Competitive Adsorption of Binary Mixtures of Diblock Copolymers onto Solid Substrates

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ABSTRACT: We have studied the competitive adsorption of binary mixtures of diblock copolymers, differing in molecular sizes of the two blocks, from solution in toluene onto mica and oxidized silicon substrates. We have considered three systems in which the two molecules are both poly(2-vinylpyridine) (PVP)−polystyrene (PS) diblock copolymers and one case where one of the molecules is a PVP−PS diblock copolymer and the other molecule is a poly(2-vinylpyridine)−polyisoprene (PI) diblock copolymer. Toluene is a selective solvent for the block copolymers, poor for PVP and good for both PS and PI. We find that in the case where there are small differences in the PVP block sizes and large differences in the PS block sizes, the adsorption favors the molecule with the smaller PS block size. In the case where there is a small difference in the PS block sizes and a large difference in the PVP block sizes, the adsorption favors the molecule with the larger PVP block. In the case where there is a difference in the chemical species, the contour length of the nonadsorbing block is the appropriate measure of size for comparing molecules to determine which molecule will be favored.

Introduction

Polymers tethered onto solid walls are used for many applications such as wetting,[1] adhesion,[2] chromatography,[3] colloid stabilization,[4] and biocompatibility.[5] The polymers may be grafted to the solid wall via chemical end groups or by using diblock copolymers in a selective solvent where one of the blocks is engineered to be insoluble and/or attracted to the wall. The other block is nonadsorbing and swells into the good solvent surrounding medium while remaining tethered to the surface by the adsorbing block. The scientific questions of interest that are posed in such situations concern the nature of the configurations adopted by the macromolecules in this environment and how changes in these configurations affect the nature of the interactions of the polymer layers with the environment. In particular, we have been interested in measuring the forces of interaction between layers of the grafted polymers and elucidating their relationship to the molecular and adsorption characteristics of the adsorbed layer. We are also interested in obtaining the relationship between the molecular characteristics such as the sizes of the diblock copolymers and adsorption characteristics such as the composition and adsorbed amounts.

Previous work in our group by Hadziioannou et al.[6] and Watanabe et al.[7] has provided information via surface force measurement[8] on the interaction between adsorbed layers of monodisperse polymer layers of the diblock copolymer poly(2-vinylpyridine) (PVP)−polystyrene (PS) adsorbed onto mica from solution in toluene. Toluene is a good solvent for PS and a bad solvent for PVP. Schematically, the adsorbed layer is as shown in Figure 1. The PVP block is attracted to the wall and the PS block is attached to the solid surface via the PVP block. Hadziioannou et al.[6] and Watanabe et al.[7] found that for these polymer layers, the range and profile of the forces of interaction depend upon the molecular weight of the two blocks and on the surface density of polymer chains as well as the quality of the solvent. Using a model developed by Patel et al.,[9] it has been shown[7] that the force−distance profiles obtained can be scaled into a dimensionless energy vs dimensionless distance form, accounting for the effect of the differences in molecular and adsorption characteristics of the adsorbed layers. The resultant data collapse onto a single curve at all but the weakest compressions, indicating the universal nature of these interactions.

Recently, we have shown how force profiles between adsorbed block copolymer layers can be tailored for specific purposes by mixing lengths of polymers.[10] We created a bimodal distribution of polymer chains on the solid surface by adsorbing from solutions containing either a binary distribution of diblock copolymers or a triblock copolymer in which a middle block is adsorbing and the two end blocks, differing in chain length, are nonadsorbing. We found that the bimodal layer force profiles[10] did not conform to the universal curve profile of the monodisperse diblock copolymers,[6,7] except in the high compression, osmotic pressure limit, where the undeformed configurations of the tethered chains are no longer relevant. This deviation was attributed to the presence of two characteristic length scales in the bimodal layer, instead of the single characteristic length determined by chain length for the monodisperse case.

