and Figure 4.3 show the results for tethering of end-functionalized polymers of three molecular weights (PS-NH$_2$-4K, PS-NH$_2$-15K, and PS-NH$_2$-44K) from dilute solution to the solid surface by means of chemical reaction between the amine end-groups of the polymer chains and the epoxide reactive sites on the surface of the substrate at room temperature. In all figures, the surface attachment density is plotted versus time; after 60 minutes, the horizontal axis is changed from linear time to log(time) to accommodate the long time to saturation for the tethering reaction. The initial, or zero time, point for each tethering reaction was the mean result of three to four replicate aliquots taken from the initial solution for analysis.
before tethering; the scatter about this mean was always less than 3%, i.e., less than the size of the symbols. Data from each member of the twins are represented by different symbols. Each data point after zero time was obtained from a single aliquot withdrawn from the reaction for analysis. As can be seen in all of the figures, twins show very good reproducibility. Figure 4.2 (a) and (b) show results for two sets of twin reactions conducted on two different batches of epoxide-derivatized substrate. The batch-to-batch reproducibility between (a) and (b) is nearly as good as within each set of twins.

The most outstanding feature of Figure 4.1, Figure 4.2, and Figure 4.3 is the appearance of three regimes of kinetics prior to saturation rather than the two regimes as predicted by theory [67]. In each figure, dotted vertical lines have been inserted to separate one regime from the next to guide the eye. The first regime lasts approximately an hour. Tethering is rapid in the first regime, during which approximately half of the final surface attachment density, \( \Sigma_{\text{sat}} \), was reached. The second regime is characterized by an extremely slow tethering rate, requiring a change in the scale of the x-axis from linear time to log(time). Tethering in the second regime appears to be proportional to log(time) with a very low slope. The third, and unpredicted, regime is characterized by a relative acceleration in tethering rate. Tethering in the third regime also appears to be proportional to log(time), but with a steeper slope than in the second regime. The third regime ends when saturation is reached. Saturation, indicated by the constancy of the last several data points spanning a long duration, cannot be considered as a regime of kinetics because nothing is occurring after saturation has been reached.

To examine the effect of temperature on the tethering process, tethering of PS-NH\(_2\)-15K and of PS-NH\(_2\)-44K was conducted at different temperatures. Figure 4.4, Figure 4.5, Figure 4.6, and Figure 4.7, plotted in the same way as Figure 4.1, Figure 4.2, and Figure 4.3, present results of tethering reactions done at elevated temperature (60 °C and 100 °C) in toluene. Reproducibility within each set of twins was very good. Three regimes of kinetics are discerned in each plot. No consistent or significant change in tethering rate with the increase in temperature was discerned. The apparent absence of a temperature effect suggests that the kinetics of the tethering process studied is not governed by the chemical reaction between the end-functional group on the polymer and the reactive site on the surface. If this chemical
reaction governed the kinetics, an increase in temperature would have enhanced the rate significantly.

To examine the effect of type of reactive site on the tethering process, the polymer to be tethered was exposed to substrate containing different types of reactive sites. These are shown in Figure 4.8, along with the chemical reaction scheme for each with the amine end-group of the polymer. It is known that the ring-strained cyclohexyl epoxide group is more reactive than the glycidoxypropyl epoxide group. However, no apparent difference was discerned between the kinetics of two tethering processes shown in Figure 4.9 (a) and (b). This result also reveals that the tethering kinetics is not controlled by the chemical reaction itself. Therefore, the rate-controlling process is something much different than the chemical reactions. Next, we discuss the control of tethering kinetics in terms of the theory presented in Chapter 1.

The first regime, according to theory, is one in which tethering kinetics is controlled by center-of-mass diffusion of the polymer chains through the solvent to the surface. Despite the fact that it was difficult to make numerous measurements within this short-lived first regime to fully characterize its time dependence, we provide evidence to support the claim that the first regime is controlled by diffusion of polymer chains.

Based on the prediction of Ligoure, the length of the first regime is related to the diffusion coefficient of the polymer chain [46]. Examples of the first regime are shown in detail for tethering of PS-NH$_2$-4K, PS-NH$_2$-15K, and PS-NH$_2$-44K in Figure 4.10, Figure 4.11, and Figure 4.12, which present data obtained by taking aliquots as fast as possible from tethering reactions. Visual inspection of Figure 4.10, Figure 4.11, and Figure 4.12 allows estimation of the time at which the first regime comes to an end. These estimated times are 40 minutes, 80 minutes, and 150 minutes for 4K, 15K, and 44K respectively. Ligoure predicted that the length of the first regime would be inversely proportional to diffusion coefficient, $D$, of the polymer chains in solution at the same mass concentration [46]. In good solvent, $D$ is proportional to $1/N^{0.6}$. Since $N \propto M_n$, it was expected that the length of the first regime would be proportional to $M_n^{0.6}$. Figure 4.13 plots the length time of the first regime versus $M_n^{0.6}$. The linear relationship in the plot is consistent with the theoretical explanation that kinetics of the first
regime should be controlled by the diffusion of the polymer through the bulk solution to the bare surface.

The second regime in Figure 4.1-Figure 4.7 seems to agree with theory, in that tethering appears to be proportional to log(time), as expected when free polymer chains are required to diffuse through a progressively increasing energy barrier. It should be recalled from Chapter 1 that the increase in energy barrier arises from the increase in density of the tethered layer. According to theory, the second regime would be expected to continue proceeding in proportion to log(time) until the natural cessation, i.e., saturation.

In practice, the tethering process in our experiments did not continue smoothly until saturation. Instead, the second regime was interrupted by an unexpected change in tethering rate. This change was manifest as a distinct increase in slope in the plots of surface attachment density vs. log(time). It was this regime of increased slope that led to saturation, as shown in Figure 4.1-Figure 4.7, and Figure 4.9. This regime was defined by us as the third regime; its increased slope revealed a relative acceleration in rate not predicted by existing theory. The relative increase in rate of the third regime had the effect of shortening the time to saturation. The actual time, experimentally observed, to reach saturation was about 14 days. By contrast, if one extrapolates the second regime in the theoretical curve (see Figure 1.3), the experimental value for saturation is reached in 100 days, which is much longer than that observed experimentally. We will present an explanation for the appearance of this unpredicted third regime in the next chapter, based on a comparison between a computer simulation and the AFM observation of the change in surface texture during the third regime.

Saturation, the end of the tethering process, is the natural point at which the benefit of chemical reaction between chain-end and surface site is offset by the entropy cost for stretching the tethered chains away from the surface.

Below, we discuss the development of the tethered layer during the course of the tethering process. The theory suggested that a mushroom layer is formed during the first regime and is completed at the end of the first regime. And then according to theory, the mushroom
stretches into a brush over the course of the second (and only remaining) regime. Thus when saturation is reached, the layer is in the form of a brush.

The completion of the mushroom layer at the end of the first regime implies that the surface attachment density at this point is inversely proportional to the square of the radius gyration of a relaxed polymer chain [46]. Figure 4.14 is a universal plot in which the surface attachment density at the end of the first regime is plotted against $1/R_g^2$ of the corresponding tethered polymer chain regardless of its molecular weight, chemical structure, and temperature, since these factors have been taken into account of computation of $R_g$. Except for the case of PS-NH$_2$-15K, surface attachment density, $\Sigma_{mush}$, is linearly proportional to $1/R_g^2$. The two outlying points at an abscissa value of 0.05 are data for PS-NH$_2$-15K. Late in this research, the sample of PS-NH$_2$-15K was subjected to elemental analysis for nitrogen by means of the Kjeldahl method. The results indicated that nearly half of PS-NH$_2$-15K chains contained two amine groups instead of one amine group per chain, as desired. (This may have resulted from an inexplicable error in polymer synthesis process.) The extra end-functional groups for this sample resulted in unusually high values of mass tethered in all the experiments where this sample was used.

Another common criterion is used to verify that the end of the first regime corresponded to completion of a mushroom layer and the saturation corresponded to formation of a brush layer. This criterion is the comparison of $d$, the average distance between tethering sites, with $2R_g$, twice the radius gyration of the relaxed polymer chain freely floating in solvent [13]. According to this criterion, if $d > 2R_g$, the tethered polymer chains have sufficient lateral space on the surface of the substrate to be relaxed and in the mushroom configuration analogous to their configurations as free chains in a solvent. On the other hand, if $d < 2R_g$, the chains are overcrowded and overlapping and must stretch away from the surface to avoid overlap. In this case, the brush configuration is indicated. The detailed computations for $R_g$ are presented in the Appendix. For PS-NH$_2$-4K, $2R_g = 4.14$ nm; for PS-NH$_2$-15K, $2R_g = 8.56$ nm; and for PS-NH$_2$-44K, $2R_g = 15.6$ nm. Table 4.3 compares $2R_g$ and $d$ at two points in the tethering process: the end of the first regime and at saturation. At the end of the first regime, the fact of $d > 2R_g$ for all cases reveals that all chains are in the mushroom configuration. If one takes a close look at the size of the difference between $d$ and $2R_g$, one finds that there is not quite enough space between
mushrooms to accommodate an additional mushroom. This provides insight into why tethering slows down so drastically at the end of the first regime. From this, we can conclude that the end of the first regime corresponds to a layer of loosely packed, randomly arranged, relaxed chains, or mushrooms. At saturation, that fact of $d < 2R_g$ in all cases reveals that all chains are crowded and would have to stretch away from the surface to avoid overlap. This is consistent with the notion of a brush, i.e., chains that are laterally compressed, and therefore stretched away from the surface.

It should be noted that the surface attachment densities at saturation are much less than 2.71 sites/nm$^2$, the area density of reactive sites on the silicate substrate prior to tethering. This means that the density of reactive sites was more than sufficient to accommodate the surface attachment density reached by the tethered chains.

Before concluding, it is worth pointing out the practical value of the distinct changes in slope in the kinetics of tethering. These three change-points can be used as benchmarks in the formation of a tethered layer, telling the experimenter where he is in the process of layer formation. For example, the experimenter who wants a mushroom layer can stop the reaction as soon as the first benchmark is reached. The experimenter who wants a brush knows he needs to keep the reaction going until three benchmarks are reached.

**Conclusion**

The kinetics of tethered layer formation by monodispersed, end-functionalized polystyrene chains in good solvent was investigated. The data showed three distinct regimes of kinetic behavior rather than the two predicted by theory. The first regime is fast and appears to be controlled by diffusion of polymer through the solvent, as predicted by theory. The second regime is slow and depends on the logarithm of time, as predicted by theory. The third regime is one in which tethering makes a relative acceleration in rate and is not predicted by theory. The three-regime kinetics is reproducible and understandable regardless of molecular weight, temperature, and type of reactive site on the surface of the substrate. The end of first regime
corresponds to the completion of a mushroom layer and saturation corresponds to the formation of a brush layer.
**Tables**

Table 4.1. Relative masses in solution of inert-ended polystyrene of two molecular weights exposed to epoxide-derivatized silicate glass beads

<table>
<thead>
<tr>
<th>Exposure time (min)</th>
<th>Mass ratio of $M_n = 40,000$ to $M_n = 4,000$</th>
<th>Deviation from initial, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.944</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.948</td>
<td>+0.42</td>
</tr>
<tr>
<td>5</td>
<td>0.961</td>
<td>+1.80</td>
</tr>
<tr>
<td>13</td>
<td>0.960</td>
<td>+1.69</td>
</tr>
<tr>
<td>40</td>
<td>0.955</td>
<td>+1.17</td>
</tr>
<tr>
<td>90</td>
<td>0.968</td>
<td>+2.54</td>
</tr>
<tr>
<td>1140</td>
<td>0.953</td>
<td>+0.95</td>
</tr>
<tr>
<td>2700</td>
<td>0.930</td>
<td>-1.48</td>
</tr>
<tr>
<td>7200</td>
<td>0.950</td>
<td>+0.64</td>
</tr>
<tr>
<td>12960</td>
<td>0.929</td>
<td>-1.59</td>
</tr>
<tr>
<td>31680</td>
<td>0.970</td>
<td>+2.75</td>
</tr>
</tbody>
</table>
Table 4.2. Contact angles made by water on modified and non-modified silicate disc surface

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle, Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine: washed in piranha solution, blow-dried and subjected to immediate contact angle measurement</td>
<td>0</td>
</tr>
<tr>
<td>Washed and aired: washed in piranha solution, rinsed, dried in vacuum and exposed to ambient air</td>
<td>21 ± 2.8</td>
</tr>
<tr>
<td>Epoxide-derivatized under anhydrous conditions</td>
<td>54 ± 3.7</td>
</tr>
<tr>
<td>Epoxide-derivatized and exposed to inter-ended PS-40K</td>
<td>57 ± 4.0</td>
</tr>
<tr>
<td>Polystyrene-tethered: epoxide-derivatized and reacted with PS-NH$_2$-44K</td>
<td>83 ± 4.6</td>
</tr>
</tbody>
</table>
Table 4.3. Characteristics of layers formed in toluene at 23 °C

