Looped Polymer Brushes Formed by Self-Assembly of Poly(2-vinylpyridine)−Polystyrene−Poly(2-vinylpyridine) Triblock Copolymers at the Solid−Fluid Interface. Kinetics of Preferential Adsorption

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ABSTRACT: The kinetics of assembly of a series of poly(2-vinylpyridine)−polystyrene−poly(2-vinylpyridine) (PVP-*b*-PS-*b*-PVP) triblock copolymers from the selective solvent toluene onto a silicon surface has been studied using phase-modulated ellipsometry. The adsorbed amount and thickness have been determined independently as functions of time. Even though the adsorbed amount as a function of time follows the traditional two-step process that is typical of the self-assembly of diblock copolymers—there is an initial fast adsorption followed by a slow buildup of the layer (brush regime)—the thickness shows an "overshoot" that corresponds to the brush regime. We attribute this phenomenon, not observed in the self-assembly of amphiphilic diblock copolymers, to having both ends of the chain tethered. The final ellipsometric thicknesses of the brush made from the triblocks are less than that expected for a single-end tethered brush made from a diblock copolymer with a buoy block of similar molecular weight. This result supports the conclusion that PVP-*b*-PS-*b*-PVP triblock copolymers adsorb mainly in a looplike conformation.

Introduction

Modifying surfaces is important for a variety of existing and emerging technologies like colloid stabilization,[1] compatibilization of polymer blends,[2] and the creation of biocompatible materials.[3] One well-known method that has been applied to create interfacial layers for such modifications is the self-assembly of amphiphilic block copolymers from dilute solution using a selective solvent. In such a solvent, one block is well solvated and the other is not, creating a situation whereby the insoluble block is driven to the surface, tethering the well-solvated block at the solid−fluid interface by its end. At sufficiently high surface density the tethered chains stretch into the solvent phase, creating a so-called "polymer brush" structure.[4] Because of this tethering mechanism and layer structure, the insoluble and well-solvated blocks are typically referred to as the "anchor" (A) and "buoy" (B) blocks, respectively.

The assembly, structure, and properties of polymer brushes made by preferentially assembled A−B diblock copolymers have been the focus of much research, both theoretical and experimental, for the past two decades and are very well understood.[5−9] However, much less attention has been devoted to studies of polymer brushes created by more complex, multiblock copolymer architectures such as stars, combs, and triblocks copolymers. Using these copolymer architectures to create brushes may allow layer height, conformation of chains, degree of stretching, and tethering density to be manipulated in ways not possible with simple linear polymers. Consequently, these differences allow surface properties, such as adhesion, friction, or resistance to deposition of foreign molecules, to be enhanced. For example, Sofia et al. showed[3] that looped layers formed by preferential assembly of polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) stars were more effective in preventing the nonspecific adsorption of proteins than surfaces modified by singly tethered chains formed by the corresponding PS-*b*-PEO diblock copolymer. Also, looped polymer chains self-organized at polymer−polymer interfaces can be used as the basis for a "molecular velcro", which can strengthen the interface in a polymer blend system by facilitating and promoting entanglements.[10] These examples highlight the utility of interfacial modification using complex macromolecular amphiphilic block copolymers and underscore the importance of understanding how surface density, polymer architecture, macromolecular composition, and size affect the adsorption, structure, and properties of the resulting brushes.

In this work we report on the kinetics of preferential adsorption of polymer brushes created using poly(2-vinylpyridine)−polystyrene−poly(2-vinylpyridine) (PVP-*b*-PS-*b*-PVP) triblock copolymers assembled from the selective solvent toluene onto a silicon surface. With this type of architecture and composition it is expected that these block copolymers will attach by both ends to the surface and will form, at sufficiently high surface densities, looped polymer brushes.

The kinetics of adsorption of A−B−A triblock copolymers onto surfaces has been studied by others;[11−16] however, there are two important differences that distinguish this contribution: First, previous studies of the adsorption behavior of A−B−A triblock copolymer adsorption have involved mainly PEO−PS−PEO copolymers assembled from the nonselective, good solvent toluene onto silicon substrates. Because PEO has a weak affinity for silicon and because the interaction between PEO chains in toluene is repulsive, highly asymmetric block copolymers with short PEO blocks are needed to create a