An important quantity in the above interactions is the dimensionless surface density of polymer chains ($\sigma = a^2/d^2$, where a as defined in eq 3 is the monomer length and d is the average distance between polymer chains on the surface). For adsorption of monodisperse diblock copolymers onto solid substrates, the adsorbed amount depends on the sizes of the two blocks in the molecule. Parsonage et al.[11] have measured the amount for adsorption from solution in toluene of a series of PVP−PS diblock copolymers on a mica surface. They found that the adsorbed amount plotted in terms of a normalized dimensionless surface density of chains (Σ), representing the degree of crowding or overlap of the adsorbed polymer chains, is a unique function of a dimensionless asymmetry parameter (β) which is the ratio of the projected areas of the two blocks of the molecule. For the PS block, in good solvent conditions, the projected area scales as $(N_{PS}^{3/5})^2$ while for the PVP block, in bad solvent conditions, the projected area scales as $(N_{PVP}^{1/3})^2$. Thus

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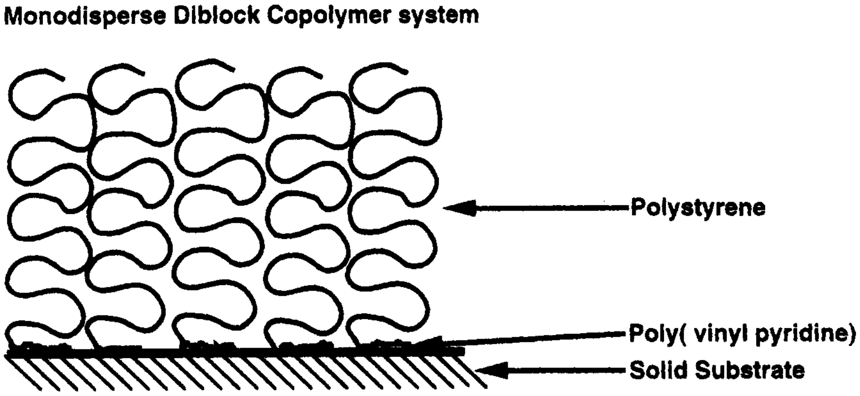

Figure 1. Schematic adsorbed layer of PVP–PS diblock copolymer adsorbed onto mica in toluene.

$$\beta = N_{PS}^{6/5}/N_{PVP}^{2/3} \quad (1)$$

and

$$\Sigma = \sigma/\sigma^* \quad (2)$$

where the critical surface density σ^* required for overlap of the polymer chains on the surface is obtained when the average distance between chains is equal to the average dimension of the chains in solution, i.e. the free solution radius of gyration of the chains. The radius of gyration for PS chains in toluene is given by Higo et al.[12] and can be calculated as

$$R_{PS} = aN^{\nu} \qquad a = 1.86\ \text{Å},\ \ \nu = 0.595 \quad (3)$$

so that the critical overlap surface density is given by

$$\sigma^* = a^2/R_{PS}^{\ 2} = N_{PS}^{\ -2\nu} \quad (4)$$

Parsonage et al.[11] plot all their data for their normalized dimensionless surface density Σ against β. They found that this correlation works very well to collapse all their data over wide ranges of N_{PS} and N_{PVP}, exactly consistent with the theory of Marques et al.[13] This theory predicts a universal power law behavior for the Σ against β curve, as seen in the experiments, up to a certain degree of asymmetry. This power law result is valid in a regime where the chemical potential of the adsorbing molecules in solution is fixed.

When there is more than one length of the molecules, as in the bimodal case of present interest, the adsorbed amount and the composition of molecules on the surface depend not only on the relative sizes of the two blocks for each molecule, but also on the relative lengths of the different molecules and on their proportions in solution. There is competition between the molecules of different sizes, and hence the adsorbed layer composition is not equal to that in solution. Competition is the subject of this paper.

We have created a bimodal distribution of chains on the solid surface by adsorbing from solutions containing a binary mixture of diblock copolymers differing in molecular size as well as chemical nature. The diblock copolymers used are PVP–PS and PVP–polyisoprene (PI). Toluene is a good solvent for PI, as well as for PS. We have considered three cases where both the competing molecules are PVP–PS. The sizes of the molecules were chosen to show the effect on adsorption of the relative sizes of PVP or PS blocks of different molecules, e.g. keeping the block sizes of one of PS or PVP nearly the same, while having a large difference in the other PVP or PS blocks.

