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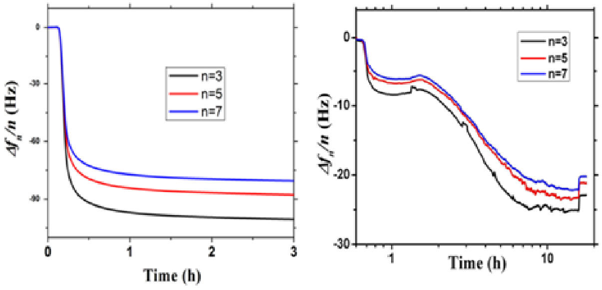

Display of three-regime kinetics requires sufficiently low temperature and concentration: too high (left) vs low enough (right).

Evidence that three-regime kinetics is inherent to formation of a polymer brush by grafting-to approach

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Abstract

Results are presented supporting the hypothesis that a three-regime kinetics profile, regardless of chemical structure of the polymer chains, molecular weight, type, of solvent and identity of the grafting surface, is inherent to polymer brushes formed by the grafting-to approach. However, the manifestation of the three-regime kinetics profile depends on grafting conditions, e.g., grafting temperature and concentration of free polymer in solution. Too high a temperature or solution concentration can lead to compression of the three distinct regimes on the time axis into what appears to be single-step brush formation, whereas low enough temperature and concentration leads to manifestation of all three regimes of kinetics. Also found was that, even when three regimes of kinetics were in evidence, grafting to a gold surface is much faster than grafting to a derivatized silica surface. Finally, the kinetics of the transition from mushroom to brush, denoted as the third regime, was found by fitting to a classical mathematical model of autocatalysis model to be consistent with an autocatalytic process.

1 Introduction

This paper focuses on the kinetics of formation of polymer brushes by means of the grafting-to approach. A polymer brush is a layer of polymer chains, all the same length, attached by one end to a surface. The surface attachment density of the chains is sufficiently high so that they are stretched vertically away from the grafting surface and contracted laterally to avoid mutual overlap.[1] Polymer brushes are typically formed in one of two ways: the grafting-from approach and the grafting-to approach. In the grafting-from approach, the chains are polymerized *in situ* from initiation sites previously installed on the solid surface. In the grafting-to approach, pre-synthesized polymer chains are attached to a solid surface by means of a strong interaction between complementary active sites on the solid surface and on the terminus of each chain. While the advantage of the grafting-from approach is that it can often lead to high grafting densities, the advantage of the grafting-to approach is that it permits the use of previously characterized polymer chains of known degree of polymerization and narrow molecular weight distribution, from which a well defined brush can be constructed. Excellent reviews are available that detail the grafting-to method specifically,[2] or provide an overview of the theory and preparation of polymer brushes,[3] or describe the increasingly important mixed brushes, which are brushes composed of two or more chemically different polymer chains.[4]

We have been studying polymer brushes for some time, and, in previous publications,[5-10] we reported the observation of three-regime kinetics for grafting of amine-functional-ended polymer chains to a single type of surface, epoxide-derivatized amorphous silica. We observed this characteristic three-regime profile for several different types of polymers as well as for different polymer architectures, molecular weights, and types of solvent. The independence of the grafting process from these system variables suggested that a three-stage process may be an inherent characteristic of the grafting-to process. The goal of work described in the present paper was to test the hypothesis that the three-regime kinetics profile is inherent to the grafting-to approach. The practical importance of the three-regime profile is that it provides a convenient window in the grafting process during which polymer solutions can be switched from one to the other for the construction of complex brushes composed of multiple types of polymers (chemistries, architectures, molecular weights) in the desired proportions. The ability to construct such brushes is crucial to the preparation of multi-functional and stimulus-responsive brushes.

A typical profile is shown in Figure 1, where the vertical dotted lines, chosen by eye, delineate the three distinct regimes. These regimes are (1) rapid initial grafting to a bare surface, (2) a latent period characterized by nearly negligible grafting, and (3) resumption of grafting until the process reaches a spontaneous conclusion at a much higher surface attachment density than achieved in the first regime.