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Table 1. Results from the Kinetics Experiments and Analyses for the Triblocks and Diblock Copolymer Studied[a]

sample	S/V	A_d (mg/m^2)	H_{elli} (nm)	$\sigma \times 10^2$ (chains/nm^2)	$\sigma_{ol} \times 10^2$ (chains/nm^2)	A_{ol} (mg/m^2)	$\sigma^* = \sigma/\sigma_{ol}$	A_d^* (mg/m^2)	t^* (s)
T252k	10/1	3.95	31	1.89	0.24	0.6	7.83	3.58	1105
T136k	10/1	4.28	19	3.79	0.50	0.7	7.54	3.73	770
T170k	4/1	3.60	23	2.55	0.45	0.8	5.69	3.05	230
T120k	4/1	3.32	8	3.33	0.68	0.7	4.91	3.02	205
T161k	1/1	2.71		2.03	0.84	1.2	2.42	1.67	498
T125k	1/1	3.02		2.91	1.13	1.2	2.57	2.06	160
T98k	1/1	2.74		3.37	1.51	1.3	2.23	2.43	165
D272k	11/1	3.55	70	0.77	0.09	0.4	9.00	2.19	720

[a] The adsorbed amounts from the plateau region, A_d, and at overlap, A_{ol}, are extracted from the kinetics experiments, as is the final swollen layer thickness, H_{elli}. The tethering density, σ, and tethering density at overlap, σ_{ol}, are calculated on the basis of an equivalent diblock model. A_d^* and t^* are the values of the adsorbed amount and corresponding time after which the model embodied by eq 8 is valid.

brushlike structure. In the concentration range where we carry out our studies, PEO/PS systems display a complex concentration dependence, where, unlike styrene/vinylpyridine systems,[17] the adsorption is sensitive to the concentration of the incubation solution and adsorbed chains can be readily exchanged from silicon surfaces.[16] Second, the general approach to study the kinetics of adsorption has been to report the adsorbed amount as a function of time, which provides no insight into the molecular-level structure. When a technique such as nulling ellipsometry is used, an average thickness may be obtained by assuming a suitable refractive index for the evolving layer and using this information to calculate the adsorbed amount.[14,16] In this work *both* the adsorbed amount and ellipsometric thickness are determined independently as functions of time. This important difference reveals more information, especially during early stages of the assembly, of the nanoscale structural evolution of the brush, and for the first time, an overshoot in the thickness is observed for these A−B−A copolymers, providing a key insight into the mechanism of self-assembly of these macromolecular amphiphiles at the solid−fluid interface.

Experimental Section

A series of triblock copolymers of PVP-*b*-PS-*b*-PVP were prepared via anionic polymerization, which allows precise control of the molecular weights and composition. As the synthesis of these materials extends our previously published methods,[18] details of the preparation and molecular characteristics of these copolymers are provided in the Supporting Information. The copolymers studied are listed in Table 1. Throughout this paper, in the table and figures, we refer to the copolymers by their total molecular weight (in thousands), S/V content, and architecture (by using T for triblock and D for diblock). One PVP-*b*-PS diblock copolymer, also anionically synthesized, was available in our laboratory and studied for comparison purposes.

Sample Preparation. Diced silicon wafers (size 1 cm × 1.2 cm) were purchased from Silicon Quest and cleaned by immersing in a freshly made 1:3 hydrogen peroxide/sulfuric acid solution (piranha solution) for 30 min at 80 °C, then rinsing with distilled water, and finally drying with filtered N_2. Substrates were prepared immediately before each experiment.

HPLC grade toluene (Sigma-Aldrich) was filtered using PTFE 0.22 μm filters (Millipore) before use in the preparation of stock solutions and to fill the experimental fluid cell at the beginning of each phase-modulated ellipsometry experiment. No further purification of the solvent was done. Stock solutions of each triblock copolymer were prepared and allowed to equilibrate for at least 1 week prior to the experiments. The concentration of the stock solutions was 78 mg/L.

Phase-Modulated Ellipsometry. The kinetics of adsorption was followed using a variable angle Beaglehole Picometer ellipsometer, which uses a He−Ne laser light source ($\lambda = 632.8$ nm) and has an angular resolution of 0.01°. In contrast to conventional nulling ellipsometers,[14] the Picometer ellipsometer uses phase modulation[19] to achieve a higher sensitivity and lower noise in the ellipsometric signal. Instead of a rotating polarizer, a photoelastic birefringence modulator is used to modulate the beam, giving response times as short as 1 ms. The ellipsometer measures the real and imaginary components of the ellipsometric ratio, ρ, defined by

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta} = \mathrm{Re}(\rho) + i\mathrm{Im}(\rho) \tag{1}$$

where r_p and r_s are the complex overall refection coefficients of the p- and s-polarizations, respectively. The real (Re) and imaginary (Im) components of the ellipsometric signal are related to the more traditional ellipsometric angles ψ and Δ by $\mathrm{Re}(\rho) = \tan \psi \cos \Delta$ and $\mathrm{Im}(\rho) = \tan \psi \sin \Delta$, where the angles ψ and Δ correspond to the ratio of attenuation of the p- and s-polarizations and the phase change between the p- and s-polarizations, respectively.[20]