Experimental Section

Materials. Tritium-labeled diblock copolymers of PVP–PS were previously synthesized anionically by the high-vacuum technique.[11] The PVP–PS and PVP–PI diblock copolymers were synthesized by regular sequential anionic polymerization.[6,7,11] Competitive adsorption experiments on four systems have been made. They are (a) 9–36 PVP–PS (sample designations refer to molecular weight of PVP–PS in thousands) and 15–152 PVP–PS diblock copolymers, with t9–32 PVP–PS (the letter t refers to the tritium-labeled polymer) used as a model polymer for 9–36 PVP–PS to determine adsorbed layer composition, (b) 62–31 PVP–PS and t9–32 PVP–PS diblock copolymers, (c) t9–32 PVP–PS and 3–36 PVP–PS diblock copolymers, and (d) t44–51 PVP–PS and 69–39 PVP–PI diblock copolymers.

The solvent toluene is glass-distilled SPEC grade and was obtained from EM Science. ASTM V-2, clear and slightly stained muscovite, ruby red mica sheets were obtained from New York Mica Corp. Rectangular mica pieces (4 cm × 1.5 cm) were carefully cut to avoid damaging the edges and freshly cleaved for use in the adsorption experiments. Silicon wafers polished on one side and containing a native oxide layer were purchased from Virginia Semiconductor, Inc. The wafers were kept in a clean glass container filled with freshly opened and filtered toluene for several days, rinsed with fresh filtered toluene and then dried by N_2 gas before being put into the incubation solutions. Adsorption onto both freshly cleaved mica and polished silicon wafers was studied. However, as also found by Parsonage et al.,[11] no measurable difference in the adsorption properties could be discerned by scintillation counting from the substrate for the tritium-labeled block copolymers. Therefore, for convenience, mica was used primarily as the substrate for the scintillation experiments, while the XPS measurements were made on the polished side of the silicon wafers.

Sample Preparation. The spectroscopic grade toluene was filtered through a 0.22 μm Millipore filter prior to use. Stock solutions of the desired copolymers were first prepared by the addition of about 8 mg of polymer to 10 mL of fresh toluene. The solutions were kept for 2–3 days to ensure dissolution. After thorough cleansing of the ground-glass containers (3 cm diameter × 6 cm) for the adsorption solutions, the containers were then incubated in a dilute solution of the desired copolymer mixture to coat the walls of the container with an adsorbed layer. After the containers were rinsed with pure solvent, solutions of nominal concentration (20–30 μg/mL) were made by dilution from the mother.

Solutions of five different compositions (0, 25, 50, 75, 100 percentage by weight) with the same total concentration were made for each copolymer pair. The solutions were kept for a few days (3–4) to ensure complete equilibration. Substrates were then allowed to remain in these incubation solutions for a period of several days (3–4). At this time, the substrates containing the adsorbed layer were removed from solution, immediately rinsed thoroughly with fresh solvent, and dried under vacuum for 24 h. Samples were stored under vacuum until the measurements were made.

The time dependence of block copolymer adsorption has been the subject of experimental work. Pefferkorn et al.[14] studied the adsorption of radio-labeled PVP–PS diblock copolymers adsorbed from solution in toluene onto silica. They observed changes in the adsorbed amount over a period of 2 months. We have observed from our surface forces experiments that the force profile is insensitive to the time for adsorption after a few hours. The PVP blocks in the PVP–PS diblock copolymers used by Pefferkorn et al.[14] were larger than the PVP blocks used in this study and that may be the reason why we did not observe changes in the force profiles with time. In the present work, we did not attempt to study this time dependence systematically but kept the substrates in the solution for at least 3–4 days. Slower, time-dependent changes may occur but are not of primary interest or significance for the work reported here.

X-ray Photoelectron Spectroscopy (XPS). Spectroscopic data for dried adsorbed layers on polished silicon substrates were acquired using a Physical Electronics Model 5400 spectrometer with angle-resolved capability and fitted with a nonmonochromatized Mg Kα X-ray (1253.6 eV) source of power 300 W. The pass energy of the spectrometer was set at 35.8 eV, and the resolution was about 0.9–1.0 eV. Integrated intensities for the Si_{2p}, C_{1s}, and N_{1s} signals were measured for a vector of takeoff angles ranging from 90° (normal) to 15° (grazing). Integrated signals were normalized to their 90° values.

Fadley et al.[15] have quantified the technique by assuming an exponential dependence of the escape probability on the escape depth of the photoemitted electrons in the sample. For a uniform film atop a silicon substrate,[16] the total integrated intensity should vary as

$$\ln\left[\frac{\mathrm{Si}_{2p}(\theta)}{\mathrm{Si}_{2p}(90°)}\right] = -\frac{\tau}{\lambda}\left[\frac{1}{\sin(\theta)} - 1\right] \qquad (5)$$

where τ is the thickness of the film, λ is the mean-free path of the Si_{2p} electrons in the film, and θ is the takeoff angle.