<table>
<thead>
<tr>
<th>Polymer being tethered</th>
<th>chains/nm², from data</th>
<th>$d$ (nm) from data</th>
<th>$2R_g$ (nm) from theory</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>At the end of the first regime</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS-NH₂-4K</td>
<td>0.019</td>
<td>7.3</td>
<td>4.14</td>
</tr>
<tr>
<td>PS-NH₂-15K</td>
<td>0.0094</td>
<td>10</td>
<td>8.56</td>
</tr>
<tr>
<td>PS-NH₂-44K</td>
<td>0.0024</td>
<td>20</td>
<td>15.6</td>
</tr>
<tr>
<td><strong>At saturation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS-NH₂-4K</td>
<td>0.066</td>
<td>3.9</td>
<td>4.14</td>
</tr>
<tr>
<td>PS-NH₂-15K</td>
<td>0.024</td>
<td>6.5</td>
<td>8.56</td>
</tr>
<tr>
<td>PS-NH₂-44K</td>
<td>0.0056</td>
<td>13</td>
<td>15.6</td>
</tr>
</tbody>
</table>
Figure 4.1. Plot of surface attachment density versus time for tethering PS-NH$_2$-4K in toluene at 23 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol.
Figure 4.2. Plot of surface attachment density versus time for tethering PS-NH₂-15K in toluene at 23 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol. 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.
Figure 4.3. Plot of surface attachment density versus time for tethering PS-NH$_2$-44K in toluene at 23 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol. 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.
Figure 4.4. Plot of surface attachment density versus time for tethering PS-NH$_2$-15K in toluene at 60 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol. 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.
Figure 4.5. Plot of surface attachment density versus time for tethering PS-NH$_2$-15K in toluene at 100 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol. 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.
Figure 4.6. Plot of surface attachment density versus time for tethering PS-NH$_2$-44K in toluene at 60 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol. 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.
Figure 4.7. Plot of surface attachment density versus time for tethering PS-NH₂-44K in toluene at 100 °C. The x-axis is linear up to 60 minutes and is logarithmic thereafter. Each data point represents one aliquot removed from reaction mixture for analysis. Error bars for multiple analyses of a single aliquot are smaller than the symbol. 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.
Figure 4.8. (a) Gycidyl epoxide group on the surface + primary amine at one of ends of polystyrene. (b) Cyclohexyl epoxide group on the surface + primary amine at one of ends of polystyrene.
Figure 4.9. Plot of surface attachment density versus time for tethering PS-NH$_2$-15K in toluene at 60 °C on the surface of epoxide-derivatized glass beads (a), or of cyclohexyl-epoxide-derivatized silicate glass beads (b).
Figure 4.10. Surface attachment density versus time for tethering PS-NH₂-4K in toluene at 23 °C, showing first regime and beginning of second in more detail. Each data point represents one aliquot removed from reaction mixture for analysis.
Figure 4.11. Surface attachment density versus time for tethering PS-NH$_2$-15K in toluene at 23 °C, showing first regime and beginning of second in more detail. Each data point represents one aliquot removed from reaction mixture for analysis.
Figure 4.12. Surface attachment density versus time for tethering PS-NH$_2$-44K in toluene at 23 °C, showing first regime and beginning of second in more detail. Each data point represents one aliquot removed from reaction mixture for analysis.
Figure 4.13. The length of the first regime of each tethering reaction versus $M_n^{0.6}$ of the polymer chain being tethered. Error in the time length is ± 10 min for PS-NH$_2$-4K and ± 15 min for PS-NH$_2$-15K and PS-NH$_2$-44K.
Figure 4.14. Surface attachment density at saturation versus $1/R_g^2$ of the polymer being tethered at the end of the first regime. See text for an explanation for outlying points.
Chapter Five
An Explanation for the Appearance of the Third Regime

Introduction

In this chapter, we present an explanation for the appearance of an unexpected third regime observed for all of the irreversible tethering reactions in our experiments. In the previous chapter, we reported that the observed tethering process at first followed the first and second regimes predicted by theory, and then diverged from theory to display an unpredicted third regime. We also verified that the end of the first regime corresponds to the completion of the mushroom layer, and that saturation corresponds to the formation of the brush. The fact that the surface attachment density increased only a small fraction in the second regime but nearly doubled in the third regime strongly supports the identification of the third regime as the transition from mushroom to brush.

Furthermore, we interpret the third regime by examining the implications of the relative increase in slope observed for the third regime with respect to the second regime. Theory describes the second regime as corresponding to the gradual formation of a brush as the increasing surface attachment density forces the tethered chains gradually to stretch away from the surface to avoid overlap. In other words, the second regime is associated with the gradual addition of chains to the surface in a spatially random fashion. However, the unpredicted third regime we observed was characterized by a steeper slope, indicating an abrupt, relative decrease in the energy barrier. This implied, in the third regime, the energy barrier to diffusion of incoming chains through the tethered layer to reach the substrate does not increase as rapidly as it did in the second regime. Unlike the uniform (random) tethering of the second regime, tethering must proceed nonuniformly in the third regime, the chains adding to the surface at preferred locations where the energy barrier to diffusion through the layer is lower than it would be in a random process.

Thus, we made the hypothesis that the transition from mushroom to brush takes place mainly in the third regime and, that it occurs in a spatially nonuniform manner. To test this
hypothesis, we observed the change in surface texture before, during, and after the third regime by means of atomic force microscopy, and compared the AFM images with the time-step snapshots generated by a Monte Carlo simulation for the tethering process. This simulation was based on a random sequential deposition model, in which like objects of simple geometry, analogous to polymer chains, are deposited on a flat surface.

**Experimental**

The procedure for conducting tethering reactions on the surface of the GPS-derivative silicate disc for AFM imaging is as follows. After the procedure for derivatization, the test tube containing the epoxide-derivative silicate disc was removed from the vacuum oven, and the top of the test tube was sealed with a rubber septum, through which argon was passed to fill the test tube. To start the tethering reaction on the surface of the silicate disc at the room temperature, 3 ml of PS-NH$_2$-15K or PS-NH$_2$-44K toluene solution at the concentration of 0.255 mg/ml was injected by means of an air-tight syringe into the test tube blanketed with argon. The silicate disc was removed from the test tube to interrupt the tethering reaction at a certain stage, based on the kinetics of the equivalent tethering reaction conducted on the silicate glass beads. The silicate disc was extracted with toluene in a Soxhlet apparatus for 16 hours to remove non-tethered polymer chains on the surface, deposited during solution run-off. The silicate disc was thoroughly rinsed with HPLC-grade methanol right after it was taken out from the Soxhlet thimble. Then the silicate disc was dried under the flow of high-purity nitrogen and was adhered to a 15-mm metal stub (Ted Pella, Inc., Redding, CA). The silicate disc was subjected to AFM imaging immediately so as to avoid any possible contamination.

**Results and Discussion**

**Atomic force microscopy (AFM)**

The AFM image of a clean silicate disc is shown in Figure 5.1, indicating that the pristine surface of the silicate disc is nearly flat on an atomic scale since its root-mean-square roughness
(RMS) is only 0.106 nm.

Figure 5.2 shows a typical AFM image of the surface of the epoxide-derivatized silicate disc, which has a RMS of 0.4 nm. This value is in agreement with the value in the literature for an epoxide monolayer on a flat surface [68]. As expected, the roughness of the epoxide-derivatized surface is slightly greater than the roughness of the pristine silicate surface.

Next, we present the supporting evidence by means of AFM for the hypothesis that the third regime corresponded to a spatially nonuniform transition from mushroom to brush. AFM images of the surface with a growing tethered layer of PS-NH$_2$-15K or PS-NH$_2$-44K were obtained by interruption of the tethering process at various points, serving as the snapshots to signify the local change in surface texture before, during, and after the transition from mushroom to brush.

Images of (a), (b), (c) and (d) in Figure 5.3 show AFM images of surfaces to which PS-NH$_2$-15K was tethered from mushroom to brush. Image (a) depicts a completed uniform mushroom layer, interrupted at a point in the middle of the second regime. Uniformly distributed roughness characterizes the mushroom layer. The RMS of the mushroom layer is 0.8 nm, which is more than twice as great as the epoxide-derivatized surface of Figure 5.2. Images (b) and (c) are from interruption of tethering early and late in the third regime, respectively. They depict early and late times in the transition from mushroom to brush, showing a nonuniform texture having large bumps emerging from the surface. Finally, image (d) depicts a tethered layer that was allowed to proceed without interruption until saturation. Here the surface texture has returned to a uniform roughness. The AFM images clearly show the uniform roughness of the layer before and after the third regime, and the nonuniform roughness during the third regime. Images of only four discs are presented here; the remaining four discs in the
series were removed at redundant times and gave no new information.

Images of (a), (b), (c) and (d) in Figure 5.4 show AFM images of surfaces to which PS-NH$_2$ 44K was tethered from mushroom to brush. Like those of Figure 5.3, these images show the evolution of surface texture before, during, and after the third regime. Image (a) typifies the a completed mushroom layer before the third regime, images (b) and (c) depict early and late times in the third regime, and image (d) typifies a saturated brush layer after the third regime. The nonuniformity of the surface texture in images (b) and (c) compared with the relative uniformity of texture in images (a) and (d) is striking.

Our hypothesis is that the large bumps in the surface texture during the third regime correspond to local areas of much higher surface attachment density [67, 69]. In good solvent, the chains in the most crowded areas would be stretched away from the surface in mutual avoidance. AFM images obtained in air of the third regime are able to provide a representation of the nonuniformity of the layer in good solvent, because each chain is fixed at one end and confined to an area within its own contour length during the evaporation of solvent and resultant collapse of the chains onto the surface beneath. This limitation on mobility of each chain prevents any significant evening out of the texture by migration of chains from areas of high density to areas of lower density during solvent evaporation. Thus, areas of high surface attachment density would appear as bumps (higher concentrations of incompressible mass) on a field of low level, background roughness.

Hence, the distinct difference between (b), (d) and (a), (d) in Figure 5.3 and Figure 5.4 supports our hypothesis that the nonuniform transition from the mushroom to brush takes place in the third regime. The emergence and disappearance of nonuniformity in the surface texture indicates that the relative acceleration of tethering in the third regime originates in the preferential tethering at local areas of high surface attachment density.

*Comparison of AFM images with a computer simulation*

We compare the real AFM images of a tethered layer with the time-step snapshots generated by a simulation model [67], which simulated the tethering as a process of random
sequential deposition, i.e., the deposition sites are chosen randomly on the surface and are filled irreversibly during deposition [70-72]. The computer simulation was conducted by Dr. Stephen E. Rankin. In the model, hemispheres, all of equal radii were used to represent the monodispersed, end-functionalized polymer chains to be tethered [73]. The hemispheres were allowed to deposit at random on the smooth surface of a substrate. Mutual interactions between an incoming hemisphere and already deposited hemispheres were included in the model as the ability to deform in order to eliminate overlap. These interactions were not important in the beginning of the process, when no overlap occurred, but became important later in the process, when incoming hemispheres always overlapped the hemispheres on the crowded surface to some extent. Since the volume of each hemisphere was specified to be the same throughout the process [73], the hemispheres were forced to contract laterally to eliminate overlap. Simultaneously, they would extend vertically to conserve volume, becoming cylinders topped by hemispherical caps [73, 74]. In the Monte Carlo simulation, the overall probability of depositing an additional hemisphere within a Monte Carlo time-step was dependent on two probabilities. One probability was related to, and diminished with, the area of overlap between an incoming hemisphere and the hemispheres already deposited on the underlying surface. The other probability was related to the energy required to accomplish the deformation, described above, that eliminated overlap between incoming and already deposited hemispheres. Each Monte Carlo step was an attempted addition of a hemisphere to the surface of the substrate. The addition of the incoming hemisphere to the surface was accepted according to the Metropolis criterion for Monte Carlo simulations [75].

The Monte Carlo simulation showed three regimes of kinetics rather than two, in accordance with the results of our experiments. In the simulation, the first regime was one in which hemispheres deposited randomly and without overlap on the bare surface. Thus the first regime corresponded to the construction of the mushroom layers. The first regime was followed by the second regime in which deposition was accompanied by small mutual deformations to eliminate the small overlap between incoming and already deposited hemispheres. In the second regime, hemispheres continued to be deposited at random locations. However, the simulation showed an increase in the surface density of the hemispheres in the second regime that was only a small fraction of the total amount. Then, suddenly, the third regime appeared, in which
hemispheres began to deposit more frequently than in the second regime until the substrate was covered with vertically extended (strongly stretched) hemispheres.

For comparison between AFM images and Monte Carlo simulation, several time-step snapshots at relevant points in the tethering process are shown in Figure 5.5 (a-e). These images show the evolution of surface texture of the tethered layer before, during, and after the transition from mushroom to brush. Snapshot (a) typifies the surface texture of the fully formed mushroom layer. The uniform surface texture shown for the completed mushroom layer persists and is stable throughout the second regime. This persistence of uniform texture is perhaps due to the fact that the surface density of hemispheres increases so little during the second regime; even by the end of the second regime, the layer is only a slightly more crowded mushroom layer. Snapshots (b), (c) and (d) depict the evolution of surface texture during the third regime, where the hemispheres deposit rapidly and the nonuniform texture emerges. In snapshot (b), the beginning of the third regime, spikes of vertically extended hemispheres have started to appear. In snapshot (c), the middle of the third regime, the spike-like islands are increasing in number and in size. In snapshot (d), late in the third regime, the islands of vertically extended hemispheres have broadened, so that they are nearly merged. Finally, snapshot (e) typifies the surface texture when saturation has been reached. At saturation the islands of vertically extended hemispheres have completely merged, making the surface texture again uniformly rough, but now farther from the underlying substrate. In summary, the simulation depicts: the first regime as the mushroom layer being formed, the second as the fully formed mushroom layer, the third as the transition from mushroom to brush, and saturation as the brush.

