Comparison of Tethering of Linear and Four-Arm Poly(ethylene oxide)

Heqing Huang,[†] Erin C. Fulchiero,[‡] and Lynn S. Penn*,[†]

Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky 40506-0046, and Chemistry Department, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010

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Introduction

The tethering of linear, amine-end-functionalized poly(ethylene oxide) to the surface of a solid substrate was compared to the tethering of four-arm, amine-end-functionalized poly(ethylene oxide) to the same type of substrate. Both end-functionalized polymers had the same molecular weight ($M_n = 10\,000$ g/mol), and both were similarly monodisperse ($M_w/M_n = 1.08$). While the linear polymer (designated linear PEO-NH_2) had one amine end group per molecule, the four-arm star (designated four-arm PEO-NH_2) had four amine end groups per molecule. We wanted to determine the effect of architecture and number of end-functional groups on the kinetics of tethering.

Experimental Section

Introduction of Reactive Sites to Substrate (Derivatization). Prior to derivatization, the substrate (silica powder S-5631, Sigma, St. Louis, MO) was cleaned with piranha solution. Then, epoxide reactive groups were introduced to the surface of the substrate by exposure to a solution of 3-glycidoxypropyltrimethoxysilane (Aldrich, Milwaukee, WI) in anhydrous toluene at reflux for 16 h.[1,2] A 20-fold excess of silane was used in the reaction mixture, based on 5−9 native hydroxyl groups/nm^2 on the surface of the cleaned silica substrate[3] and nominal reaction of one silane molecule with three hydroxyls. After reaction, the epoxide-derivatized silica was separated from the supernatant by filtration and was exhaustively extracted in a Soxhlet to remove any silane adsorbed to but not reacted with the surface. This procedure has been shown to produce 2.71 ± 0.24 epoxide groups per nm^2 of silica surface.[4] Values for specific surface area were determined by means of the Brunauer−Emmett−Teller (BET) method on a Tristar 300 gas adsorption analyzer (Micrometritics, Norcross, GA).

Tethering Reactions. Linear PEO-NH_2 or four-arm PEO-NH_2 (Polymer Source, Inc., Quebec, Canada) were tethered to the epoxide-derivatized surface of the silica substrate.[3,5,6] This involved room temperature exposure (with stirring) of the derivatized substrate to a solution of carefully weighed polymer in toluene (0.80 mg/mL). The solution also contained a known amount of inert-ended PEO of $M_n = 2000$ g/mol and $M_w/M_n = 1.05$ (Polymer Source) as internal standard.

Real-Time Monitoring of Kinetics. The disappearance of the PEO-NH_2 from the solution was monitored by means of a real-time, off-line method made quantitative by the unchanging internal standard in each reaction mixture.[1,2,6] Briefly, small aliquots were removed from the stirring reaction mixture at frequent intervals. The silica substrate was removed from each aliquot by filtration, and the solution was analyzed by size exclusion chromatography (SEC) for PEO-NH_2. Analysis of peak area ratios from digitized chromatograms gave mass depleted from solution, which is equivalent to mass tethered. Mass tethered for each aliquot was converted to surface attachment density, expressed as chains/nm^2, with knowledge of precise values of polymer molecular weight and total surface area of the substrate.

Test for Segmental Adsorption. Segmental adsorption of PEO to the surface of the substrate was evaluated by a method described previously,[1,2,6] which consisted of exposure of the substrate to a solution containing carefully weighed amounts of inert-ended, monodiperse PEO of $M_n = 2000$ and 8000 g/mol. The solution was monitored with SEC, in which the digitized areas of the two peaks were compared over time. The absence of segmental adsorption is characterized by a peak area ratio that remains constant at its initial value over time, while the presence of segmental adsorption is characterized by a changing the peak area ratio reflecting the preferential adsorption of the higher-molecular-weight polymer.[7]

Colorimetric Analysis for Amine. The number of primary amine groups on the surface of silica powder was determined by colorimetric dye analysis specific to primary amine, as described in refs 8 and 9. Briefly, this involved formation of a 1:1 complex of Ponceau 3R dye molecules with the primary amine groups contained in polymer molecules linked to the surface. Any excess (noncomplexed) dye was removed from the surface by thorough rinsing of the silica, after which the complex was cleaved with a change in pH, and the cleavage medium was quantitatively analyzed at a wavelength of 510 nm in the UV spectrometer by comparison with a calibration curve based on known concentrations of Ponceau 3R. Only systems that had reached saturation were analyzed because the analysis required a substantial amount of reacted substrate, and the starting materials used in the tethering reactions were limited in supply. The harsh conditions of the colorimetric analysis procedure are known to cleave some of the bonds linking the amine to the surface of the substrate.[8] For this reason, repeat analyses of the same substrate were conducted, and the results were extrapolated to the preanalysis value.