Parsonage et al.[11] have measured λ for the diblock copolymer system of PVP–PS for three different molecular weights and found it to be fairly insensitive to the composition of the particular polymer. They obtained an average value of λ = 1.57 nm, which was then used in angle-resolved XPS measurements to calculate the adsorbed amounts. From the above equation, if we plot the attenuation of the Si_{2p} signal as a function of $(1/\sin(\theta) - 1)$, we get $(-\tau/\lambda)$ as the slope. Since we already know λ, the thickness of the adsorbed layer can be obtained. Assuming a bulk density of 1.04 g/cm^3, the total adsorbed amount of polymer per unit area can be calculated. The error in (τ/λ) was 3% as measured by the standard deviation from the average of replicate runs.

Scintillation Counting. Substrates of mica possessing an adsorbed layer containing tritium-labeled polymer are directly placed in the scintillation vials and filled with a high-efficiency scintillation liquid for β emission (Beta Max, ICN Radiochemicals). The intensity of light emitted from the scintillation cocktails was measured with a Beckman LS 6800 liquid scintillation counter.

The composition of the molecules on the surface having a mixture of two polymers, one of which is tritium-labeled, was determined in the following manner. The intensity of light emitted by this substrate was measured using scintillation counting. The amount of the tritium-labeled polymer on this substrate was calculated by comparing this measured intensity of light to that measured for a substrate having a known amount of only the labeled polymer. The amount in the latter case was determined using XPS. The total amount of polymer on the substrate having a mixture of two polymers was determined using XPS. The amount of the nontritiated polymer was then obtained by difference from the total adsorbed amount.

The error in the scintillation experiments was 10%, as measured by the standard deviation from the average of replicate runs. The error bars in Figures 2–5 were obtained in the following manner. The error in the total adsorbed amount as measured from the XPS measurements is 3%. Combining the XPS and scintillation experiments results in a computed error of 10 and 11%, as measured by the standard deviation, in the amount and composition, respectively, of the tritium-labeled component. The calculated error, as measured by the standard deviation, in the amount and the composition of the nonlabeled component depends upon the values of both the total adsorbed amount and the amount of the tritium-labeled component.