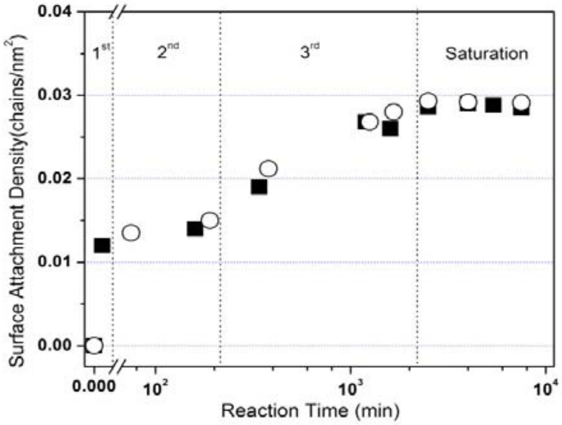

Fig. 1 Plot of surface attachment density versus time for the grafting of amine-ended, monodisperse polystyrene, M_n = 15,000; M_w/M_n <1.04, to epoxide-derivatized silica. Grafting was conducted in toluene at 25°C, concentration of 0.17 mM. Filled squares and open circles represent data taken from simultaneous, twin reactions. Abscissa shows 0-60 min in linear time before the axis break and log time thereafter. [Adapted with permission from Ref. 6, L.S. Penn, H. Huang, M. Sindkhedkar, S.E. Rankin, K. Chittenden, R.P. Quirk, R.T. Mathers, and Y. Lee, *Macromolecules*, 35, 7054-7066 (2002).

Before describing the experiments, we present a strictly physics-based explanation of the existence of a three-regime profile for the grafting-to process. The advantage of a physics-based explanation is that it is not system dependent, i.e., is not specific to a particular type of polymer or to a particular type of surface.

The first regime can be represented by a process of random sequential adsorption (RSA), or random sequential deposition, in which uniform objects adsorb randomly to, or are deposited randomly on, a bare surface until none of the remaining spaces is large enough to accommodate another object of the same size.[11-13] This point, at which 55% of the underlying surface is covered by the uniform objects and 45% of the surface remains uncovered, is called the jamming limit in the RSA literature. In the grafting-to process, solvated polymer chains are the uniform objects, and they are deposited from solution and grafted w*ithout distortion from the spherical conformations* they would have as free chains in solution.[1, 14-16] The first regime ends when the jamming limit is reached, i.e., the point at which the surface is covered with a layer of solvated, nonoverlapping, grafted polymer chains, each in the spherical conformation. These nondistorted, grafted chains form what is termed a "mushroom" layer. The surface attachment density of chains in the mushroom layer is inversely related to the radius of gyration of the monodisperse grafted chains in solution. Because the chains forming the mushroom layer are not distorted from the spherical conformations they would have as free chains in solution, they experience loss only of *translational* entropy and essentially no loss of segmental rotational or vibrational entropy upon being grafted.

The second regime, a latent period during which very little grafting occurs, is the logical consequence of an energy barrier to further grafting presented by the completion of the mushroom layer.[15,16] The barrier originates in the same excluded volume effects that cause polymer chains in solution to avoid mutual overlap. Free chains diffusing through solution and encountering the mushroom layer simply diffuse away without penetrating it.