Kinetics of Preferential Adsorption Measurements. The basic protocol for the kinetics of adsorption experiments follows that described by Toomey et al.:[9] a clean silicon wafer with a well-defined SiO_2 layer (1.5 nm thick, as measured by ellipsometry) is mounted on a Teflon platform situated in the center of a home-built, cylindrical glass fluid cell. The total volume of the fluid cell is 14 mL. After aligning the fluid cell so that the laser beam impinges on the silicon wafer at its center and enters normal to the walls of the fluid cell, the cell is filled with pure filtered toluene. The incident angle is adjusted to the Brewster angle for the SiO_2−toluene interface. This is done by adjusting in tandem the arms of the ellipsometer so that the real component of the ellipsometric ratio is equal to zero. At the Brewster angle $\Delta = 90°$. After determining the Brewster angle, the real and imaginary components of the ellipsometric ratio are followed for 15 min to verify that no adventitious adsorption due to contamination within the system was occurring and to obtain the baseline for the measurements. If the signals do not change, a small volume (typically 1−5 mL) of toluene is removed from the fluid cell using a syringe and replaced with an equal volume of the previously equilibrated stock solution containing the block copolymer in order to make a final concentration inside the fluid cell of 30 mg/L. It has been shown[21] that for PVP-*b*-PS-*b*-PVP triblock copolymers the lower limit for micelle formation is 0.5 wt %. The concentration used here is 2 orders of magnitude below this limit. (We also have checked for the presence of micelles at this concentration using light scattering measurements.) During each adsorption experiment the ellipsometric signals were recorded every 5 s until a plateau in the signals is reached (at least 3000 s). After an adsorption experiment is completed, the polymer-modified silicon wafer is removed from the fluid cell, rinsed with pure toluene, and thoroughly dried with filtered dry nitrogen. The dry layer thickness is then measured using multiangle ellipsometry.

Data Analysis. The adsorbed amount and layer thickness are determined independently as functions of time following the analysis described by Toomey et al.[9] The interested reader is referred to the Supporting Information for a fuller description. In brief, when the measurements are done at the Brewster angle, two simple expressions that relate $\mathrm{Re}(\rho)$ to the zeroth moment, Γ_0, and $\mathrm{Im}(\rho)$ to the first moment, Γ_1, of the refractive index profile are obtained, which enables the adsorbed amount, A_d (mg/m^2), and ellipsometric

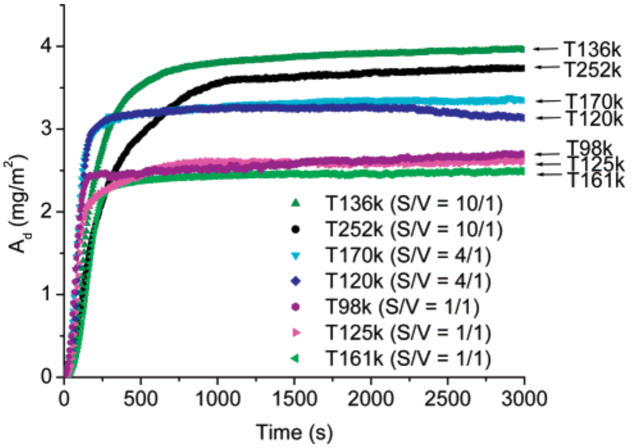

Figure 1. Adsorbed amounts for seven triblock copolymers as a function of time. A rapid assembly is observed at early times (fast initial regime) followed by a slower regime as the surface becomes crowded (brush regime) and finally a plateau region is reach. All experiments were conducted at 30 mg/L.

thickness, H_{elli}, to be determined as functions of time:

$$A_{\text{d}} = \Gamma_0\left(\frac{\text{d}n}{\text{d}c}\right)^{-1} \quad (2)$$

$$H_{\text{elli}} = 2\left(\frac{\Gamma_1}{\Gamma_0}\right) \quad (3)$$

As Toomey et al. noted,[9] the refractive index increment, dn/dc, for the PS/PVP system is almost independent of the composition of the copolymer; therefore, a constant value of 0.102 mL/g is used for all the copolymers studied. To check the validity of this assumption, the final adsorbed amounts at the end of the kinetics experiments (from the plateau region) are compared with the adsorbed amounts obtained from the dry layer thickness measurements.[22] It should be noted that the ellipsometric thickness corresponds to an average thickness, which will be equal to the overall thickness only in the case of a perfectly homogeneous layer with a boxlike density profile.[9]