We emphasize that the comparison between AFM images and simulation snapshots is qualitative only. Qualitatively speaking, our hypothesis equated the large bumps in the AFM images and the spikes in the simulation snapshots during the third regime to local areas of much higher surface attachment density. We suggest that these bumps in the AFM images correspond to the areas where preferential tethering is taking place, forcing the tethered chains to make the transition from mushroom to brush. The appearance and disappearance of bumps on the surface imaged by means of AFM was confirmed by the rising and merging of spikes on the surface simulated by means of Monte Carlo simulation. In the simulation, the third regime begins with
the appearance of sharp spikes, i.e., a small cluster of severely contracted hemispheres. These spikes emerge at only the most crowded location in the mushroom layer, suggesting that a critical overlap is necessary to initiate strong lateral contraction and vertical extension of interacting hemispheres. Spike formation starts as a random and rare event, but once it begins in a particular location on the surface, it becomes autoaccelerating. The acceleration in the simulation arises from a particular feature built into the model: axisymmetric lateral contraction. Because of this feature a strong lateral contraction on the part of an already deposited hemisphere exposes the bare surface on the side opposite that of the incoming hemisphere. This nearly exposed the bare surface then makes it easier for an additional incoming hemisphere to be accepted. The result is the preferential deposition of incoming hemispheres at the periphery of a cluster in which the deposited hemispheres have been severely contracted into cylinders. As additional hemispheres are deposited on the periphery of an existing cluster, the cluster grows laterally in the surface plane until it impinges upon other growing clusters. Finally, when the simulation area is covered with vertically stretched cylinders, the surface texture becomes uniform again.

**Conclusion**

The third regime shown in the kinetics of the tethering of monodispersed, end-functionalized polymer corresponded to a transition from mushroom to brush. AFM images at different times during the process of tethering revealed that the surface texture is fairly uniform in the mushroom stage (from the end of the first regime to the end of the second regime), is nonuniform during the third regime when the surface attachment density is increasing strongly, and returns to uniformity at saturation, when the layer has become a brush, and tethering has ceased. The nonuniform stage of the evolution of the tethered layer occurred during the third regime, as shown in the AFM images as well as in the Monte Carlo simulation. This is the first time the process of change from mushroom to brush has been elucidated.
Figure 5.1. Typical AFM image of the surface of the pristine silicate disc before organosilane has been introduced to it.
Figure 5.2. Typical AFM image of the surface of the epoxide-derivatized silicate disc before any polymer chains have been tethered to it
Figure 5.3. AFM images of surfaces containing tethered polystyrene of \( M_n = 15,000 \) g/mol. These images show the surface texture (a) in the mushroom stage, (b) early in the third regime, (c) late in the third regime, and (d) in brush stage.
Figure 5.4. AFM images of surfaces containing tethered polystyrene of $M_n = 44,000$ g/mol. These images show the surface texture (a) in the mushroom stage, (b) early in the third regime, (c) late in the third regime, and (d) in the brush stage.
Figure 5.5. Time-step snapshots from the Monte Carlo simulation of deposition process conducted by Dr. S. E. Rankin. These snapshots show the surface texture (a) in the mushroom stage, (b) early in the third regime, (c) the middle of the third regime, (d) late in the third regime, and (e) in the brush stage. \( R_g \) in the snapshots is the radius of the undeformed hemisphere.
Chapter Six

Effect of Architecture of Polymer on Tethering Kinetics

Introduction

In this chapter, we describe our studies of the tethering kinetics of two end-functionalized polymer chains of vastly different architectures: linear and four-arm. The two polymers chosen for this study were linear, amine-ended poly(ethylene oxide) and four-arm, amine-ended poly(ethylene oxide). For a valid comparison of linear and four-arm architectures, both polymers were procured at the same molecular weight ($M_n = 10,000$ g/mol) and both were monodispersed ($M_w/M_n = 1.08$). In addition, all tethering reactions were conducted under the same conditions of concentration, solvent, and temperature. The data obtained from monitoring the reactions showed that three-regime kinetics was displayed by polymer chains of both architectures, but that the surface attachment density was much higher for the four-arm architecture than for the linear one.

Experimental

Verification of functionality of PEO-NH$_2$

For verification the presence of a primary amine group at one end of the linear architecture and at all four ends of the four-arm architecture, a procedure was developed to quantitatively analyze for primary amine. This procedure was based upon current assays for primary amine groups in peptide [76]. Fluorescamine (Aldrich, Milwaukee, WI), is normally a non-fluorescent compound that reacts with primary amine to form a fluorophor having an excitation wavelength of 390 nm and an emission wavelength of 475 nm, as shown in Figure 6.1. The reaction between fluorescamine and a primary amine is completed in only 100-500 msec, and fluorometry can be used subsequently to determine the fluorescence of the product of the reaction. In our quantitative analysis procedure, a calibration curve for emission intensity at 475 nm versus amine concentration was made by reacting four glycine solutions at pH 9 buffer with fluorescamine. The molar concentration of glycine solutions ranged from 0.010 to 0.060 µmol/mL. To do this, 24 mL of each of the four solutions was mixed with 1 mL of
fluorescamine solution in acetone (0.20 mg/mL) to allow all amine groups to be converted to fluorophor. Emission spectra of the fluorescamine-glycine compound were collected for each solution in an Aminco-Bowman Spectrofluorometer (Thermo Electron Cooperation, Woburn, MA), and then the calibration curve was plotted. Subsequently, three buffer solutions (pH 9) of linear and four-arm PEO-NH₂-10K were prepared at concentrations in the range 0.020 to 0.050 µmol/mL, which is in the linear range of the calibration curve. The emission spectrum of the fluorescamine-polymer compound at each concentration was acquired, and the fluorescence amplitude of each was compared with the calibration curve. From these comparisons, the relative amine functionalities of the linear and four-arm architectures were determined.

**Tethering reaction**

Tethering of linear or four-arm PEO-NH₂-10K was conducted at room temperature in a manner similar to the procedure described in Chapter 4, except that epoxide-derivatized silica powder was used instead of beads. The high specific surface area of the powder permitted use of the high concentration of PEO needed to compensate for the low response of the RI detector to PEO. Each tethering reaction was monitored by means of the real-time method described in Chapter 3.

**Results and Discussion**

**Functionality of polymer**

In determining functionalities of linear and four-arm PEO-NH₂-10K, a problem was revealed immediately. Although the fluorescamine-glycine compound is a standard compound used for calibration curve in the analysis of amine groups in peptides, the fluorescamine-glycine compound could not be used as a standard in our case. This was because a significant difference existed between response factors per amine group of the fluorescamine-glycine compound and the fluorescamine-polymer compound in the fluorometry. Thus, it was invalid to use glycine as a calibration for absolute amine content of linear and four-arm PEO-NH₂-10K, even though all exhibited a good linear relationship in a concentration range from 0.01 to 0.06 µmol/mL. Not surprisingly, the fluorescamine-linear-PEO-NH₂ compound and the fluorescamine-four-arm-
PEO-NH₂ compound had the same response factor per amine group in the fluorometry. Therefore relative functionality of linear and four-arm PEO-NH₂-10K could be determined by fluorometry. At the same mass concentration, the emission intensity of the fluorescamine-four-arm-PEO-NH₂ compound at 475 nm was 4-fold stronger than that of fluorescamine-linear-PEO-NH₂ compound, in accordance with the presence of one amine group at the end of each arm of the four-arm architecture and the presence of a single amine group per chain for the linear architecture.

**Tethering Kinetics**

The results for tethering of linear PEO-NH₂ of Mₐ = 10,000 and four-arm PEO-NH₂ of Mₐ = 10,000 are shown in Figure 6.2 and Figure 6.3, respectively. The figures show that both of these polymers, of vastly different architectures, displayed three-regime kinetics. No discernable difference was observed in the length of the three regimes in either case. However there was a substantial difference in surface attachment density at all times during tethering.

Tethering rate in the first regime was slightly more rapid for the four-arm architecture than for the linear architecture. This could be ascribed to the fact that the radius of gyration, Rₐ, of four-arm PEO-NH₂-10K (Rₐ = 2.63 nm) is smaller than that of linear PEO-NH₂-10K (Rₐ = 3.10 nm). The computation of the radius of gyration of linear PEO-NH₂-10K and four-arm PEO-NH₂-10K is presented in the Appendix. The length of the second and third regimes was approximately the same for both architectures. This similarity is unexpected and can only be explained if the increased tethering activity of four amines per molecule in the four-arm architecture is offset by the faster build-up of the energy barrier of the already tethered layer in the case of the four-arm architecture. The time to reach saturation was approximated same for both architectures – 10,000 minutes.

At any moment of tethering, the surface attachment density of four-arm PEO-NH₂-10K was about 4 to 5 times more than that of linear PEO-NH₂-10K. As presented in Table 6.1, the surface attachment density (Σᵢₘₖᵤₛ) of four-arm PEO-NH₂-10K was 4.5 times higher at the end of the first regime than Σᵢₘₖᵤₛ of linear PEO-NH₂-10K, while the surface attachment density (Σᵢₖₛₚₐᵗ) of
four-arm PEO-NH$_2$-10K was 4.9 times higher at saturation than $\Sigma_{\text{sat}}$ of linear PEO-NH$_2$-10K. The closeness to four of this value suggests that the difference in surface attachment density between four-arm and linear PEO-NH$_2$-10K might originate more in the number of reactive end-groups per molecule than in the architecture itself. It was at least four times more likely for four-arm PEO-NH$_2$-10K to be affixed at the surface than for linear PEO-NH$_2$-10K. If architecture were the dominant factor in the surface attachment density at saturation (or anywhere during tethering), then it would have been expected that the surface attachment density would be correlated to $R_g$. However, the $R_g$ of the four-arm architecture is nowhere near four times smaller than that of the linear architecture.

A remaining question is whether all amine functional-ends of the four-arm PEO-NH$_2$-10K had reacted with epoxide groups on the surface of the substrate. The number of unreacted primary amine groups in the tethered layer was determined by means of the colorimetric analysis described in Chapter 3. Before this analysis was conducted on tethered layer, the method itself was evaluated by applying it to the surface of amino-derivatized silica powder. The result was 1.57 ± 0.03 amine groups per nm$^2$. This standard deviation among six independent specimens is less than 2%. The average value is very reasonable and is comparable to other such analyses for silicate surface derivatized with small molecules. Both remarkable accuracy and consistency confirmed the validity of colorimetric analysis for free amine attached to, but not reacted directly with, a surface. The results from the measurement of the silica powder containing tethered four-arm PEO-NH$_2$-10K indicated that three out of four arms of tethered four-arm PEO-10K chains were not detected by the colorimetric analysis and therefore had reacted with epoxide groups on the surface of the substrate.

**Conclusion**

In summary, data showed that polymer architecture did not alter the kinetics profile of the tethering from dilute solution to the epoxide-derivatized substrate by means of chemical reaction. For both linear and four-arm amine-ended poly(ethylene oxide), three-regimes of kinetics were in evidence. However, the surface attachment density of four-arm chains was more than 4-fold higher than that of linear chains. The higher surface attachment density may be due to the
presence of more end-functional groups per molecule for the four-arm architecture over the linear architecture.
## Tables

Table 6.1. Surface attachment density for both architectures

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma_{\text{mush}}$</th>
<th>$\Sigma_{\text{sat}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four-arm PEO-NH$_2$-10K</td>
<td>0.030</td>
<td>0.094</td>
</tr>
<tr>
<td>Linear PEO-NH$_2$-10K</td>
<td>0.0067</td>
<td>0.018</td>
</tr>
</tbody>
</table>
Figures

\[ R = -(\text{CH}_2-\text{CH}_2-\text{O})_n^- \] (poly(ethylene oxide))

or \( \text{C(CH}_3)_2\text{COOH} \) (glycine)

Figure 6.1. Reaction between fluorescamine and primary amine
Figure 6.2. Tethering of linear PEO-NH$_2$ of $M_n = 10,000$ onto the surface of the epoxide-derivatized silica powder in toluene at 23 °C
Figure 6.3. Tethering of four-arm PEO-NH$_2$ of $M_n = 10,000$ onto the surface of the epoxide-derivatized silica powder in toluene at 23 °C
Chapter Seven
Effect of Solvent Quality on Tethering Kinetics

Introduction

This chapter describes experiments performed to determine the effect of solvent quality, as expressed by $\chi$-parameter between polymer and solvent, on the kinetics and outcome of tethered layer formation. In all tethering reactions conducted, experimental variables were held constant except the $\chi$-parameter. Variation in $\chi$-parameter was achieved by the use of a series of nonpolar, organic solvents. The distinct three-regime kinetics, typical of tethering reactions run in good solvent and in the absence of segmental adsorption, was observed over the range of values for $\chi$-parameter. As expected, an increase in $\chi$-parameter (decrease in solvent quality) did result in increased tethering density, but, contrary to expectation, no increase in tethering rate was observed.

The issue of solvent quality has been addressed before, both theoretically and experimentally. It has been suggested that tethering from poor solvent would yield a more densely tethered layer than tethering from good solvent, because the poor solvent conditions would nullify the unfavorable steric interactions between adjacent tethered chains [42, 53]. However, in experimental studies of solvent quality performed up to now, systems were used in which the changes in solvent quality were accompanied by other effects, such as segmental adsorption [53], changes in ionic strength [42], changes in temperature [22, 77], or detachment of loosely bound tethered chains [77]. As a result, the effect of a change in solvent quality alone still has not been clarified.

We sought a system in which the solvent quality could be varied without simultaneous changes in ionic strength or temperature, and without the occurrence of segmental adsorption or detachment of already-tethered chains. After numerous preliminary trials, we identified a set of systems in which the solvent quality, and the corresponding $\chi$-parameter, could be varied systematically in the absence of other effects. Variation of the $\chi$-parameter was achieved by using a family of nonpolar, aromatic solvents.
Our work in the previous chapters focused on the study of the tethering kinetics for monodispersed, end-functionalized polymers in a good solvent. The goal of our work described in the present chapter was to explore the effect of solvent quality alone, with all other variables eliminated or held constant, on the kinetics and outcome of tethering. In this chapter, we made the hypothesis that, in the absence of segmental adsorption of the polymer to the substrate, a decrease in solvent quality would result in the retention of the three-regime kinetics and only a modest increase in surface attachment density and tethering rate.