The third regime, in which grafting resumes and proceeds to a spontaneous conclusion (saturation), is the most difficult to explain. In fact, once the third regime gets started, the incremental resistance to grafting appears to diminish. In an earlier publication, we called this diminishing resistance "layer assisted" grafting.[5] By the end of the third regime, the mushroom layer has been transformed into a brush, i.e., a layer of densely grafted chains stretched normal to the surface. The very existence of the third regime indicates that the barrier presented by the mushroom layer can be overcome eventually. It is reasonable to assume that the natural thermal fluctuations occurring during the latent period would provide, at some point, transient openings here and there in the mushroom layer -- openings large enough to accommodate a portion of the length of a free chain. Once a portion of a free chain has penetrated the mushroom layer, the remainder of the chain can penetrate more easily, because the size of the nondistorted portion of the chain outside the layer is reduced, diminishing the loss of conformational entropy upon further penetration. Upon completely penetrating the mushroom layer and becoming grafted to the underlying surface, this chain and its immediate neighbors create a small cluster of overcrowded chains that must extend vertically away from the surface and contract laterally to avoid mutual overlap. Concerted lateral contraction may result in a slightly reduced polymer segment concentration at the perimeter of the small cluster, where additional free chains can more readily penetrate to become grafted. As chains add to the cluster at the periphery, the perimeter of reduced segment concentration would move outward and become longer, providing *even greater* opportunity for continued grafting, reminiscent of an autocatalytic phenomenon. From the overall viewpoint, clusters would be initiated at random locations on the surface, and would grow laterally until they impinged on each other to create a brush over the whole solid surface.

The above explanation for the transition from mushroom to brush clearly describes a spatially nonuniform process for the third regime. The predicted nonuniformity was demonstrated experimentally by atomic force microscopy images of the surface taken at frequent intervals in the third regime.[10] (Spatial nonuniformity during brush construction also has been noted for other systems.[17]) A typical image is shown in Figure 2, in which clusters of vertically stretched grafted chains are seen as peaks rising above a surface covered with chains comprising the previously formed mushroom layer. This image of one of many similar images of the third regime, all of which show the extremely heterogeneous topography. Images of the completed mushroom layer in the second (latent) regime as well as of the completed brush (saturation) show much smoother surfaces by comparison with that in Figure 2.

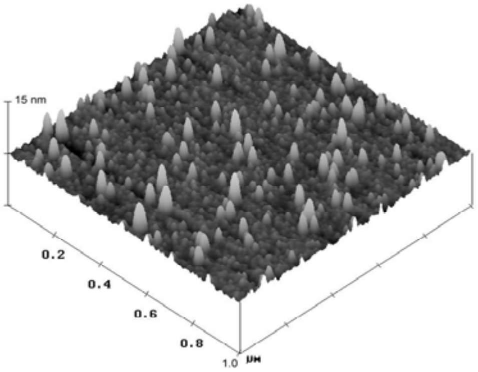

Fig. 2 Atomic force microscope image of surface of grafted layer (polystyrene chains) interrupted during transition from mushroom to brush. The peaks in the image correspond to areas of higher surface attachment density, i.e., clusters of stretched, grafted chains. (Image obtained as described in Ref. 10).

In concert with our explanation above, especially those aspects that focus on time and thermal fluctuations, is the supposition that higher temperatures and solution concentrations could shorten the latent period and speed up the transition to brush. In the extreme, the three regimes would be compressed into a single regime with respect to time. In our previous studies of grafting to derivatized silica, we were not able to test this notion, because the solution depletion method that we used to monitor grafting kinetics severely limited the allowable variation of temperature and concentration. Had we been able to increase the temperature sufficiently, we would have expected the observed three regimes to collapse into one. However, another system investigated in our lab, thiol-ended polystyrene grafted to a gold surface *did show only a single regime*.[18] To determine if this single-regime behavior was indeed a compressed three-regime behavior, we explored lower temperatures and lower solution concentrations as grafting conditions.

Our hypothesis was that three-regime kinetics is inherent to the grafting-to process, and that the three regimes are manifest under conditions of sufficiently low temperature and/or solution concentration. Stated differently, we posit that an apparently single-regime, grafting-to process can be expanded to reveal three regimes by the appropriate reduction of temperature and/or solution concentration. In addition to testing this hypothesis, we sought support for our description of the transition from mushroom to brush as a “layer-assisted” process by applying a mathematical model of autocatalysis to the data. In contrast to our previous studies, in which grafting kinetics was monitored indirectly by means of solution depletion analysis, grafting kinetics in the present study was followed with the quartz crystal microbalance (QCM). This technique provided continuous, direct, and real-time gravimetric analysis of the addition of mass to the grafting surface.