Results and Discussion

The kinetics of preferential adsorption of the seven triblock copolymers onto silicon substrates is reflected by the evolution of the adsorbed amount (Figure 1) and ellipsometric thickness (Figure 2). To interpret the nanoscale assembly of these materials, we analyze and discuss first the kinetics of assembly in terms of the adsorbed amount and then in terms of the thickness evolution. Finally, a comparison of the preferential adsorption of a PVP-*b*-PS-*b*-PVP triblock copolymer and a corresponding PVP−PS diblock copolymer is offered.

Analysis of the Adsorbed Amount. Figure 1 shows that the kinetics of assembly, based on the adsorbed amount, of PVP-*b*-PS-*b*-PVP triblock copolymers follows the traditional two-step process observed for the self-assembly of A−B diblock copolymers.[9,14] A fast initial adsorption occurs at early times when there is sufficient free surface area and therefore little interaction among tethered chains. While this regime is often labeled as a “diffusion-limited” regime, at this stage we refer to this regime more generally as the fast initial regime. It is followed by a slower buildup of the layer as the surface become crowded and chains start to interact and rearrange so that more chains can be tethered to it. This second regime is referred to as the brush regime. Finally, a plateau region is reached where further densification of the layer occurs, if at all, at a very slow rate.

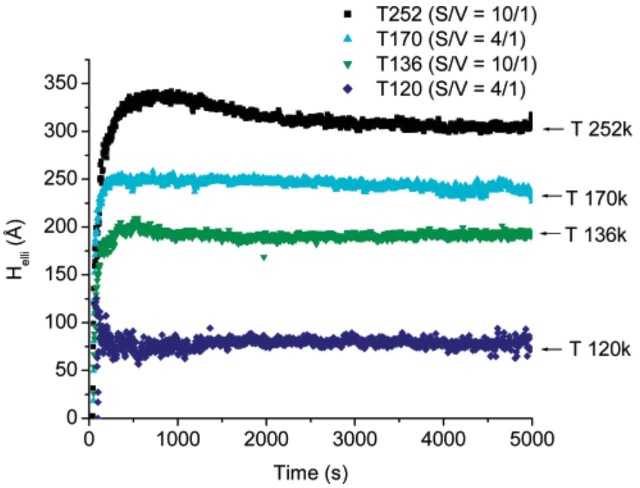

Figure 2. Ellipsometric thicknesses as a function of time for four of the triblock copolymers. An overshoot that corresponds to the transition to the brush regime is observed. This overshoot may be related to surface and molecular rearrangements as the surface becomes crowded and surface reorganization is needed in order for the triblock copolymer to assembly both ends. All experiments were conducted at 30 mg/L.

Fast Initial Regime. For the fast initial regime, assuming it is diffusion-controlled, an equation that relates the adsorbed amount as a function of time, t, has been derived:[16]

$$A_{\text{d}}(t) = 2C_0\sqrt{\frac{D_{\text{eff}}t}{\pi}} \quad (4)$$

In this expression, C_0 is the concentration inside the fluid cell and D_{eff} is an effective diffusion coefficient for the copolymer. Many authors have used eq 4 to describe the fast initial regime and calculate diffusion coefficients.[11,16,23] However, eq 4 is based on the following assumptions:[9] (a) there are no interactions between an incoming chain and previously attached chains, and (b) every chain that approaches the surface instantaneously attaches to it. These two conditions are unlikely to be true in a real system; the incoming polymer must have a conformation whereby the anchoring end units access the surface. In the case of the A−B−A triblocks, the polymer must present one or both of the PVP blocks to the surface to tether the chain. Therefore, eq 4 represents an ideal upper bound for the adsorption process in the absence of a convective driving force. To compare the ideal behavior described by eq 4 with the experimental data, a plot of log(A_{d}) vs log(t) is shown in Figure 3. It shows the ideal preferential adsorption behavior of one triblock copolymer (T120k, 4/1 S/V), calculated using eq 4 and the effective diffusion coefficient measured from dynamic light scattering ($D_{\text{eff}} = 4.5 \times 10^{-7}$ cm^2/s), and the corresponding experimental results for three representative triblock copolymers of different S/V ratios. Two observations can be made from this plot. First, the diffusion-limited behavior embodied by eq 4 gives always greater adsorbed amounts representing the upper limit for adsorption and the scaling $A_{\text{d}}(t) \sim t^{1/2}$ is not obtained—a stronger time dependence is observed. Second, the adsorbed amount where the data begin to deviate from the power law corresponds to the point where chains start to overlap, indicating the transition to the brush regime. These values of the adsorbed amount at overlap, A_{ol}, are reported in Table 1. For all of the triblocks, the power law of the initial “fast” time dependence of the adsorbed amount varies between 1.8 and 3.4. Although there is a stronger time dependence, the overall rate of adsorption is slower. This deviation from mass-transfer-limited behavior may be due to desorption (rejection) or reconfiguration of