Results and Discussion

In the test for segmental adsorption to the epoxide-derivatized substrate, two molecular weights of inert-ended PEO in solution maintained a constant ratio of 0.733 ± 0.014 for the duration of the exposure (20 h). The constancy of the ratio verified the absence of segmental adsorption.

The results for tethering of linear PEO-NH_2 and four-arm PEO-NH_2 of the same molecular weight are shown in Figures 1 and 2, respectively. The figures show that both of these polymers, although of different architecture, displayed the three-regime kinetics characteristic of irreversible tethering of polymer from dilute solution in the absence of segmental adsorption.[1,2,5,6,10]

The most notable difference between the tethering process for the two architectures was that the surface attachment density of four-arm PEO-NH_2 was about 4−5 times greater than that of linear PEO-NH_2 at all times during the tethering process, indicating a higher tethering rate for the four-arm PEO-NH_2. In the tethering process, diffusion of the polymer molecule to the surface rather than its chemical reaction with the surface is the rate-determining step.[1,2,5,6,10] Since rate of diffusion through solvent is inversely proportional to R_g, four-arm PEO-NH_2, with $R_g = 2.63$ nm,[11] would diffuse only 18% faster than linear PEO-NH_2, with $R_g = 3.10$ nm.[12] Thus, the effect of polymer architecture,

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[†] University of Kentucky.
[‡] Bryn Mawr College.
* Corresponding author: Ph 859-257-7897; Fax 859-257-7897; e-mail penn@engr.uky.edu.

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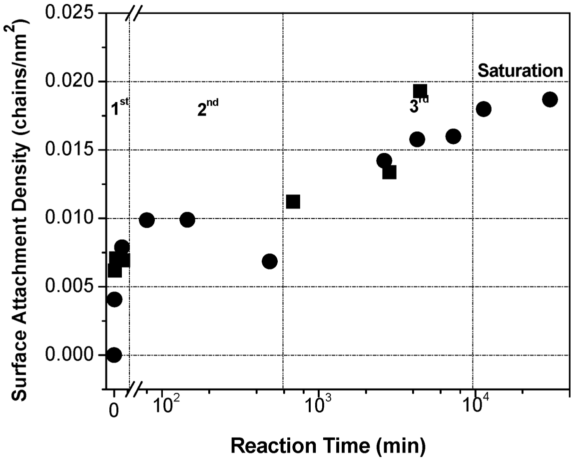

Figure 1. Tethering of linear PEO-NH$_2$ of M_n = 10 000 onto the surface of the epoxide-derivatized silicate powder in toluene at 23 °C. The x-axis changes from linear to logarithmic at 60 min. The two different symbols represent duplicate tethering reactions conducted to illustrate reproducibility.

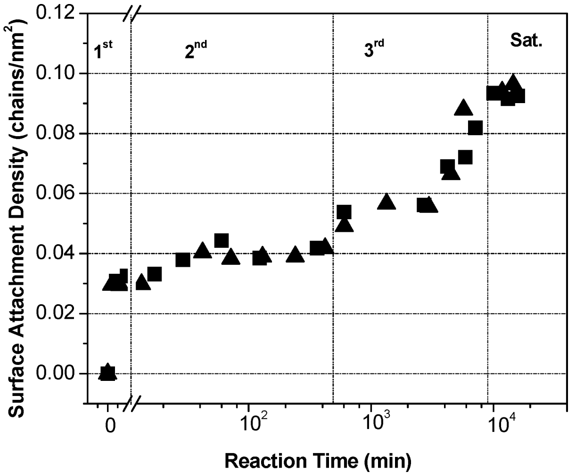

Figure 2. Tethering of four-arm PEO-NH$_2$ of M_n = 10 000 onto the surface of the epoxide-derivatized silicate powder in toluene at 23 °C. The x-axis changes from linear to logarithmic at 10 min. As above, the two different symbols represent duplicate reactions.