2 Experimental

The polymer samples used were monodisperse, thiol-ended polystyrene of M_n = 5,300 g/mol ($M_w/M_n \leq 1.10$) and M_n = 50,000 g/mol ($M_w/M_n \leq 1.06$) purchased from Polymer Source, Inc. (Dorval, Quebec). HPLC grade (>99.9%) toluene used as solvent for grafting was purchased from Sigma Aldrich. The concentration of each solution of free chains was rendered effectively constant during the grafting process by the use of a large reservoir of solution.

An E4 QCM instrument (Q-Sense Inc., Gothenburg, Sweden) was used, in which the sensing element was an AT-cut piezoelectric quartz crystal disc (14 mm in diameter and 0.3 mm thick) coated on the top side with a 100-nm-thick layer of gold. On the other side of the disc was a deposited electrode that made the crystal part of a circuit. These piezoelectric crystals vibrate at a resonant frequency of 4.95 MHz ± 50 kHz in the absence of mass deposited from the surroundings, and the vibrational frequency becomes lower when mass is deposited on the top surface. In the absence of significant viscous character, the mass of the deposited layer is proportional to the reduction in frequency and can be computed from the Sauerbrey equation.[19] In a typical experimental run, the crystal is situated in a flow cell, and the pure solvent or solution of interest is drawn from an argon-blanketed reservoir through the cell by a peristaltic pump at a rate of 0.088 mL/min. The polymer solutions used were all in the dilute range. Data from three vibrational modes, n = 3, 5, and 7, were collected. These data were obtained as the change in vibrational frequency, $\Delta f_n / n$, of the piezoelectric sensor crystal of the QCM versus time. The flow cells were temperature-controlled to a precision of ± 0.02 ^{o}C; the lowest temperature available was 10 ^{o}C.

3 Results and Discussion

Assuming that the manifestation of three-regime kinetics is condition-dependent, we systematically changed conditions for the grafting of thiol-ended polystyrene chains to gold, finding ultimately that the single regime observed at room temperature could be resolved into three regimes at reduced temperatures and concentrations. The results are summarized in Figures 3 and 4, which show data obtained with the quartz crystal microbalance for the grafting of thiol-ended polystyrene chains (M_n = 50,000 g/mol) to gold. Figure 3 shows a profile for grafting conducted at room temperature from a solution of ~ 1 mM concentration. There is a single regime, characterized by such rapid grafting that saturation is reached in approximately one hour. It appears that, for this materials system, the grafting temperature is high enough to help the free chains surmount the energy barrier presented by the mushroom layer, and the concentration is high enough to provide an ample supply of free chains to do this. The result is compression of the three distinct regimes on the time axis into what appears to be single-step brush formation. When both temperature and concentration were lowered substantially, three regimes of kinetics appeared, as shown in Figure 4.

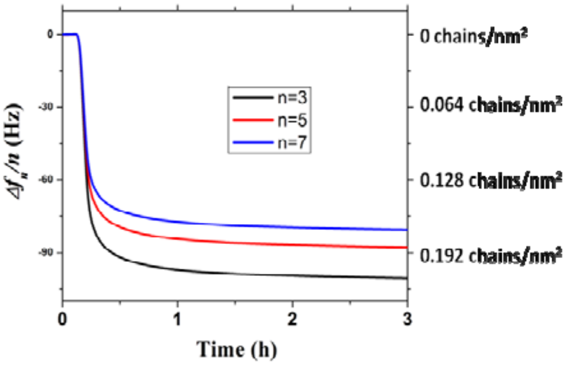

Fig. 3 Plot of $\Delta f_n/n$ (vibrational mode numbers $n = 3, 5, 7$) vs. time for exposure of gold-coated crystal to a solution of thiol-end-functionalized polystyrene (HS-PS, M_n = 50,000 g/mol), ~1.0 mM in toluene at room temperature. Different regimes of kinetics are not in evidence at room temperature.