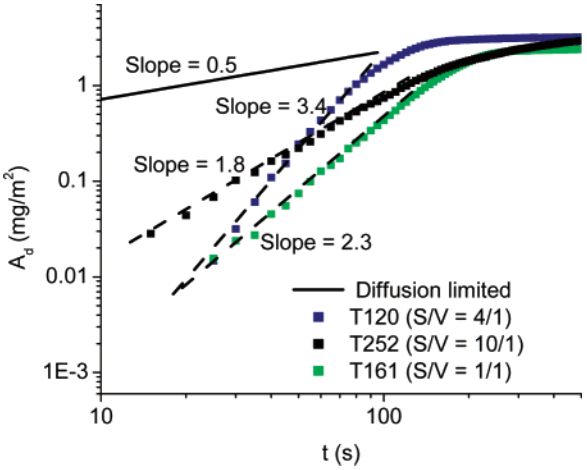

Figure 3. Adsorbed amounts as a function of time for three representative triblock copolymers. The solid line is the ideal diffusion-controlled behavior ($t^{1/2}$ time dependence) calculated using eq 4 and the effective diffusion coefficient obtained from dynamic light scattering measurements on the T120k (S/V = 4/1) triblock copolymer. This ideal diffusion-limited behavior represents and upper limit for the adsorption process. The stronger time dependence observed for the triblocks may be the result of interaction between incoming chains and already attached chains or desorption of molecules that do not arrive at the surface in a conformation amenable for tethering through the PVP blocks.

macromolecules that do not arrive at the surface in the correct conformation and/or the result of interaction between incoming chains and already attached chains. The already attached chains, even at these early stages, may block unoccupied surface area, creating a barrier for incoming chains to reach the surface; this effect is likely to be more important when there are two tethering end blocks that need to be adsorbed in order to form the looped structure.

Brush Regime. As the surface becomes crowded and chains start to interact and rearrange to accommodate more chains arriving at the surface, there is a transition to a slower regime. In the case of A−B−A triblock copolymers we have two A blocks, one at each end of the B block; therefore, the brush regime for these materials is likely to involve extensive surface or molecular rearrangements in order for an arriving chain to penetrate the already formed layer and tether by both ends to the surface. Because of this influence of architecture, this regime is better understood when compared with the corresponding brush regime for singly tethered polymers, so a more detailed discussion of this regime will be presented later.

Plateau Region. After long times in the brush regime, a plateau is reached where further densification of the layer, if any, occurs at a very slow rate. Even though much longer time experiments would be needed to obtain true equilibrium adsorbed amounts,[9] the adsorbed amounts from the plateau region can be used to verify the existence of a brush structure. (And that detailed analysis of the equilibrium structure of the looped brushes will be treated in a future paper.) A useful quantity to verify the existence of a brush structure is the reduced tethering density, σ^*, which is defined as the ratio of the tethering density divided by the theoretical tethering density at overlap: $\sigma^* = \sigma/\sigma_{\mathrm{ol}}$.[17] A value of $\sigma^* > 1$ means that the chains are overlapping, and beyond this σ^*, there are sufficient lateral interaction between chains to cause the chains to swell away from the tethering surface,[24,25] resulting in the brushlike structure. The theoretical tethering density at which the chains should start overlapping, σ_{ol}, can be calculated using eq 5:[17]

$$\sigma_{\mathrm{ol}} = \frac{1}{\pi R_{\mathrm{gB}}^{\ 2}} \tag{5}$$

In eq 5, R_{gB} is the radius of gyration of the buoy block, which for polystyrene in toluene can be calculated on the basis of the results from Higo et al., $R_{\mathrm{gPS}} = 1.86N_{\mathrm{PS}}^{0.595}$.[26] Here N_{PS} is the degree of polymerization of PS. The tethering density can be calculated from the measured adsorbed amount, A_{d}, using eq 6.[17]

$$\sigma = \frac{A_{\mathrm{d}}N_{\mathrm{a}}}{M_{\mathrm{PS}} + M_{\mathrm{PVP}}} \tag{6}$$

In eq 6, N_{a} is Avogadro's number and M_{PVP} and M_{PS} are the molecular weights of the anchor block and the buoy block, respectively. The adsorbed amount obtained from the plateau region of each of the seven triblock copolymers is listed in Table 1.