Table 1. Surface Attachment Density for Both Architectures (Avg ± 1 Std Dev)

tethered polymers	Σ_{mush}, chains/nm^2	Σ_{sat}, chains/nm^2
four-arm PEO-NH$_2$	0.030 ± 0.002	0.094 ± 0.002
linear PEO-NH$_2$	0.0067 ± 0.0005	0.018 ± 0.001

i.e., four-arm vs linear, on diffusion through the solvent is relatively minor, and the explanation of the dramatic increase in rate and surface attachment density must lie elsewhere.

Table 1 shows values for surface attachment density at the two key benchmarks in the process: the end of the first regime, at which the mushroom layer is complete, and saturation, at which tethering has stopped and the layer is in the brush configuration. The surface attachment density of the mushroom layer (Σ_{mush}) was 4.5 times higher for four-arm PEO-NH$_2$ than for linear PEO-NH$_2$, while the surface attachment density at saturation (Σ_{sat}) was 5.2 times higher. These enhancements in Σ are not the same statistically (at $p < 0.05$) as four, but their closeness to four prompted us to consider the role of the four-to-one ratio of number of reactive end-functional groups per polymer molecule in producing the observed difference in surface attachment density.

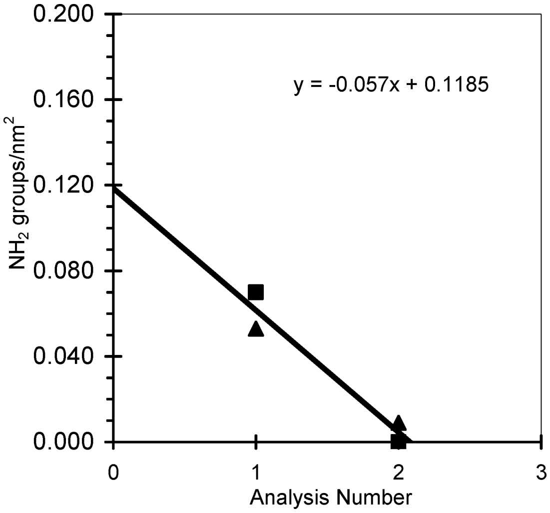

Figure 3. Plot of primary amine groups detected vs analysis number.

One effect of four vs one end-functional group would be to increase the probability that four-arm PEO-NH$_2$ would become tethered during an encounter with the surface rather than diffusing away. This enhancement would occur for all three regimes of kinetics, leaving the characteristic three-regime kinetics profile intact. While an enhanced probability of tethering can explain the increase in rate, it cannot explain why surface attachment density of the four-arm polymer would reach a higher value that that of the linear polymer. The results of colorimetric analysis offer some insight into this. These results are shown in Figure 3, where detectable primary amine (groups per nm^2 of substrate surface) is plotted vs analysis number. Extrapolation to the pre-analysis value gives 0.12 amines/nm^2, and division of this value by 0.094 chains/nm^2 yields 1.25, close to a value of one detectable (free) amine per tethered four-arm polymer molecule. These results show that *three* of the end-functional groups of the four-arm PEO-NH$_2$ had reacted with the surface, leaving one free. (Theoretical treatments of tethered multiarm polymers have predicted that it would be energetically unfavorable for more than one arm to be attached to the underlying surface;[13,14] however, the energy benefit of the chemical reaction of end-functional groups with active sites on the surface was not included in these models.)

The attachment of three of the four arms to the surface can be regarded as an explanation of the dramatically higher tethering density achieved by the four-arm polymer, if one assumes that it leads to reduced lateral dimensions in the tethered state. Reduced lateral dimensions for the four-arm polymers would allow them to reach higher surface attachment densities at all times in the tethering process. This notion is particularly clarified by the values for surface attachment density at the end of the first regime (Σ_{mush} in Table 1). Here, where the substrate has just become fully covered with a layer of nonoverlapping tethered polymer molecules, only reduced lateral dimensions would permit a 4.5-fold greater value of Σ_{mush} for the four-arm polymer over the linear polymer.

Conclusions

The tethering behavior of linear and four-arm poly(ethylene oxide) was evaluated. The linear polymer possessed one amine-end-functional group, while the four-arm polymer possessed four such end-functional groups. Both linear and four-arm polymers exhibited three-regime kinetics when tethered from dilute solution, but the four-arm polymer exhibited 4−5 times greater surface attachment density than the linear polymer at all times in the process. Quantitative analysis for primary amine revealed that three of the four end-functional groups in the four-arm polymer had undergone chemical reaction with the surface of the substrate. This apparently produced a change in configuration of the tethered polymer molecules in the form of a reduced lateral dimension, which contributed to the enhanced surface attachment density.

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