**Experimental**

To study the effect of solvent quality on the kinetics, tethering reactions were conducted for each of the three individual systems listed in Table 7.1, from which it can be seen that solvent is the only variable. Reaction conditions and initial quantities are also given in Table 7.1. The experimental details of the twin tethering reactions run in different solvents were similar to those in good solvent described in Chapter 4. For each reaction, 20.0 mL of PEO-NH₂ solution (0.800 mg/mL) was added to a reaction flask containing 3.20 g of epoxide-derivatized silica powder at 50 °C. The reason for conducting the tethering reaction at this temperature was to ensure that PEO remained in solution, especially in cases of p-xylene and ethylbenzene. At 50 °C, the polymer remained in solution indefinitely, while at temperatures lower than 50 °C, PEO chains had a tendency to precipitate from p-xylene and ethylbenzene. The reaction flask was tightly covered with aluminum foil. Small aliquots of the reaction mixture were removed at frequent intervals for quantitative analysis by real-time, off-line monitoring as described in Chapter 3.

**Results and Discussion**

Prior to the study of tethering, auxiliary experiments were conducted to check for segmental adsorption in each of the three aromatic solvents at 50 °C. In these experiments, GPS derivatized silica powder was exposed to a solution of two molecular weights of inert-ended PEO (PEO-8K and PEO-2K), as described in Chapter 3. Our previous experience in testing for segmental adsorption taught us that a change in mass ratio would occur in within one hour if
segmental adsorption were present. As shown in Table 7.2, the constancy (within 3.5% of initial) of the mass ratio of the two molecular weights in solution verified the absence of segmental adsorption of PEO.

For a comparison study such as ours, in which temperature, molecular weight, and initial concentration are held constant, consistent values of $\chi$ can be obtained by calculation from the following semi-empirical expression [78]:

$$\chi = \frac{V_s}{RT} (\delta_p - \delta_s)^2 + 0.34, \text{(Equation 7.1)}$$

where $V_s$ is the molar volume of the solvent; $\delta_p$ and $\delta_s$ are solubility parameters of the polymer and solvent, respectively; $R$ is the universal gas constant; $T$ is the temperature; and the last term on the right is the contribution of entropy [78]. For use in Equation 7.1, a value of $\delta_p = 20.0$ (J/cm$^3$)$^{1/2}$ for PEO was taken from the literature [79]. Solubility parameters for the solvents were also taken from the literature[80, 81], as were the values for molar volume [82]. These values are listed in Table 7.3. The last column in Table 7.3 shows the value of $\chi$ for each solvent with PEO computed from Equation 7.1.

It is of interest to note that experimental values of $\chi$ for PEO in the three solvents of interest are available in the literature. Values of 0.40, 0.54, and 0.69, were found for PEO in toluene, $p$-xylene, and ethylbenzene respectively [79, 83, 84]. However, these values were obtained under different conditions of temperature, concentration, and molecular weight from each other and from our conditions. In practice, for a single set of conditions, it is difficult to achieve a wider range of $\chi$-values than we have achieved in present study. If one attempts to extend the range of $\chi$ by use of other solvents from the same family, one finds that there is no single temperature at which all of the solutions are soluble without precipitation of the polymer; if one goes to mixed solvents in which the polymer is soluble at one given temperature, the range of achieved for $\chi$ is no larger than what we have achieved with the aromatic family of solvents used in the present study.

Figure 7.1-Figure 7.3 show the experimental results for tethering PEO-NH$_2$ in the three aromatic solvents that provided successively increasing values of $\chi$. In these figures, surface
attachment density is plotted versus time, and after 60 minutes, the horizontal axis is changed from linear time to log(time) to accommodate the lengthy time to saturation for each reaction. As can be seen from the figures, all three systems showed three distinct regimes of kinetics (delineated by thin, vertical lines to guide the eye), which agrees with the hypothesis stated in the introduction. However, contrary to our hypothesis, there was no perceptible increase in rate as solvent quality decreased. As shown in Figure 7.1-Figure 7.3, the first regime (rapid tethering to form the mushroom layer) finished within 60 minutes, after which the tethering process entered the slow, second regime. The second regime lasted for approximately the same length of time in each system. The third regime, of relative acceleration with respect to the second regime, also was comparable in length in all three systems. Finally, all systems reached saturation at about the same time.

We had anticipated a modest increase in tethering rate, i.e., a shortened time to saturation, based on two factors. These two factors are the decrease in $R_g$ with decrease in solvent quality and the nullification of steric repulsion with decrease in solvent quality, each of which is discussed below.

The computed values for $R_g$ were 3.55 nm, 3.25 nm, and 2.86 nm in toluene, $p$-xylene, and ethylbenzene, respectively. The computations of $R_g$ are shown in the Appendix. A smaller $R_g$ imparts a higher diffusion coefficient to a polymer in solution, leading to the expectation of faster diffusion [85]. Because, during the first regime, the rate of the overall tethering process is governed by diffusion of polymer through the solution to the bare surface [46], a shorter first regime would have been expected for lower values of $R_g$. While we did not discern a shortening of the first regime with decrease in $R_g$, it is possible that we simply were not able to resolve it with our monitoring method.

The other factor leading to the expectation of faster tethering is the progressive nullification of polymer-to-polymer steric repulsion that occurs with an increase in $\chi$ (decrease in solvent quality) [53]. Reduction of steric repulsion would be expected to lower the energy barrier to diffusion of free polymer chains through the already-tethered layer. As a result, shorter second and third regimes would have been expected. However, we did not observe any of these
expected increases in rate. A possible explanation for the lack of increase in rate is that lowering of the energy barrier to diffusion of free polymer chains through the already-tethered layer would also allow the density of the tethered layer to increase faster. The increase in density would produce a corresponding increase in energy barrier to diffusion, which would offset the above-mentioned decrease in energy barrier. The net result would be the absence of an observed rate increase. The results presented below, on surface attachment density, are consistent with the notion that an increase in surface attachment density offsets the benefit of nullification of steric interactions where the tethering rate is involved.

The surface attachment density, \( \Sigma \), was examined at two of the key benchmarks of the tethering process: the end of the first regime and saturation. Table 7.4 reports values for surface attachment density at both of these benchmarks [86]. For the first benchmark, the end of the first regime, a point in the process that corresponds to the completion of the mushroom layer, there appears to be no apparent difference among the three systems given the scatter in the data. This is confirmed by the lower plot in Figure 7.4, of \( \Sigma_{\text{mush}} \) versus \( \chi \), for which the regression line is nearly horizontal. (Note that the scatter for the first two points is smaller than the size of the symbol.)

The surface attachment density at the other benchmark, saturation, does show the influence of the \( \chi \)-parameter. In the upper plot in Figure 7.4, the values for \( \Sigma_{\text{sat}} \) from Figure 7.4 are plotted against \( \chi \). As can be seen, the highest \( \chi \)-parameter we investigated, \( \chi = 0.55 \), resulted in a 25% increase in \( \Sigma_{\text{sat}} \) over that achieved in good solvent. This is a statistically significant but modest increase, as predicted by the hypothesis stated in the introduction.

**Conclusion**

In summary, we evaluated the effect of solvent quality alone, in the absence of other effects or variables, on the kinetics and outcome of the tethering process. Solvent quality was expressed as \( \chi \), the interaction parameter between the solvent and the polymer in the solution at dilute concentrations. All three systems studied displayed the expected three-regime kinetics, regardless of solvent quality. As expected, an increase in \( \chi \)-parameter for the system brought
about a modest increase in surface attachment density, but contrary to expectation, an increase in $\chi$-parameter did not perceptibly increase the rate of tethering. In other words, the results of this study suggest that decreasing the solvent quality alone, without otherwise changing conditions, is not an effective way to make substantial increases in tethering density.
Table 7.1. Three tethering systems

<table>
<thead>
<tr>
<th>Tethered Polymer</th>
<th>Internal Standard</th>
<th>Mass of substrate</th>
<th>Volume of solution</th>
<th>Initial conc.</th>
<th>Temp.</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-NH$_2$-10K</td>
<td>PEO-CH$_3$-2K</td>
<td>3.20 g</td>
<td>20.0 mL</td>
<td>0.800 mg/mL</td>
<td>50 ºC</td>
<td>Toluene</td>
</tr>
<tr>
<td>PEO-NH$_2$-10K</td>
<td>PEO-CH$_3$-2K</td>
<td>3.20 g</td>
<td>20.0 mL</td>
<td>0.800 mg/mL</td>
<td>50 ºC</td>
<td>p-Xylene</td>
</tr>
<tr>
<td>PEO-NH$_2$-10K</td>
<td>PEO-CH$_3$-2K</td>
<td>3.20 g</td>
<td>20.0 mL</td>
<td>0.800 mg/mL</td>
<td>50 ºC</td>
<td>Et-benzene</td>
</tr>
</tbody>
</table>
Table 7.2  Relative masses in solution of inert-ended poly(ethylene oxide), PEO, of two molecular weights exposed to epoxide-derivatized silica powder

<table>
<thead>
<tr>
<th>Mass ratio of PEO-8K/PEO-2K</th>
<th>Solvent</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>p-Xylene</td>
<td>Et-Benzene</td>
</tr>
<tr>
<td>Initial</td>
<td>0.748</td>
<td>1.19</td>
<td>0.841</td>
</tr>
<tr>
<td>1 hour</td>
<td>0.728</td>
<td>—</td>
<td>0.865</td>
</tr>
<tr>
<td>20 hour</td>
<td>0.722</td>
<td>1.17</td>
<td>0.846</td>
</tr>
</tbody>
</table>
Table 7.3. Properties of solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_s$ (J/cm$^3$)$^{1/2}$</th>
<th>$V_s$ (cm$^3$/mol)</th>
<th>T (K)</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>18.2</td>
<td>106.8</td>
<td>323</td>
<td>0.47</td>
</tr>
<tr>
<td>$p$-Xylene</td>
<td>18.0</td>
<td>123.9</td>
<td>323</td>
<td>0.52</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>17.9</td>
<td>123.1</td>
<td>323</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Table 7.4. Surface attachment density at different stages achieved in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\chi$</th>
<th>$\Sigma_{\text{mush}}$, at the end of 1\textsuperscript{st} regime (chains/nm\textsuperscript{2})</th>
<th>$\Sigma_{\text{sat}}$, at saturation. (chains/nm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.47</td>
<td>0.00595 ± 0.00028</td>
<td>0.0182 ± 0.0015</td>
</tr>
<tr>
<td>$p$-Xylene</td>
<td>0.52</td>
<td>0.00688 ± 0.00007</td>
<td>0.0198 ± 0.0009</td>
</tr>
<tr>
<td>Et-benzene</td>
<td>0.55</td>
<td>0.00642 ± 0.00083</td>
<td>0.0227 ± 0.0010</td>
</tr>
</tbody>
</table>
Figure 7.1. Surface attachment density vs. time for tethering of PEO-NH$_2$-10K to the surface of epoxide-derivatized silica in solvent of toluene at 50 °C. 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 to show the reaction-to-reaction reproducibility.
Figure 7.2. Surface attachment density vs. time for tethering of PEO-NH₂-10K to the surface of epoxide-derivatized silica in solvent of p-xylene at 50 °C. Other features of plot are the same as described in the caption to Figure 7.1.
Figure 7.3. Surface attachment density vs. time for tethering of PEO-NH$_2$-10K to the surface of epoxide-derivatized silica in solvent of ethylbenzene at 50 °C. Other features of plot are the same as described in the caption to Figure 7.1.
Figure 7.4. Surface attachment density at the end of the first regime (lower part) or at saturation (upper part) versus polymer-solvent interaction parameter, $\chi$
Chapter Eight
Kinetics of Tethered Layer Formation
in the Presence of Segmental Adsorption

Introduction

In this chapter, we study the kinetics and outcome of tethering monodispersed, amine-ended polystyrene to the surface of epoxide-derivatized silicate glass beads in the poor solvent of cyclohexane, which allows segmental adsorption. The tethering process was monitored in real time by means of a procedure that allowed chains tethered to the surface by chemical bonds to be distinguished from those held to it by segmental adsorption. Compared with tethering in the absence of segmental adsorption, the presence of segmental adsorption fundamentally altered the tethering process and led tethering to saturation earlier with a higher surface attachment density.

The previous studies on formation of tethered layers focused on systems in which segmental adsorption was absent. However, segmental adsorption of polymer chains coexists with tethering in many systems of interest. It is important to study the tethering process in the presence of simultaneous segmental adsorption.

Segmental adsorption in polymers occurs when the interaction between a segment in the polymer chain and the surface of the solid is more favorable than the interaction between the solvent and surface. Segmental adsorption leads the backbone of the polymer chain to adhere to the surface in a tail-loop-train configuration (Figure 8.1).

The energy of physical bonding for each adsorbed segment along the polymer chain can be as small as one $kT$. Thus at equilibrium, some segments that form trains can easily become part of loops or trails, and vice versa. However, the adsorption energy of a whole adsorbed chain can be as large as hundreds of $kT$ if there are a large number of adsorbed segments along the polymer chain. The detachment of an adsorbed chain can be accomplished by changing the solvent or by taking other actions to reduce segment-surface interaction.
Segmental adsorption is a rapid process, as shown in Figure 8.2. The overall kinetics of polymer adsorption and desorption consists of four steps: 1) transport onto the surface by either diffusion or convection; 2) attachment to the surface; 3) space rearrangement on the surface, which involves the change from the free-coil configuration in the solution into a “train-loop-tail” configuration on the surface of the substrate; and 4) detachment from the surface, which is diffusion-limited and usually very slow. Most segmental adsorption reaches saturation in a period of hours, much shorter than any tethering process we studied.

Segmental adsorption coexisting with tethering has been predicted by theory and noticed experimentally [53]. Some scholars predicted that segmental adsorption should inhibit tethering [87, 88] since the energy barrier to diffusion of a free polymer chain to the surface would be elevated by the presence of adsorbed chains. Some experimenters noticed the existence of segmental adsorption during tethering [23] and assumed that it had a negligible effect on the results of tethering [53]. However, up to now no experimental effort has been put forth to determine the effect of segmental adsorption on tethering kinetics.