In the case of doubly bound brushes made from the end-tethering triblocks the key issue in using eqs 5 and 6 is how to choose the molecular weights. We use an "equivalent diblock" model in using these equations. This equivalent diblock model assumes that each triblock adsorbs in a looped conformation, and therefore, each tethered triblock is considered to be made of two diblock copolymers that have a PS block of one-half the molecular weight of the PS block of the triblock copolymer and a PVP block equal to one of the end blocks of the triblock. There is precedent for this model: Patel et al.[27] used this model to reduce surface forces profiles of PVP-*b*-PS-*b*-PVP triblock copolymers and showed that these scaled force profiles collapse to the master curve formed by singly tethered brushes made from PVP-*b*-PS diblock copolymers. So in applying eq 6 to our system, M_{PVP} and M_{PS} are equal to the molecular weights of one of the end blocks and one-half of the middle block of the triblock copolymer, respectively. The values of σ and σ_{ol} for the seven triblock copolymers calculated using the equivalent diblock model are presented in Table 1. On the basis of this model, it is seen that the seven triblock copolymers form a brush structure because in all cases σ^* is greater than 1. This reduced surface density decreases as the styrene-to-vinylpyridine ratio (S/V) ratio decreases. Evidence of loop formation will be provided in the next section.

As mentioned in the Experimental Section, for comparison purposes the adsorbed amounts also have been calculated from the dry layer thickness using eq 7.[22]

$$A_{\mathrm{dDRY}} = L_{\mathrm{d}}(M_{\mathrm{PVP}} + M_{\mathrm{PS}})\left(\frac{M_{\mathrm{PVP}}}{\rho_{\mathrm{PVP}}} + \frac{M_{\mathrm{PS}}}{\rho_{\mathrm{PS}}}\right)^{-1} \tag{7}$$

In this expression, L_{d} is the dry layer thickness measured with ellipsometry and ρ_{PVP}, ρ_{PS} and M_{PVP}, M_{PS} are the densities and molecular weights of the PVP and PS blocks, respectively. To enable comparison with the adsorbed amounts obtained directly from the kinetics of assembly measurements, A_{dDRY} is also calculated using the equivalent diblock model. Good agreement between the adsorbed amounts calculated from dry layer thicknesses and plateau values obtained from the kinetics experiments demonstrates the robustness of the technique. (The measured L_{d} and calculated A_{dDRY} values are presented in Table SI in the Supporting Information.)

Analysis of Ellipsometric Thickness. Figure 2, which shows the evolution of layer thickness as a function of time, provides more insights into the kinetics of preferential adsorption of the triblock copolymers. As expected, as the PS block size increases,

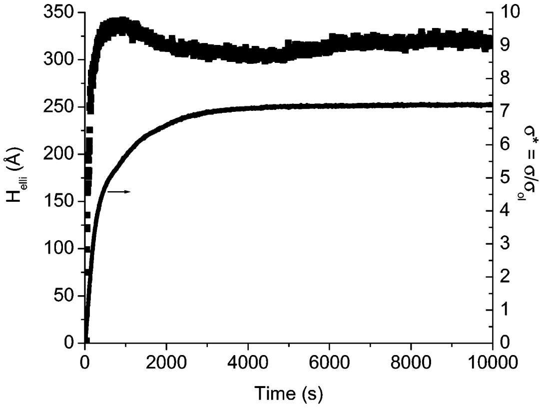

Figure 4. Ellipsometric thickness and reduced tethering density as functions of time for the highest molecular weight triblock, T252k. The plot clearly shows that the overshoot in the thickness corresponds to the transition to the brush regime, where chains start to overlap and rearrange in order to allow more chains to self-assemble onto the surface.

the thickness of the looped brush also increases. No thicknesses were detected for the 1:1 S/V copolymers. This is because the lower limit detection for the experimental technique is ∼5 nm,[9] and these are the least overlapped (and therefore the least stretched) of the triblocks. As embodied by the calculated σ^* values, all the triblocks examined form an extended conformation based on the measured plateau values of the adsorbed amounts and copolymer composition. So the fact that a thickness was not measured for the 1:1 S/V triblocks is not because they do not form a brush structure, but rather because of technique (thickness resolution) limitations.