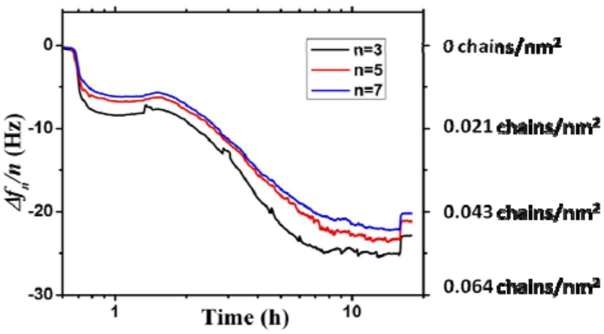

Fig. 4. Plot of $\Delta f_n/n$ (vibrational mode numbers $n = 3, 5, 7$) vs. time for exposure of gold-coated crystal to a solution of thiol-end-functionalized polystyrene (HS-PS, M_n = 50,000 g/mol), 0.0005 mM in toluene at 10 ^{o}C. Three regimes of kinetics have emerged. The small step change in $\Delta f_n/n$ at the extreme right side of the plot is caused by the switch from polymer solution to pure solvent.

While it is fully expected that decreasing the temperature of a process would slow it down, it may be less obvious that decreasing the concentration would slow the process. Proof of the role of concentration in making the three regimes of kinetics manifest is shown in Figures 5-7. The figures show grafting experiments in which the temperature is held constant at 10^{o}C while the concentration is progressively reduced. At the highest concentration (Fig. 5), even a lowered temperature does not expand the process into three regimes. However, when the concentration is lowered (Figs. 6 and 7), three regimes appear. At lower concentrations, fewer free chains would approach the surface per unit time, which would stretch the process out with respect to time.

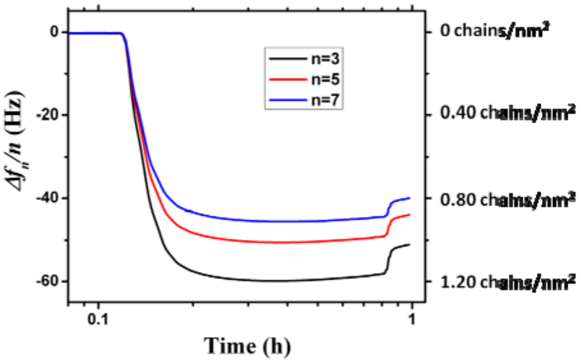

Fig. 5. Grafting of 0.3 mM PS-SH, M_n = 5,300 g/mol, at 10 °C.

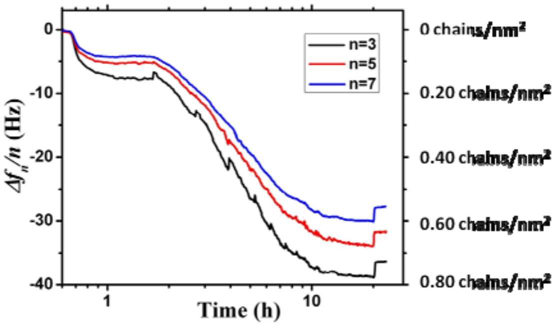

Fig. 6 Grafting of 0.01 mM PS-SH, M_n = 5,300 g/mol, at 10 °C.

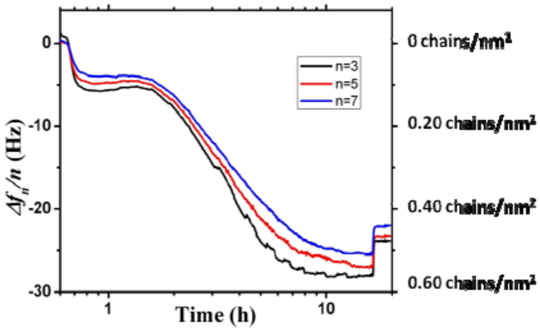

Fig. 7 Grafting of 0.005 mM PS-SH, M_n = 5,300 g/mol, at 10° C.