The primary goal of the study in this chapter was to estimate the impact of segmental adsorption on the tethering process. The study of the solvent effect on the tethering kinetics described in the previous chapter clarified that three-regime kinetics is manifest for any system in which segmental adsorption is absent, regardless of solvent quality. Considering that the adsorption of segments along the polymer chain backbone to the substrate would interfere with the ability of the tethered chains to retain traditional mushroom and brush configuration, the hypothesis we made was that segmental adsorption would alter the tethering process, changing the kinetics and the outcome of the tethering. This chapter reports results of experiments designed to test this hypothesis.
Experimental

Tethering reaction in cyclohexane

The experimental details of the twin tethering reactions run in the presence of segmental adsorption were similar to those performed in the absence of segmental adsorption (i.e. in toluene). In brief, the end-functionalized polystyrene of the desired $M_n$ was dissolved ahead of time in dried, reagent grade cyclohexane at a concentration of 0.225 mg/mL. A carefully weighed amount of internal standard was added to this solution. The solution was quantitatively analyzed to establish the area ratio for end-functionalized polymer to internal standard at zero time. Then all 20 mL of the polymer solution was added to 18.1 g of epoxide-derivatized silicate glass beads, while stirring was maintained in the reaction flask, and the tethering process began immediately. Real-time monitoring was conducted as described in Chapter 4. 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.

However, to investigate the effect of segmental adsorption, procedures were changed. Instead of only running one set of twin reactions, two sets were run. This was done so that a special procedure could be used to distinguish between chains attached to the surface by chemical bonds (tethered) and those attached solely by segmental adsorption. The details of this procedure will be presented in the next section.

Procedure for distinguishing tethering from segmental adsorption

Tethering reactions for two sets of twins described immediately above were conducted under the same conditions, but the internal standards and handling of the aliquots were different.

First, the internal standards used in the two sets of twins were different: one used polyisoprene and the other used polystyrene. Inert-ended polyisoprene was selected to serve as the internal standard in one set of twins, because of the absence of segmental adsorption of polyisoprene to the substrate from the cyclohexane solvent. Inert-ended polystyrene was
selected to serve as the internal standard in the other set of twins, because of the absence of segmental adsorption of polystyrene to the substrate from the toluene solvent.

Second, the handling of the aliquots prior to quantitative analysis in one set of twins was different from the handling of the aliquots in the other set of twins. In the set of twins containing polyisoprene as the internal standard, each aliquot was quenched, filtered, and analyzed differently (see Chapter 4). In the set of twins containing inert-ended polystyrene as the internal standard, each aliquot was quenched, its solvent was evaporated and replaced with toluene, and it was filtered and analyzed. The evaporation of the cyclohexane and its replacement with toluene achieved the desorption of all nontethered polymer chains – both end-functionalized polystyrene and internal standard of inert-ended polystyrene (internal standard). While the desorption returned the physically adsorbed chains to the solution, it could not detach tethered chains from the surface.

Use of different internal standards and handling procedures for each set of twins allowed the subsequent quantitative analysis to distinguish the tethered chains from the adsorbed chains. Analysis of aliquots from the reaction containing polyisoprene as the internal standard yielded the total amount of end-functionalized polystyrene attached to the surface of the substrate including both tethered chains and physically (segmentally) adsorbed chains. On the other hand, the analysis of aliquots from the reaction containing inert-ended polystyrene as the internal standard yielded only the end-functionalized polystyrene that was tethered to the surface of the substrate. The different handling procedures and the behavior monitored for the two sets of twins are summarized in Table 8.1.

**Results and Discussion**

**Results of auxiliary studies on adsorption and desorption**

The results of auxiliary experiments that confirmed the absence of segmental adsorption of polystyrene from toluene were presented in Table 4.1. The results of auxiliary experiments confirming the absence of segmental adsorption of polyisoprene (internal standard) from
cyclohexane are presented in Table 8.2. It should be recalled that change in the mass ratio of two molecular weights of polymer in solution over time is the most sensitive measure of segmental adsorption. As seen in Table 8.2, the variation in mass ratio of the two molecular weights over a long exposure time to the substrate was less than the 3%. The constancy of this ratio confirmed that no segmental adsorption of polyisoprene to the surface of epoxide-derivatized beads occurred from cyclohexane, which was the desired result. Similar auxiliary experiments confirmed complete desorption of polystyrene from the substrate upon replacement of cyclohexane with toluene which also was the desired result.

**Tethering in the presence of segmental adsorption**

Figure 8.3 and Figure 8.4 show the results for tethering monodispersed, PS-NH₂-4K and PS-NH₂-44K, respectively, in the presence of segmental adsorption. Each data point 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 when a poor solvent (cyclohexane) is used in these experiments. The upper curve in each figure, composed of open circles for one twin and closed circles for 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 some or all of the tethered chains would have some segments along their backbones adsorbed to the substrate. However, desorption by a good solvent would not be able to detach these chains from the substrate, because they are irreversibly attached to the substrate by chemical bonding. The lower curve in each figure, composed of open triangles for one twin and closed triangles for the other twin in the set, 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 that were held to the surface by segmental adsorption alone.

Figure 8.3 and Figure 8.4 are similar in shape and timescale to those found in studies of polymer adsorption [89-93], where the kinetics is 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 the absence of segmental adsorption. 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 much more rapidly in the presence of segmental adsorption than in the absence of segmental adsorption. This more rapid tethering provides assurance that saturation is indeed reached not only without a third regime but also earlier. Specifically, without segmental adsorption, PS-NH$_2$-4K reaches saturation in about 6000 minutes, whereas it takes only 400 minutes when segmental adsorption occurs. Similarly, without segmental adsorption, PS-NH$_2$-44K reaches saturation in 4000 minutes, whereas it takes only 600 minutes when segmental adsorption occurs. To recapitulate, the presence of segmental adsorption obliterated the 3-regime tethering kinetics and reduced the duration of tethering to reach saturation by 85%.

Another effect of segmental adsorption is that higher values of tethering density were reached, not only throughout the tethering process but also at saturation. 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 tethered chains per unit area of surface belies this expectation. Surface attachment density at saturation was 67% and 78% higher for PS-NH$_2$-4K and PS-NH$_2$-44K, respectively, when segmental adsorption was present rather than when it was absent. A useful measure for comparing tethered layers constructed under different conditions is the average distance between tethering sites on the substrate, $d$. The value of $d$ is computed from the experimental value for surface attachment density, $\Sigma$; $d = \Sigma^{-1/2}$. The values shown in Table 8.3 and Table 8.4 for PS-NH$_2$-4K and PS-NH$_2$-44K, respectively, show the decrease in distance between tethering sites when segmental adsorption is allowed.

The higher tethering density achieved by constructing tethered layers in the presence of segmental adsorption has great practical potential. Whenever denser brushes are desired, chains can be tethered in a solvent that allows segmental adsorption and then can be developed into a brush by replacing the tethering solvent with a solvent in which no adsorption occurs.
We suggest an explanation for the increase in the number of chains tethered in the presence of segmental adsorption [94, 95]. First, the phenomenon of segmental adsorption involves more chains than are simply tethered, as shown in Figure 8.3 and Figure 8.4. Once the freely diffusing chains are “captured” by segmental adsorption, they are held to the surface and do not diffuse away. By contrast, a free polymer chain that does not experience segmental adsorption can diffuse away the surface without becoming tethered. Because segmental adsorption keeps the chain at the surface, it increases the probability that the chain will become tethered. Second, the existence of segmental adsorption in no way prevents tethering from happening. Segmental adsorption is a dynamic phenomenon [64], in which individual segments of an adsorbed polymer chain are repeatedly adsorbing and desorbing, to cover and uncover reactive sites. Therefore, the reactive sites on the surface are not any less accessible to the functional ends of the polymer chains than if there were no segmental adsorption. The overall result is that segmental adsorption has the effect of increasing the number of tethered chains.

When a solvent that allows segmental adsorption is replaced with a solvent that does not allow it, those chains that were segmentally adsorbed, but not tethered, are removed from the surface. For the chains that are tethered, this change of solvent would detach any adsorbed segments from the surface to produce a polymer brush. Table 8.3 and Table 8.4 show that for both molecular weights, $d < 2R_g$, confirming that the tethered layers are brushes.

**Conclusion**

The tethering process was altered significantly when segmental adsorption occurred simultaneously. The tethering 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 a solvent that allows segmental adsorption to a solvent in which no segmental adsorption occurs after tethering is complete.
### Tables

Table 8.1. Internal standard used to monitor the presence of polymer in solution

<table>
<thead>
<tr>
<th>Set</th>
<th>Internal standard</th>
<th>Aliquot handling</th>
<th>Behavior monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS-NH$_2$-44K</td>
<td>Quench, filter, and analyze</td>
<td>Tethering &amp; adsorption</td>
</tr>
<tr>
<td></td>
<td>PI-3K</td>
<td>Quench, replace solvent, filter, and analyze</td>
<td>Tethering only</td>
</tr>
<tr>
<td>2</td>
<td>PS-NH$_2$-4K</td>
<td>Quench, filter, and analyze</td>
<td>Tethering &amp; adsorption</td>
</tr>
<tr>
<td></td>
<td>PI-60K</td>
<td>Quench, replace solvent, filter, and analyze</td>
<td>Tethering only</td>
</tr>
<tr>
<td></td>
<td>PS-40K</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8.2. Relative masses in solution of inert-ended polyisoprene of two molecular weights exposed to epoxide-derivatized silicate glass beads

<table>
<thead>
<tr>
<th>Exposure time (min)</th>
<th>Mass ratio of PI-60K to PI-3K</th>
<th>Deviation from initial, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.006</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.977</td>
<td>-2.88</td>
</tr>
<tr>
<td>5</td>
<td>0.997</td>
<td>-0.89</td>
</tr>
<tr>
<td>13</td>
<td>0.992</td>
<td>-1.39</td>
</tr>
<tr>
<td>40</td>
<td>1.017</td>
<td>+1.19</td>
</tr>
<tr>
<td>90</td>
<td>0.988</td>
<td>-1.79</td>
</tr>
<tr>
<td>1500</td>
<td>0.984</td>
<td>-2.19</td>
</tr>
<tr>
<td>2880</td>
<td>0.978</td>
<td>-2.78</td>
</tr>
</tbody>
</table>
Table 8.3. Distance apart of tethered chains, PS-NH$_2$-4K ($2R_g = 4.14$ nm)

<table>
<thead>
<tr>
<th>Segmental adsorption</th>
<th>Chains/nm$^2$ at saturation</th>
<th>$d$, nm, at saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.066</td>
<td>3.9</td>
</tr>
<tr>
<td>Yes</td>
<td>0.11</td>
<td>3.0</td>
</tr>
</tbody>
</table>
Table 8.4. Distance apart of tethered chains, PS-NH$_2$-44K (2R$_g$ = 15.6 nm)

<table>
<thead>
<tr>
<th>Segmental adsorption</th>
<th>Chains/nm$^2$ at saturation</th>
<th>$d$, nm, at saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0.0056</td>
<td>13</td>
</tr>
<tr>
<td>Yes</td>
<td>0.010</td>
<td>10</td>
</tr>
</tbody>
</table>
**Figures**

Figure 8.1. Cartoon of an adsorbed chain in tail-loop-train configuration. A train is a sequence of segments along the chain in direct contact with the surface. That is, each segment in a train is adhered to the surface. A loop is a sequence of unbound segments connecting two trains. And a tail is a sequence of non-adsorbed segments at the end of the chain; the tail extends away from the surface.
Figure 8.2. Kinetics profile of a typical segmental adsorption of polymer [64]
Figure 8.3. Surface attachment density versus time for tethering of monodispersed, end-functionalized polystyrene, $M_n = 4,000$, in cyclohexane. 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 8.4. Surface attachment density versus time for tethering of monodispersed, 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.
Chapter Nine

Competitive Tethering

Introduction

In this chapter, we discuss the construction of the mixed tethered layers by means of competitive tethering, in which end-functionalized polystyrenes of two molecular weights ($M_n = 4,000$ and $M_n = 44,000$) were tethered from solution to the surface of the silicate glass beads. The initial ratio of two polymers in solution was varied to obtain a set of mixed layers with different ratios of short-to-long chains. The kinetics of both molecular weights was monitored to evaluate the impact of competition between two polymers on the tethering process. Three-regime kinetics for each molecular weight was observed in competitive tethering even though the short chains dominated the tethering throughout the formation of the mixed layer.

In the previous chapters, we focused on the construction of the simple tethered layer, i.e., a layer constructed from polymer chains of a single chemical structure and a single molecular weight. Further advances in surface science demand the fabrication of a more complex tethered layer, i.e., a layer composed of different types of polymers of different molecular weights. Complex layers have the potential to be responsive: to be hydrophobic or hydrophilic [96], to be conductive or nonconductive, and to release or adsorb species in response to external environmental incentives such as light [97], electrical field [98], temperature [52], pressure [99], pH, etc. Responsive tethered layers could be widely used in many areas, including membrane separation [100], biosensor [101, 102], and surface patterning [97, 103].