From Figure 2 it is observed that an overshoot in thickness is present during the early stages of assembly. This overshoot is most evident and extended in the case of the T252k copolymer, which has the highest molecular weight and asymmetry ratio. Figure 4 shows a plot of the reduced tethering density, σ^*, and ellipsometric thickness as functions of time for this copolymer that clearly shows that the overshoot phenomena corresponds to the transition to the brush regime, where the chains start to rearrange on the surface in order to allow more chains to be added to the layer. We attribute this overshoot to complexities in the way the polymer approaches the surface and attaches to it, especially as the surface becomes crowded and surface reorganization and/or molecular rearrangement is needed in order for incoming triblocks to attach by both ends and form the looped brush. Figure 5 shows a plot of the thickness evolution and adsorbed amount as a function of the degree-of-overlap for the same triblock (T252k 10/1). It is seen that in the range of $\sigma^* \sim 2$ there is a pseudo-plateau where the thickness remains nearly constant while material continues to add to the adsorbed layer. Following this pseudo-plateau there is a transition region, after which the thickness scales with $\sigma^{1/3}$, which is expected for brushes in good solvent. This figure also shows that the pseudo-plateau region corresponds to the "weak overlap" regime and that for all times the adsorbed amount shows a monotonic increase with degree of overlap until the plateau region is reached. The pseudo-plateau and transition regions indicate that, in terms of the thickness evolution, there is an extended transition from the fast initial regime (where chains are not overlapping) to the brush regime. Interestingly, there are no corresponding signatures for the overshoot or pseudo-plateau in the adsorbed amount traces (Figure 1).

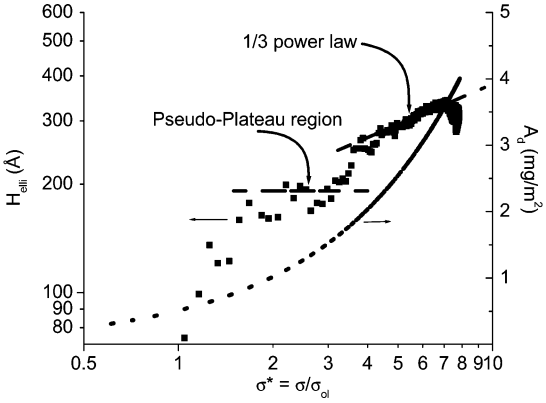

Figure 5. Ellipsometric thickness and adsorbed amount as a function of degree of overlap for the T252k 10/1 copolymer. A pseudo-plateau region where the chains are weakly overlapped and the thickness remains basically constant is observed in the ellipsometric thickness. After the pseudo-plateau and transition regions, the layer height begins to increase with a 1/3 power-law dependence on tethering density.

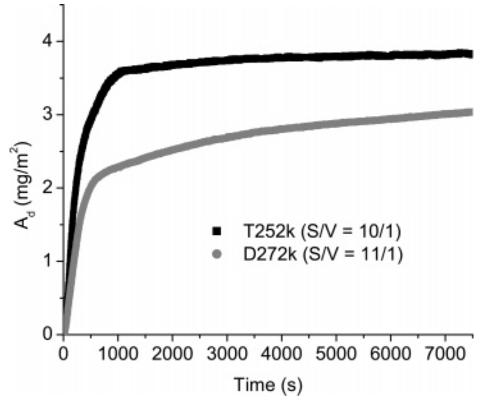

Figure 6. Comparison of the adsorbed amount as a function of time for one triblock and one diblock with similar molecular weights and S/V ratios. In the self-assembly of the triblock, the transition to the brush regime occurs at a higher adsorbed amount and longer time. Also, the buildup of the layer after the fast initial regime occurs at a slower rate in the case of the triblock. Both differences may be attributed to the triblock having two anchor blocks.

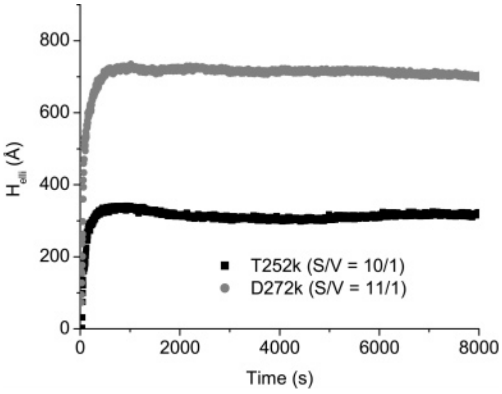

Figure 7. Comparison of the ellipsometric thickness as a function of time for one triblock and one diblock of similar molecular weights and S/V ratio. The ellipsometric thickness of the layer formed from the triblock is much less than that of the diblock (less than half), and an overshoot is observed in the case of the triblock.