The observation of three-regime kinetics for grafting to two vastly different surfaces, gold and epoxide-derivatized silica, plus the previously determined independence of the process from polymer chemical structure, polymer architecture, molecular weight, and solvent, establishes that the three-regime profile of kinetics is inherent to the grafting-to process.

The opportunity to make brushes composed of different types of polymer is offered by the second regime (latent period) during which polymer solutions can be switched. Thus, experimenters making complex, tailored brushes need to be aware of the duration of the second regime, in order to know how much time they have to interrupt it. The duration of the second regime is influenced by the nature of the grafting surface. Of the two grafting surfaces investigated by us, the second regime for grafting to gold was much shorter than the second regime for grafting to derivatized silica: ~ 420 min versus ~ 2000 min, respectively. From a physical point of view, one would expect the thermal fluctuations providing entry of a free chain into the mushroom layer would be the same for all mushroom layers. Therefore, the difference in the length of the latent period for these two grafting surfaces must originate in the nature of the grafting surface itself. It is possible that the greater density of active sites on the gold surface than on the epoxide-derivatized silica surface is important. The former has ~5 active sites/nm^2 (each site being a trio of gold atoms), while the latter has ~1.5 epoxide groups/nm^2.[20] Thus, to a free chain penetrating the mushroom layer, the gold surface presents more chances for grafting than does the epoxide-derivatized silica surface. It is also possible that the coordination reaction between the terminal thiol group on the polymer chain and the gold surface has lower steric requirements than does the chemical reaction between the terminal amine group on the polymer chain and the epoxide group on the surface, resulting in an additional advantage for grafting to gold.

Regardless of the length of the second regime, once the third regime starts, the opportunity for controlled manipulation of the chemical composition of the brush ends. If the third regime is indeed autocatalytic, it would be difficult to interrupt this part of the process at a precise surface attachment density to switch polymer solutions. We sought support for our description in the introduction of the mushroom-to-brush transition (Regime 3) as autocatalytic by fitting the data for Regime 3 to a classical model of autocatalysis. In such a model, we can let A represent the free chains in solution that will become grafted during Regime 3, and we can let B represent grafted chains. Thus A's will convert to B's during the grafting process. The time-dependence of the concentration of *B* (grafted chains) is given by,[21]

$$B(t) = \frac{A_0 + B_0}{1 + \dfrac{A_0}{B_0} e^{-k(A_0+B_0)t}},$$

where subscript zero indicates value at t = 0, i.e., at the start of the transition from mushroom to brush. We have fitted the data from Figure 1 to this functional form, allowing A_0, B_0 and the rate constant, *k*, to be fitting parameters. The analysis gives A_0 = 0.019 chains/nm^2 as the number of chains per available surface that start as *free* chains at the beginning of the mushroom-to-brush transition and become grafted during the transition. The analysis gives B_0 = 0.0091 chains/nm^2, which closely matches the experimental value (0.011 chains/nm^2) for surface attachment density of grafted chains at the beginning of the mushroom-to-brush transition. At $t = \infty$ the value for B is $B_\infty = 0.028$ chains/nm^2, which matches the experimental value for surface attachment density at the end of the mushroom-to-brush transition, i.e., when saturation is reached. By the law of conservation of matter in a chemical process, the sum of A_0 and B_0 must equal B_∞, and it does. The value of k obtained from the fit was 0.15 nm^2/chain·s. These parameter values are quite robust, changing by less than 15% with variation of the time window considered. Figure 8 compares, on a log time axis, the experimental data (black diamonds) to the dotted red line that represents the classical mathematical model of an autocatalytic process. The good fit of the data to the model underscores that the third regime exhibits autocatalytic behavior, as purported. The data points do not include the first regime, since the *formation* of the mushroom layer is a distinctly different process from the transition from mushroom to brush. Rather, the data include the third regime, the latent period that precedes it, and saturation that succeeds it. The data from Figures 4, 6, and 7, for grafting to gold, also fit this functional form, and exhibit compliance with the law of conservation of matter. However, it should be noted that values obtained for the fitting parameters, including the rate constant, do not provide general design guidance, because they pertain only to one part of the grafting process, i.e., the transition from mushroom to brush (Regime 3), and are specific to polymer molecular weight and grafting temperature.