Over the past decade, interest in mixed tethered layers consisting of at least two polymers different in chemical structure and/or molecular weight has been growing, both from theoretical [104-110] and from experimental [28, 103, 111-123] points of view. Some of these mixed tethered layers demonstrate the responsive properties mentioned above [103, 116, 117, 121]. In this chapter, we describe the kinetics of a mixed tethered layer formed by means of competitive tethering. We made a hypothesis that the composition of the bi-dispersed layer would be different from the initial composition of the solution.
**Experimental**

Three competitive tethering reactions were conducted for mixtures of amine-ended polystyrene of $M_n = 44,000$ g/mol and $M_n = 4000$ g/mol, present in different ratios. The experimental procedure for conducting competitive tethering was similar to that for simple tethering as described in Chapter 4, except that the toluene solution for competitive tethering contained three polymers: the two amine-ended polystyrenes of different molecular weight and the inert-ended polystyrene ($M_n = 13,000$ g/mol) serving as the internal standard. The internal standard was always present at a concentration of 0.255 mg/mL. Table 9.1 lists the concentrations of both amine-ended polystyrenes in the solution for each competitive tethering reaction. Each competitive tethering reaction was monitored by means of the real-time method described in Chapter 3.

**Results and Discussion**

The results of competitive tethering for the 5:1, 1:1, and 1:5 initial mass ratio of PS-NH$_2$-4K to PS-NH$_2$-44K are shown in Figure 9.1, Figure 9.2, and Figure 9.3. In each figure, surface attachment density is plotted against time. The time axis is linear at first and then changes to logarithmic at about 60 minutes to accommodate all the data. The upper plot of each figure depicts the tethering of long chains, PS-NH$_2$-44K, while the lower plot depicts the tethering of short chains, PS-NH$_2$-4K.

The figures show that both molecular weights in each competitive tethering reaction displayed three-regime kinetics, similar to that in simple tethering. The parallel kinetics of 44K and 4K in the third regime underscores the cooperative nature of tethering in the third regime, as discussed in Chapter 5, and shows that it embraces both molecular weights present in the system.

The figures also show a decided advantage of the 4K over the 44K in the competition between the two molecular weights. This is better seen in Table 9.2, which gives data about the mushroom layers. The 4K dominated the mushroom layer even when the initial mass in solution was five times less than that of 44K. This result is not surprising for the formation of a
mushroom layer, where the chains diffuse through solution to the bare surface, because the small chains will diffuse much faster through solution than the large chains. Table 9.3 lists the surface attachment density of each molecular weight at saturation for the three cases. For saturation, as for the mushroom layer, the 4K dominated the 44K even when the initial mass ratio of 4K in solution was unfavorable. This suggests that 4K more easily diffused through the existing tethered layer to become tethered than did 44K.

Next, we will discuss the structure of the bi-dispersed tethered layer in terms of stratification that was predicted by theory [105-107, 109] and supported by neutron reflectivity [111-113]. Theoretical and computer simulation studies proposed that a bi-dispersed brush can be viewed as consisting of “inner” and “outer” strata. It was reasoned that the inner stratum of the bi-dispersed brush, adjacent to the plane of the bare substrate, is composed of short chains as well as portions of the long chains. The outer stratum of the bi-dispersed layer then must contain the remaining portions of the long chains. The portions of the long chains in the inner stratum of the brush are interspersed among the short chains, with both being equally stretched. The portions of the long chains that are in the outer stratum are stretched or not stretched, depending on their surface attachment density.

The stratification of each bi-dispersed layer prepared in this work can be predicted by the use of the common criterion that judges the configuration of chains in each stratum of the layer. In this criterion, if \( d \), the average distance between attachment points of the chains, is smaller than twice \( R_g \), the radius of gyration, the polymer chains are stretched to from a polymer brush. For the inner stratum, \( d_{inner} \) is taken to be the average distance between attachment points of all chains—long and short—on the surface. \( R_g (inner) \) is taken to be the radius of gyration of the short chains in the bi-dispersed layer. For the outer stratum, \( d_{outer} \) is taken to be the average distance between attachment points of long chains only, and \( R_g (outer) \) is taken to be the radius of gyration of that portion of the chain that extends beyond the inner stratum.

When \( d_{inner} \) is smaller than \( 2R_g (inner) \), while \( d_{outer} \) is larger than \( 2R_g (outer) \), the bi-dispersed layer in this case can be viewed as a mushroom layer surmounting a short brush layer, as depicted in drawing “a” of Figure 9.4. When \( d_{inner} \) is smaller than \( 2R_g (inner) \), while \( d_{outer} \) is smaller
than $2R_g$ (outer), both inner stratum and outer stratum are expected to be brushes, as illustrated in drawing “b” of Figure 9.4. Table 9.4 presents the values of $d$ in the inner or outer stratum and $2R_g$ of equivalent chains in each stratum for the bi-dispersed layer consisting of 44K and 4K, as well as the expected stratification of the corresponding bi-dispersed layer. As shown in the table, the structure of each bi-disperse layer varied with the composition of the initial solution.

The examples of competitive tethering described in this study also bring out an inherent limitation. This is the existence of a practical lower limit on the ratio of short-to-long chains in the tethered layer at saturation. The faster diffusion of short chains with respect to long chains means that the only way to greatly reduce the relative number of short chains in the tethered layer is to reduce the number of them in solution initially. However, reduction below a certain point causes a problem of quantitative accuracy for the monitoring method. In other words, when the number of short chains in the solution gets too close to the detection limit, the measurement of changes in concentration will become less accurate. The problem of quantitative accuracy for small numbers of short chains in the solution is a general problem, because most measurements for quantitative analysis are based on the mass of the polymer instead of molar amount. Therefore the existence of a practical lower limit for the ratio of short-to-long chains in the tethered layer is general. This practical limitation will be encountered whenever different molecular weights are being tethered, no matter what the chemical structure of the polymer.

**Conclusion**

Bi-dispersed layers consisting of mixtures of PS-NH₂-44K and PS-NH₂-4K were constructed by means of competitive tethering reactions. Competitive tethering of two molecular weights gave three-regime kinetics as observed for simple tethering. In competitive tethering, short chains dominated over long chains. The composition of the tethered layer was strongly influenced by the relative number of chains of each molecular weight initially placed in the solution.
### Tables

Table 9.1. Concentration of amine-ended polystyrenes in each competitive tethering

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration mg/mL</th>
<th>Mass ratio of 4K to 44K</th>
<th>Molar ratio of 4K to 44K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PS-NH$_2$ 4K</td>
<td>0.513</td>
<td>5:1</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$ 44K</td>
<td>0.105</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PS-NH$_2$-4K</td>
<td>0.255</td>
<td>1:1</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$ 44K</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PS-NH$_2$ 4K</td>
<td>0.104</td>
<td>1:5</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$ 44K</td>
<td>0.523</td>
<td></td>
</tr>
</tbody>
</table>
Table 9.2. Surface attachment density of each molecular weight in the mushroom layer

<table>
<thead>
<tr>
<th>mass ratio of 4K to 44K in initial solution</th>
<th>5:1</th>
<th>1:1</th>
<th>1:5</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass ratio of 4K to 44K in mushroom layer</td>
<td>13:1</td>
<td>15:1</td>
<td>3.9:5</td>
</tr>
<tr>
<td>$\Sigma_{\text{mush}}$ of 4K</td>
<td>0.042 chains/nm$^2$</td>
<td>0.040 chains/nm$^2$</td>
<td>0.017 chains/nm$^2$</td>
</tr>
<tr>
<td>$\Sigma_{\text{mush}}$ of 44K</td>
<td>0.00030 chains/nm$^2$</td>
<td>0.00025 chains/nm$^2$</td>
<td>0.0020 chains/nm$^2$</td>
</tr>
<tr>
<td>Percent of chains in mushroom layer that are 4K</td>
<td>99.3</td>
<td>99.4</td>
<td>89.5</td>
</tr>
</tbody>
</table>
Table 9.3. Surface attachment density of each molecular weight in the brush layer

<table>
<thead>
<tr>
<th>Mass ratio of 4K to 44K in initial solution</th>
<th>5:1</th>
<th>1:1</th>
<th>1:5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass ratio of 4K to 44K in brush layer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12:1</td>
<td>4.6:1</td>
<td>1.9:5</td>
</tr>
<tr>
<td>( \Sigma_{sat} ) of 4K</td>
<td>0.17 chains/nm²</td>
<td>0.076 chains/nm²</td>
<td>0.053 chains/nm²</td>
</tr>
<tr>
<td>( \Sigma_{sat} ) of 44K</td>
<td>0.0013 chains/nm²</td>
<td>0.0015 chains/nm²</td>
<td>0.014 chains/nm²</td>
</tr>
<tr>
<td>Percent of chains in brush layer that are 4K</td>
<td>99.2</td>
<td>98.1</td>
<td>80.3</td>
</tr>
</tbody>
</table>
Table 9.4. Data for evaluating stratification of bi-disperse layers

<table>
<thead>
<tr>
<th>Mass Ratio in solution</th>
<th>Mass Ratio at sat.</th>
<th>$d_{\text{inner}}$ (nm)</th>
<th>$2R_g(\text{inner})$ (nm)</th>
<th>$d_{\text{outer}}$ (nm)</th>
<th>$2R_g(\text{outer})$ (nm)</th>
<th>Stratification</th>
</tr>
</thead>
<tbody>
<tr>
<td>4K : 44K</td>
<td>44K : 4K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 : 1</td>
<td>12 : 1</td>
<td>2.42</td>
<td>4.14</td>
<td>27.7</td>
<td>14.8</td>
<td>mushroom over brush</td>
</tr>
<tr>
<td>1 : 1</td>
<td>4.6 : 1</td>
<td>3.59</td>
<td>4.14</td>
<td>25.8</td>
<td>14.8</td>
<td>mushroom over brush</td>
</tr>
<tr>
<td>1 : 5</td>
<td>1.9 : 5</td>
<td>3.86</td>
<td>4.14</td>
<td>8.77</td>
<td>14.8</td>
<td>Brush over brush</td>
</tr>
</tbody>
</table>
Figure 9.1. Surface attachment density versus time for competitive tethering of polystyrene of two different molecular weights, $M_n = 4000$ and $M_n = 44,000$. Mass ratio of long to short chains in solution initially is 5:1.
Figure 9.2. Surface attachment density versus time for competitive tethering of polystyrene of two different molecular weights, $M_n = 4000$ and $M_n = 44,000$. Mass ratio of long to short chains in solution initially is 1:1.
Figure 9.3. Surface attachment density versus time for competitive tethering of polystyrene of two different molecular weights, $M_n = 4000$ and $M_n = 44,000$. Mass ratio of long to short chains in solution initially is 1:5.
Figure 9.4. The stratification of the bi-disperse tethered layer. Drawing (a) depicts the outer stratum is mushroom and the inner stratum is in brush. Drawing (b) depicts both the outer and inner strata are brush.
Chapter Ten
Sequential Tethering

Introduction

In this chapter, we report our second approach to constructing the mixed tethered layers on the silicate substrates, in which the relative amounts of the two polymers could be controlled to the desired value. This was done by exploiting the three-regime kinetics found for tethered layer formation of single-polymer systems. Two end-functionalized polymers, different either in molecular weight or in chemical structure, were tethered sequentially: the first polymer was tethered to the surface from the solution to form a mushroom layer; then, after the slow second regime had started, the solution of the first polymer was replaced by a solution of the second polymer. We then allowed tethering of the second polymer to proceed. All tethering reactions were monitored quantitatively, in real time, throughout the process. Our hypothesis concerning the sequential approach was that the first polymer would exhibit the first regime and part of the second regime, after which the second polymer would exhibit the remainder of the second regime (a mushroom layer of the first polymer already being present on the surface) and then would continue though the third regime to saturation.

Using sequential tethering, we formed mixed tethered layers of two types: bi-dispersed (two different molecular weights) and bi-component (two chemical structures). In these sequential tethering experiments, we found that the kinetics did not proceed according to our hypothesis. In addition to a second and third regime, the second polymer in the sequence exhibited its own first regime, in spite of the mushroom layer of the first polymer already existing on the surface.

Experimental

Four sequential tethering reactions were conducted to construct bi-dispersed layers and two sequential tethering reactions were conducted to construct bi-component layers. In addition, as a control, two sequential tethering reactions were conducted with a single polymer. Each
sequence in the sequential tethering reactions was conducted in the same manner as for simple tethering described in Chapter 4. Table 10.1 lists the combination used for each of eight sequential tethering reactions. As a typical example, we describe below the procedure for sequential tethering of PS-NH₂-4K followed by PS-NH₂-44K.

A reaction vessel was charged with 19.9 g GPS-derivatized silicate glass beads. To this was added 22 mL toluene solution of the first polymer to be tethered, PS-NH₂-4K at 0.255 mg/mL and an equal amount of inert-ended polystyrene (PS-40K), serving as internal standard. After tethering of the first polymer proceeded through the first regime and entered the sluggish, plateau-like second regime, indicating completion of the mushroom layer, the tethering reaction was halted by separation of the substrate from the polymer solution as follows. The reaction mixture was decanted into a filtration funnel on a Fisherbrand® vacuum filtration apparatus fitted with a 0.1-µm membrane to allow the substrate to be separated from the polymer solution by vacuum filtration. The substrate (silicate glass beads containing a mushroom layer) containing the first tethered polymer chains was subjected to thorough extraction for one day with toluene in a Soxhlet apparatus under positive pressure of argon. After extraction, the substrate was dried in a vacuum at 60 °C overnight. Then 18.1 grams of this substrate was weighed and placed in a reaction vessel. The second sequence of tethering started when 20 mL of PS-NH₂-44K in toluene (0.255 mg/mL) was added to the flask. The reaction proceeded until saturation was reached. Note that there was a slight and inevitable loss in the mass of silicate glass beads between two sequences of the tethering reaction, owing to filtering and extraction. This was the reason for starting with slightly more GPS-derivatized silicate glass beads and polymer solution than usual.