Comparison between Diblock and Triblock Copolymers. It is useful to compare the kinetics of assembly of A−B−A triblock copolymers with that of A−B diblock copolymers to see the differences between these two systems. These differences are evident when examining Figures 6 and 7 in which one triblock and one diblock are compared. The triblock and diblock copolymers selected for this comparison have similar molecular weights and S/V ratio. First, Figure 6 shows that the transition from the fast initial regime to the brush regime occurs at higher

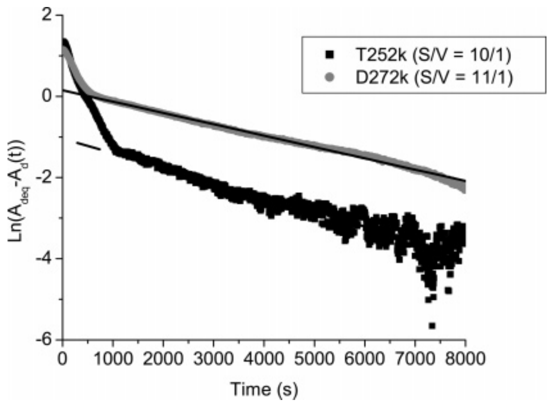

Figure 8. Comparison of the adsorption behavior in the brush regime for one triblock and one diblock copolymer. An exponential function describes the preferential assembly of both the diblock and triblock copolymers, with the triblock assembling more quickly.

adsorbed amounts and longer times in the case of the triblock. Also, the buildup of the layer after the initial fast adsorption occurs at a slower rate in the case of the diblock. These two differences can be explained if we consider that each self-assembled triblock contributes two tethering points (i.e., two equivalent diblocks) to the brush structure. For diblock copolymers, it has been shown that the assembly of the layer, once an overlapped brush is established on the surface, follows an exponential time decay dependence:[14]

$$A_d(t) = (A_{deq} - A_d^*)[1 - \exp(-k(t - t^*))] + A_d^* \quad (8)$$

In eq 8, A_{deq} is the plateau value of the adsorbed amount, A_d^* and t^* are the values of the adsorbed amount and corresponding time after which the exponential model is valid, respectively, and k is the rate constant for this regime. Values of A_d^* and t^* are reported in Table 1 for all copolymers studied. Figure 8 shows the data for the D272k diblock and T252k triblock copolymers plotted according to eq 8, from which the value of k can be calculated from the slope of the linear portion of the plot. Equation 8 adequately describes the self-assembly in the brush regime of the brushes made from diblocks and triblocks. The rate constant, k, for the triblock is greater than that of the diblock (3.6×10^{-4} and 2.8×10^{-4} s^{-1}, respectively), reflecting the observation that the triblock assembles more quickly. Even though eq 8 describes the brush regime for both copolymers, the assembly in this regime is more complex in the case of the triblock copolymer. This contention is supported by the two distinct differences in the thickness evolution as a function of time behavior seen in Figure 7: First, and as noted previously, the triblocks display an overshoot in the first 2000 s of assembly, which as mentioned before can be a result of a slow surface reorganization as the assembly proceeds. Second, the final thickness of the layer made from the triblock is approximately one-half of that of the diblock. This suggests that the triblocks assemble mostly in a looplike conformation. Even though these two copolymers have slightly different molecular weights (T252k and D272k) and S/V ratios, the significant difference in layer height observed cannot be explained as a sole consequence of this molecular weight difference.

Conclusions

By independently measuring the adsorbed amount and ellipsometric thickness, additional details of the molecular-level structural evolution during preferential adsorption of triblock copolymers are revealed, providing insight into the role of architecture on the self-assembly of the looped polymer brushes. The complexity of tethering both ends of the chains, as compared to the singly tethered counterpart, manifests primarily in an overshoot in the measured ellipsometric thickness, which occurs in the transition to the brush regime. The kinetics of adsorption as expressed by the adsorbed amount shows no corresponding overshoot. That a preferentially adsorbed triblock forms a layer that is approximately one-half the thickness of the corresponding singly tethered layer made from preferentially adsorbed diblock suggests that the PVP-*b*-PS-*b*-PVP copolymers adsorb mainly in a looped configuration (tethered through both PVP end blocks) after extensive surface and molecular rearrangements, which are likely permitted by the slow nature of the adsorption. These experiments show that polymer architecture impacts the adsorption behavior of preferentially adsorbed polymer amphiphiles; the equilibrium properties of the looped brushes and a more extensive comparison with their singly tethered counterparts will be presented in a future publication.

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Supporting Information Available: Detailed description of synthesis and characterization of triblock copolymers and expanded description of data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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