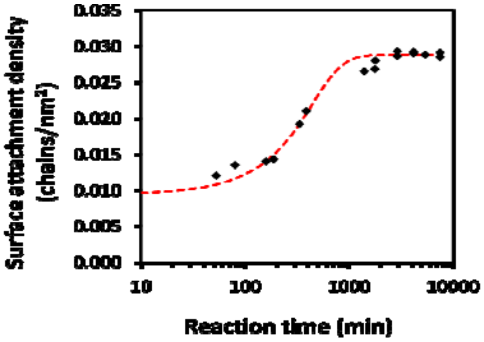

Fig. 8 Data points and solid line showing good fit for surface attachment density versus log time for transition from mushroom to brush. Black dots represent data from Fig. 1 (which states grafting conditions) and red dashed line represents model.

Finally, as noted before by us and others, final grafting density depends on solution concentration.[22,23] Figures 9 and 10 show semi-log plots of surface attachment density at saturation versus solution concentration, all at 10°C. The red lines in the figures are the best fit through the data. Thus, although solution concentration of free chains has no influence on the surface attachment density of the mushroom layer (which is determined entirely by radius of gyration of the nondeformed chains), concentration can influence grafting density subsequent to formation of the mushroom layer and therefore can serve as another control over the final characteristics of the brush.

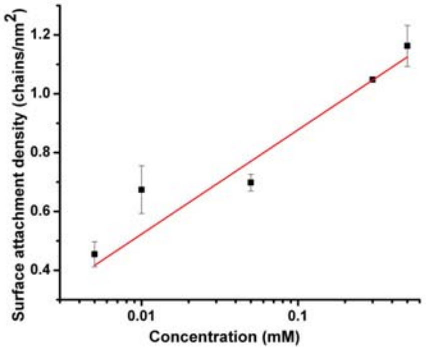

Fig. 9 Surface attachment density at saturation vs solution concentration for PS-SH chains of M_n = 5,300 g/mol. Data obtained at 10 °C.

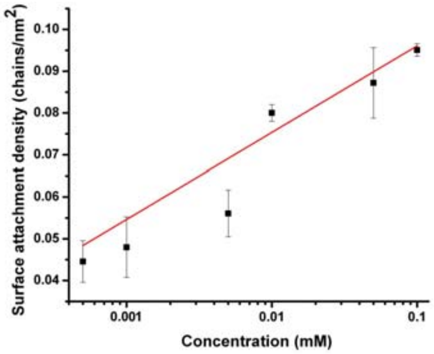

Fig. 10 Surface attachment density at saturation vs solution concentration for PS-SH chains of M_n = 50,000 g/mol. Data obtained at 10 °C.

4 Conclusion

The work reported in the present paper, taken together with previously reported work, shows that three-regime kinetics is inherent to polymer brush formation by means of the grafting-to approach, regardless of the chemical structure, polymer architecture, molecular weight of the grafting chains, and solvent used in the grafting process, and *identity of the grafting surface*. However, the accessibility of the three distinct regimes of kinetics to experimental observation depends on conditions, e.g., grafting temperature and concentration of free polymer in solution. For a given materials system, sufficiently high temperatures (and concentrations) help the free chains surmount the energy barrier presented by the mushroom layer, leading to compression of the three distinct regimes on the time axis into what appears to be single-step brush formation. Sufficiently low temperatures (and concentrations) lead to the manifestation of three distinct regimes of kinetics. Conditions leading to three regimes are desirable when complex, multi-component brushes need to be prepared. Finally, the transition from mushroom to brush was found to be consistent with an autocatalytic process, justifying use of the term "layer-assisted" grafting to describe this transition.

5 Acknowledgements

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