**Results and Discussion**

Plots of sequential tethering reactions conducted to form bi-dispersed mixed layers are shown in Figure 10.1-Figure 10.4 [124]. These figures consist of a left-hand and a right-hand part: tethering of the first polymer is shown on the left and tethering of the second polymer is shown on the right. The time axis of the left-hand part is linear, whereas the time axis of the right-hand part is linear at first, but changes to logarithmic at about 60 minutes to accommodate
all the data. Note that the vertical scales at left and right are different: the scale for the polymer of lower molecular weight is an order of magnitude larger than that of the polymer of higher molecular weight. As can be seen in each of the figures, tethering of the first polymer was allowed to proceed until the mushroom layer was complete and tethering had entered the second regime. Then the solution was switched and tethering of the second polymer began. Tethering of the second polymer in the sequence was permitted to proceed until saturation (natural cessation of tethering) in each case. The second polymer in the sequence exhibited its own first regime, contrary to the hypothesis presented in the introduction. This will be discussed later in this chapter.

The final surface attachment densities for the two molecular weights in each of the four bi-dispersed layers depicted in the figures are summarized in Table 10.2. The surface attachment density of the low-molecular-weight polymer always exceeds that of the high-molecular-weight polymer, no matter which was tethered first. This is not surprising, given the relative sizes of the chains. The last column shows the number ratio of short chains to long chains achieved in each final layer. Note that widely different ratios of short-to-long chains were achieved by simply reversing the tethering sequence.

Although we allowed the tethering of the second polymer in the sequence to proceed until saturation, its tethering could have been stopped at any selected time before saturation was reached. Removal of the solution containing the second polymer at various time-points in the process would lead to a set of different ratios of short-to-long chains in the final mixed tethered layer. For example, in the case of PS-NH$_2$-44K followed by PS-NH$_2$-4K, removal of the PS-NH$_2$-4K solution well before saturation would result in a ratio of short-to-long chains much lower than the ratio of 28:1 reported in Table 10.2. The only restriction on this tactic is that removal of the second polymer in the sequence cannot be done with precision during its (the second polymer’s) first regime, because first-regime kinetics is so fast. With this in mind, the experimenter can achieve ratios of short-to-long chains anywhere in the range 28:1 to 10:1 by removal of the PS-NH$_2$-4K solution at the appropriate time after its first regime. The reverse sequence, PS-NH$_2$-4K followed by PS-NH$_2$-44K, provides access to ratios of short-to-long chains anywhere within the range 10:1 to 4.4:1 simply by removal of the second solution at
selected time-points in the process. Overall, ratios of short-to-long chains spanning the range 28:1 to 4.4:1 can be achieved for a bi-dispersed layer of these two molecular weights.

Plots of sequential tethering reactions conducted to form bi-component (PS and PEO) mixed layers are shown in Figure 10.5 and Figure 10.6. As above, these figures consist of a left-hand and a right-hand part: tethering the first polymer on the left, and, after the solutions are switched, tethering the second polymer on the right. As can be seen in both figures, tethering the first polymer was allowed to proceed until the mushroom layer was complete and tethering had entered the second regime. Then the solution was switched and tethering the second polymer began. Tethering the second polymer in the sequence was permitted to proceed until saturation. Again, the second polymer in the sequence exhibits its own first regime, contrary to the hypothesis presented in the introduction. This will be discussed later in this chapter.

The final surface attachment densities for the two components of both bi-component layers depicted in Figure 10.5 and Figure 10.6 are summarized in Table 10.3. The last column shows the ratio of PEO to PS achieved in each final layer. Note the substantial difference in final composition of the two bi-component tethered layers even though the molecular weights of the linear and star PEO’s were identical. Part of the difference may be due to the linear versus star architecture, but part may be due to the fact that the star polymer has four amine end-functional groups (one at the end of each arm), while the linear polymer has only one, as discussed in Chapter 6.

Now, we consider the unexpected display of a first regime by the second polymer in the sequence, a phenomenon that was not in accordance with the hypothesis presented in the introduction. Consideration of the literature on random sequential deposition of regularly shaped objects to a flat surface, led us to propose that this unexpected phenomenon might be due entirely to a size difference between the first and second polymers in the sequence. To test this, we conducted control experiments in which the first and second polymers tethered in the sequence were identical in type and in size. The results (Figure 10.7 and Figure 10.8) show that the second polymer in the sequence did not exhibit its own first regime. Rather, when first exposed to the substrate, the second polymer underwent extremely slow tethering, typical of
second-regime behavior. This was followed after a long while by the accelerated tethering typical of the third regime and subsequently by saturation. According to the results of these control experiments, when the second polymer in the sequence is the same size as the first, the second polymer exhibits only the second and third regimes of kinetics. These results support our proposed explanation that the second polymer in the sequence exhibits its own first regime only if its size is different from that of the first polymer.

Drawing on the concept of random sequential deposition, we can develop a more detailed explanation for the first regime kinetics exhibited by the second polymer in sequential tethering of polymers of different sizes. In the random deposition of rigid circular objects of a given uniform size, deposition occurs easily and rapidly until a jamming limit is reached [71, 72]. This is the point at which no further objects can be deposited without overlap. Mathematically, the surface coverage at the jamming limit is about 55%, leaving 45% of the substrate surface area empty [71, 72]. After reaching the jamming limit, continued deposition of the same-sized objects cannot be done without relaxing the original constraints on the system. Changing the deposition of smaller rigid circular objects would overcome this constraint. These smaller objects could be deposited into the empty spaces between the larger objects as easily as the larger objects were deposited onto the bare surface before their jamming limit was reached [72]. In construction of a tethered layer from polymer chains, a completed mushroom layer can be regarded as equivalent to a surface that contains objects deposited to their jamming limit. We first consider a mushroom layer comprised of tethered chains of high molecular weight, i.e., large mushrooms. Once the mushroom layer is complete, subsequent tethering of polymer chains of the same large size is difficult, but tethering smaller polymer chains to the empty areas between large chains would be expected to occur easily, giving an apparent first regime for the second – and smaller – polymer in the sequence. Then, when the smaller polymer chains had filled the empty areas, the second polymer in the sequence would begin its own second regime.

The reverse case, in which a large polymer is tethered second in the sequence and displays its own first regime, can also be explained by the relative difference in size. In this case, the first polymer tethered is of low molecular weight and the mushroom layer is comprised of small mushrooms. These, too, are at their jamming limit, and 45% of the surface of the
substrate is unoccupied. The unoccupied surface is in the form of many, very small empty areas. A large polymer chain approaching a mushroom layer of small chains is approaching a layer that is shallow relative to its own large size. Entry into an empty area of the mushroom layer by the functionalized free end of a large polymer chain would require only a small thermal excursion relative to the size of the large chain. Such a thermal excursion is relatively easy for two reasons; the free ends of a chain are able to respond more rapidly to thermal fluctuations than are the internal segments, and the free ends tend to spend more time at the periphery of the coil than buried inside it. Thus, large chains could be tethered quite rapidly to the empty areas of a mushroom layer of small chains, giving an apparent first regime for the second – and larger—polymer in the sequence.

Finally, the stratification of the mixed layers constructed by sequential tethering is subjected to the aforementioned criterion in Chapter 9. Here the configuration of the chains in each stratum is evaluated separately by use of two quantities: $d$, the average distance between attachment points of the chains (computed from experimental data), and $R_g$, the radius of gyration of analogous free chains in a good solvent. Table 10.4 shows that the only case in which $d_{inner} < 2R_g\ (inner)$ is for mixed layers comprised of PS-NH_2-15K and PS-NH_2-44K, tethered in either order. This indicates that the chains in the inner stratum are sufficiently crowded to be stretched away from the surface of the substrate. For all other combinations, $d_{inner} > 2R_g\ (inner)$, which indicates that the chains in the inner stratum have enough room to be included in the mushroom configuration.

For the outer stratum, $d_{outer}$ is taken to be the average distance between attachment points of the long chains only, and $R_g\ (outer)$ used for the comparison is the radius of gyration computed for that portion of the chain that extends beyond the inner stratum. Table 10.4 shows that when the long chains were tethered first in the sequence, the outer stratum is clearly in the mushroom configuration ($d_{outer} > 2R_g\ (outer)$). This was the expected result, because when long chains were first in the sequence, tethering was stopped after they completed a mushroom layer. For all of the remaining mixed layers in Table 10.4, $d_{outer} \approx 2R_g\ (outer)$, which indicates a borderline case between mushroom and brush for the outer stratum. If the suggestion is followed that a disproportionately large amount of the contour length resides in the outer stratum to gain
entropy, while the residual length in the inner stratum is stretched, the calculated values of $2R_g^{(outer)}$ become slightly larger, so that $d_{outer} < 2R_g^{(outer)}$. Stretching the chains in the outer stratum would be the expected result from a sequence in which long chains were tethered second to saturation. This is because stretching plays a role in bringing the tethering to a natural halt (saturation) [12]. Recall that, in all these examples, when tethering the second polymer in the sequence reaches saturation, there are still ample numbers of epoxide reactive sites remaining on the substrate. This underscores the fact that tethering halts because of the entropy cost of stretching and not because the reactive sites on the surface have been consumed.

**Conclusion**

Several mixed tethered layers, composed of polymers either of two molecular weights or two chemical structures, were constructed by means of sequential tethering. Mixed layers of known and controlled composition were achieved by exploiting the unique, three-regime kinetics established previously for monodispersed, single-component tethered layers. The two polymers for the mixed layer were tethered sequentially; the first polymer was allowed to form a mushroom layer, and then the solution in contact with the substrate was switched to that of a second polymer. The second polymer was then allowed to become tethered to saturation. These experiments showed that a wide range of ratios of the two polymers in the mixed layer can be achieved by means of a sequential tethering approach. Our hypothesis for the sequential tethering was that once the first polymer had exhibited the first regime, the second polymer in the sequence would exhibit only a second and third regime, giving a total of three regimes, similar to tethering a simple, one-polymer system. However, contrary to our hypothesis, the second polymer in the sequence exhibited an unexpected first regime, as well as the second and third regimes. We determined that the unexpected first regime originated in the size difference between the first and second polymers in the sequence.
### Tables

Table 10.1. Combination for sequential tethering reactions

<table>
<thead>
<tr>
<th>Purpose</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; tethering reaction</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; tethering reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepare bi-disperse tethered layer</td>
<td>PS-NH$_2$ 44K</td>
<td>PS-NH$_2$ 4K</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$ 4K</td>
<td>PS-NH$_2$ 44K</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$ 44K</td>
<td>PS-NH$_2$ 15K</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$ 15K</td>
<td>PS-NH$_2$ 44K</td>
</tr>
<tr>
<td>Prepare bi-component tethered layer</td>
<td>PS-NH$_2$-4K</td>
<td>Linear PEO-NH$_2$-10K</td>
</tr>
<tr>
<td></td>
<td>PS-NH$_2$-4K</td>
<td>Four-arm PEO-NH$_2$-10K</td>
</tr>
<tr>
<td>Test hypothesis</td>
<td>PS-NH$_2$ 44K</td>
<td>PS-NH$_2$ 44K</td>
</tr>
<tr>
<td></td>
<td>Linear PEO-NH$_2$-10K</td>
<td>Linear PEO-NH$_2$-10K</td>
</tr>
</tbody>
</table>
Table 10.2. Final compositions of bi-dispersed mixed layers

<table>
<thead>
<tr>
<th>1st polymer:2nd polymer</th>
<th>Σ (chains/nm²)</th>
<th>Number ratio of chains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st: 2nd</td>
<td>short: long</td>
</tr>
<tr>
<td>PS-NH₂-4K: PS-NH₂-44K</td>
<td>0.019: 0.0043</td>
<td>4.4: 1</td>
</tr>
<tr>
<td>PS-NH₂-44K: PS-NH₂-4K</td>
<td>0.0016: 0.045</td>
<td>28: 1</td>
</tr>
<tr>
<td>PS-NH₂-15K: PS-NH₂-44K</td>
<td>0.015: 0.0045</td>
<td>3.3: 1</td>
</tr>
<tr>
<td>PS-NH₂-44K: PS-NH₂-15K</td>
<td>0.0015: 0.025</td>
<td>17: 1</td>
</tr>
</tbody>
</table>
Table 10.3. Final compositions of bi-component mixed layers

<table>
<thead>
<tr>
<th>1&lt;sup&gt;st&lt;/sup&gt; polymer : 2&lt;sup&gt;nd&lt;/sup&gt; polymer</th>
<th>Σ (chains/nm&lt;sup&gt;2&lt;/sup&gt;)&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Number ratio of chains PEO: PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-NH&lt;sub&gt;2&lt;/sub&gt;-4K: Linear PEO-NH&lt;sub&gt;2&lt;/sub&gt;-10K</td>
<td>0.013: 0.023</td>
<td>1.8: 1</td>
</tr>
<tr>
<td>PS-NH&lt;sub&gt;2&lt;/sub&gt;-4K: Four-arm PEO-NH&lt;sub&gt;2&lt;/sub&gt;-10K</td>
<td>0.013: 0.071</td>
<td>5.6: 1</td>
</tr>
</tbody>
</table>
Table 10.4. Data for evaluating configurational status of mixed layers

<table>
<thead>
<tr>
<th>1st polymer: 2nd polymer</th>
<th>$\Sigma$, chains/nm²</th>
<th>Inner stratum</th>
<th>Outer stratum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st, 2nd</td>
<td>$d_{inner}$ nm</td>
<td>$2R_{g_s(outer)}$ nm</td>
</tr>
<tr>
<td>PS-NH₂-4K: PS-NH₂-44K</td>
<td>0.019: 0.0043</td>
<td>6.55</td>
<td>4.14</td>
</tr>
<tr>
<td>PS-NH₂-44K: PS-NH₂-4K</td>
<td>0.0016: 0.045</td>
<td>4.63</td>
<td>4.14</td>
</tr>
<tr>
<td>PS-NH₂-15K: PS-NH₂-44K</td>
<td>0.015: 0.0045</td>
<td>7.16</td>
<td>8.56</td>
</tr>
<tr>
<td>PS-NH₂-44K: PS-NH₂-15K</td>
<td>0.0015: 0.025</td>
<td>6.14</td>
<td>8.56</td>
</tr>
<tr>
<td>PS-NH₂-4K: Linear PEO-NH₂-10K</td>
<td>0.013: 0.023</td>
<td>5.27</td>
<td>4.14</td>
</tr>
</tbody>
</table>
Figure 10.1. Surface attachment density versus time for sequential tethering of PS-NH$_2$-4K followed by PS-NH$_2$-44K. The left and right vertical axes indicate the individual surface attachment densities of PS-NH$_2$-4K and PS-NH$_2$-44K, respectively.
Figure 10.2. Surface attachment density versus time for sequential tethering of PS-NH₂-44K followed by PS-NH₂-4K. The left and right vertical axes indicate the individual surface attachment densities of PS-NH₂-44K and PS-NH₂-4K, respectively.
Figure 10.3. Surface attachment density versus time for sequential tethering of PS-NH$_2$-15K followed by PS-NH$_2$-44K. The left and right vertical axes indicate the individual surface attachment densities of PS-NH$_2$-15K and PS-NH$_2$-44K, respectively. Twin tethering reactions (open and closed symbols) were run to show run-to-run reproducibility.
Figure 10.4. Surface attachment density versus time for sequential tethering of PS-NH$_2$-44K followed by PS-NH$_2$-15K. The left and right vertical axes indicate the individual surface attachment densities of PS-NH$_2$-44K and PS-NH$_2$-15K, respectively. Twin tethering reactions (open and closed symbols) were run to show run-to-run reproducibility.
Figure 10.5. Surface attachment density versus time for sequential tethering of PS-NH$_2$-4K followed by linear PEO-NH$_2$-10K. The left and right vertical axes indicate the individual surface attachment densities of PS-NH$_2$-4K and linear PEO-NH$_2$-10K, respectively.
Figure 10.6. Surface attachment density versus time for sequential tethering of PS-NH$_2$-4K followed by four-arm-PEO-NH$_2$-10K. The left and right vertical axes indicate the individual surface attachment densities of PS-NH$_2$-4K and four-arm PEO-NH$_2$-10K, respectively. The left-hand side of this figure appears identical to the left-hand side of Figure 10.5, because the first part of the sequence was the same and then the substrate was divided for the second part of the sequence of two different mixed layers.
Figure 10.7. Surface attachment density versus time for sequential tethering of PS-NH$_2$-44K followed by PS-NH$_2$-44K. The left and right vertical axes indicate the individual surface attachment densities for the first and second parts of the sequence, respectively. Twin tethering reactions (open and closed symbols) were run to show run-to-run reproducibility.
Figure 10.8. Surface attachment density versus time for sequential tethering of linear PEO-NH$_2$-10K followed by linear PEO-NH$_2$-10K. The left and right vertical axes indicate the individual surface attachment densities for the first and second parts of the sequence, respectively.
Chapter Eleven

Overall Conclusions

The work described in this dissertation constitutes the first comprehensive investigation ever done of the kinetics of irreversible tethering of end-functionalized polymer chains to the surface of a solid. The data showed three distinct regimes of kinetics rather than the two predicted by theory. The three-regime kinetics was found to be an inherent feature of the system regardless of molecular weight of tethered polymer, reaction temperature, or type of reactive site on the surface of the substrate. Once the discovery of three-regime kinetics was made, much of the subsequent work was devoted to determining the cause of the unexpected third regime and to determining how to exploit its features to construct controlled and complex tethered layers.

Systems were investigated in which amine end-functionalized polystyrene or poly(ethylene oxide) were tethered from dilute solution to the surface of the epoxide-derivatized solid substrate. For all systems, the end of the first regime was found to correspond to a mushroom layer, i.e., a layer of relaxed, nonoverlapping chains, and saturation was found to correspond to a brush, i.e. a layer of crowded chains, all stretching away from the surface like the bristles in a brush. The first regime was fast and was controlled by diffusion of the polymer through solution to the bare surface of the solid. The second regime was slow and was controlled by the diffusion of polymer through the already-tethered layer to reach the surface to react. The third regime was determined to be due to a spatially nonuniform transition from mushroom to brush. AFM images obtained at different times during the process of tethering revealed the nonuniform surface texture of the third regime, as compared with the uniform texture of the mushroom stage and the uniform texture of brush at saturation.

The effect of polymer architecture on the tethering kinetics was investigated. The experimental data obtained in this investigation showed that polymer architecture did not alter the kinetics profile. For both linear and four-arm amine-ended poly(ethylene oxide), three-regimes of kinetics were in evidence. However, the surface attachment density of four-arm chains was more than 4-fold higher than that of linear chains. The higher surface attachment
density is attributed to the presence of more end-functional groups per molecule for the four-arm architecture over the linear architecture.

The effect of solvent quality alone on the kinetics and outcome of the tethering process was investigated. Solvent quality was expressed as $\chi$, the interaction parameter between the solvent and the polymer in the solution at dilute concentrations. In the relatively limited range of $\chi$ (from 0.47 to 0.55) that was studied, the expected three-regime kinetics was displayed, regardless of solvent quality. As expected, an increase in $\chi$-parameter for the system brought about a modest increase in surface attachment density, but contrary to expectation, an increase in $\chi$-parameter did not perceptibly increase the rate of tethering. This points out that decreasing the solvent quality alone, without otherwise changing conditions, is not an effective way to make substantial increases in tethering density.

The effect of segmental adsorption on the tethering process was investigated. The tethering process was altered dramatically when segmental adsorption occurred simultaneously with tethering. The tethering 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.

Based on the understanding obtained in investigation of the tethering kinetics, mixed tethered layers were constructed by means of two approaches: competitive tethering and sequential tethering. First, competitive tethering reactions were conducted to construct bi-dispersed layers consisting of mixtures of two molecular weights. Competitive tethering gave three-regime kinetics as observed for simple tethering. In competitive tethering, short chains rather than long chains dominated the tethering process. The composition of the tethered layer was strongly influenced by the relative number of chains of each molecular weight initially placed in the solution.

Second, sequential tethering was used to construct several mixed tethered layers, composed of polymers either of two molecular weights or two chemical structures. In sequential
tethering; the first polymer was allowed to form a mushroom layer, and then the solution in contact with the substrate was switched to that of a second polymer. The second polymer was then allowed to become tethered to saturation. These experiments showed that a wide range of controlled ratios of different polymers in mixed layers can be achieved by means of a sequential tethering approach.
Appendix

The radius of gyration of each polymer used in this dissertation was computed according to a method developed by Flory [125]. This way, a series of consistent values of $R_g$ for a given set of conditions was achieved from the following expression,

$$R_g = \alpha \sqrt[6]{C_\infty / (6n^{1/2}l)}.$$  Equation I.1

In this expression, $\alpha$ is the expansion factor of a polymer coil in solvent: $\alpha$ is larger than 1 in good solvent, indicating expansion of a chain from its ideal value while $\alpha$ is smaller than 1 in poor solvent, indicating contraction of a chain from its ideal value; $C_\infty$ is the characteristic ratio obtained from the literature; $n$ is the number of single bonds in the backbone; and $l$ is the length of the single bonds in the backbone of the polymer chain.

The value of $\alpha$ in Equation I.1 was determined analytically for each polymer-solvent system by the use of the expression below [125]:

$$\alpha^5 - \alpha^3 = 2C_M(0.5 - \chi),$$  Equation I.2

where $C_M$ is a parameter depending on properties of the polymer-solvent system and $\chi$ is the polymer-solvent interaction parameter. $C_M$ is given by [125]

$$C_M = \left(\frac{27}{2^{5/2} \pi^{3/2}}\right)\left(\frac{v_2^2}{N_AV_1}\right)\left(\frac{\left< r^2 \right>_0}{M_n}\right)^{-3/2},$$  Equation I.3

where $v_2$ is the specific volume of the polymer; $N_A$ is Avogadro’s number; $V_1$ is the molar volume of the solvent; $<r^2>_0$ is the mean square end-to-end distance of the polymer chain in ideal solvent; and $M_n$ is the molecular weight of the polymer. The value of $\frac{\left< r^2 \right>}{M_n}$ is independent of the molecular weight of the polymer and was obtained from the literature [125]. $\frac{\left< r^2 \right>}{M_n}$ is equal to 0.0700 (nm)(mole)$^{1/2}$(g)$^{-1/2}$ for polystyrene in toluene and is equal to 0.0790 (nm)(mole)$^{1/2}$(g)$^{-1/2}$ for poly(ethylene oxide) in aromatic solvents [84]. The value of $\chi$ used in Equation I.2 for each
polymer-solvent system was obtained from the literature. (For the case of PEO in several aromatic solvents, $\chi$ was computed from an empirical expression, as described in Chapter 7.) The value used for $C_\infty$ in Equation I.1 was 10.8 [84] for polystyrene in toluene and was 6.7 for PEO in aromatic solvents [85]. The value used for $l$ in Equation 1 was 0.154 nm for each C-C single bond of polystyrene and was 0.150 nm for poly(ethylene oxide), computed as the average of two C-C bonds and one C-O bond.

Radius of gyration of four-arm PEO-NH$_2$-10K was derived from $R_g$ of linear PEO-NH$_2$-10K by the use of the following expression [126]:

$$R_{g(\text{star})} = R_{g(\text{linear})} N^{1/5} (0.5 - \chi)^{1/5}, \quad \text{Equation I.4}$$

where $R_{g(\text{star})}$ is the radius of gyration of a star polymer; $R_{g(\text{linear})}$ is the radius of gyration of a linear polymer whose molecular weight is equal to that of the star polymer; $N$ is the number of arms in each star polymer, and $\chi$ is the polymer-solvent interaction parameter. In the case of four-arm PEO-NH$_2$-10K, $N$ is equal to 4 and $R_{g(\text{linear})}$ was taken as the value of $R_g$ of linear PEO-NH$_2$-10K. Table I.1 lists parameters used and values computed for $R_g$ used in the study of simple tethered layers in Chapters 3-8.

In the study of mixed tethered layers, described in Chapters 9 and 10, an $R_g$-value had to be computed for that portion of each long chain that extended into the solvent beyond the short chains [109]. The length of this portion was taken as the difference between the length of an extended long chain and the length of an extended short chain. Thus, this type of $R_g$-value, designated $R_g(\text{outer})$, was computed for the following mixed layers: PS-NH$_2$-44K and PS-NH$_2$-4K; PS-NH$_2$-44K and PS-NH$_2$-15K; and PS-NH$_2$-4K and linear PEO-NH$_2$-10K. The method of computation of $R_g(\text{outer})$ was the same as for $R_g$. Table I.2 lists parameters used and values computed for $R_g(\text{outer})$ in mixed tethered layers.
Table I.1. Parameters used and values computed for $R_g$ in simple tethered layers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>$\chi$</th>
<th>n</th>
<th>$C_\infty$ (nm)</th>
<th>l (nm)</th>
<th>$\alpha$</th>
<th>$R_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-NH$_2$-4K</td>
<td>Toluene</td>
<td>23</td>
<td>0.40</td>
<td>77</td>
<td>10.8</td>
<td>0.154</td>
<td>1.14</td>
<td>2.07</td>
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<td>23</td>
<td>0.40</td>
<td>288</td>
<td>10.8</td>
<td>0.154</td>
<td>1.22</td>
<td>4.28</td>
</tr>
<tr>
<td>PS-NH$_2$-44K</td>
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<td>23</td>
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<td>846</td>
<td>10.8</td>
<td>0.154</td>
<td>1.30</td>
<td>7.80</td>
</tr>
<tr>
<td>Linear PEO-NH$_2$-10K</td>
<td>Toluene</td>
<td>23</td>
<td>0.39</td>
<td>456</td>
<td>4.25</td>
<td>0.150</td>
<td>1.15</td>
<td>3.10</td>
</tr>
<tr>
<td>Four-arm PEO-NH$_2$-10K</td>
<td>Toluene</td>
<td>23</td>
<td>0.39</td>
<td>456</td>
<td>4.25</td>
<td>0.150</td>
<td>N/A</td>
<td>2.63</td>
</tr>
<tr>
<td>Linear PEO-NH$_2$-10K</td>
<td>Toluene</td>
<td>50</td>
<td>0.47</td>
<td>456</td>
<td>4.25</td>
<td>0.150</td>
<td>1.05</td>
<td>3.55</td>
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<tr>
<td>Linear PEO-NH$_2$-10K</td>
<td>$p$-Xylene</td>
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<td>0.54</td>
<td>456</td>
<td>4.25</td>
<td>0.150</td>
<td>0.961</td>
<td>3.25</td>
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<tr>
<td>Linear PEO-NH$_2$-10K</td>
<td>Et-benzene</td>
<td>50</td>
<td>0.69</td>
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<td>4.25</td>
<td>0.150</td>
<td>0.845</td>
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Table I.2. Parameters used and values computed for $R_g$ (outer) in mixed tethered layers

<table>
<thead>
<tr>
<th>Mixed layer</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>$\chi$</th>
<th>n</th>
<th>$C_\infty$</th>
<th>l (nm)</th>
<th>$\alpha$</th>
<th>$R_g$ (nm)</th>
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<tbody>
<tr>
<td>PS-NH$_2$-44K &amp; PS-NH$_2$-4K</td>
<td>Toluene</td>
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<td>0.40</td>
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<td>558</td>
<td>10.8</td>
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<td>1.27</td>
<td>6.20</td>
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<td>PS-NH$_2$-4K &amp; Linear PEO-NH$_2$-10K</td>
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<td>0.39</td>
<td>402</td>
<td>4.25</td>
<td>0.150</td>
<td>1.14</td>
<td>2.91</td>
</tr>
</tbody>
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Vita

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