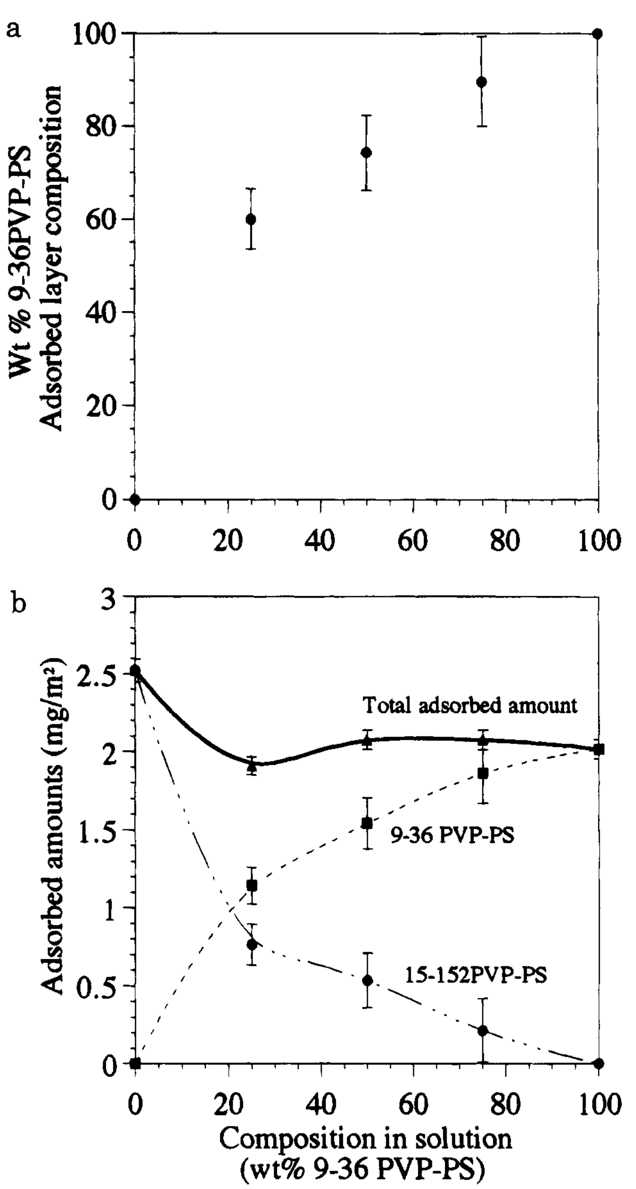

Figure 2. (a) Adsorbed layer composition by weight percentage of 9–36 PVP–PS as a function of the solution composition by weight percentage of 9–36 PVP–PS. (b) Adsorbed layer amounts of the polymers as a function of the solution composition by weight percentage of 9–36 PVP–PS for the 9–36 PVP–PS and 15–152 PVP–PS system. Smooth lines are drawn through the points to guide the eye.

Dynamic Light Scattering. Dynamic light-scattering experiments for the 9–36 PVP–PS and the 15–152 PVP–PS monodisperse diblock copolymers at the concentrations used in our experiments (20–30 μg/mL) showed the presence of only one decay rate characteristic of a single size of object in the solution. This corresponds to the size of free chains in solution and implies that we are below the observed critical micelle concentration (cmc). The molecular weights and concentrations used for other polymers used are not extremely different and we assume that we are below the cmc in these as well as in the binary mixture cases.

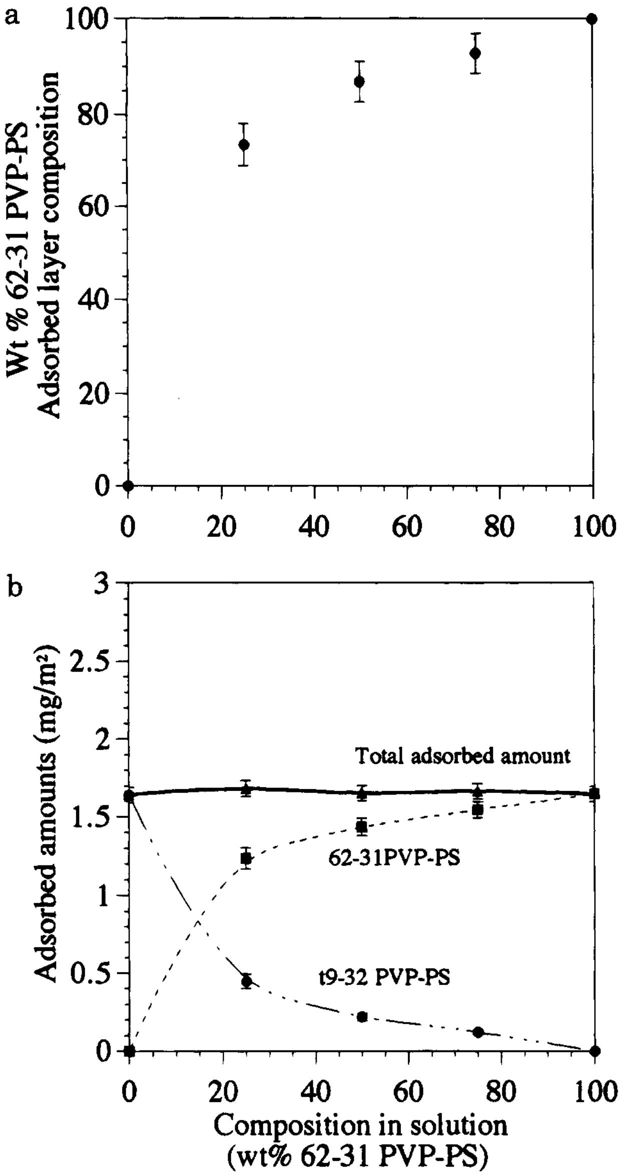

Figure 3. (a) Adsorbed layer composition by weight percentage of t9−32 PVP−PS as a function of the solution composition by weight percentage of t9−32 PVP−PS. (b) Adsorbed layer amounts of the polymers as a function of the solution composition by weight percentage of t9−32 PVP−PS for the t9−32 PVP−PS and 62−31 PVP−PS system. Smooth lines are drawn through the points to guide the eye.

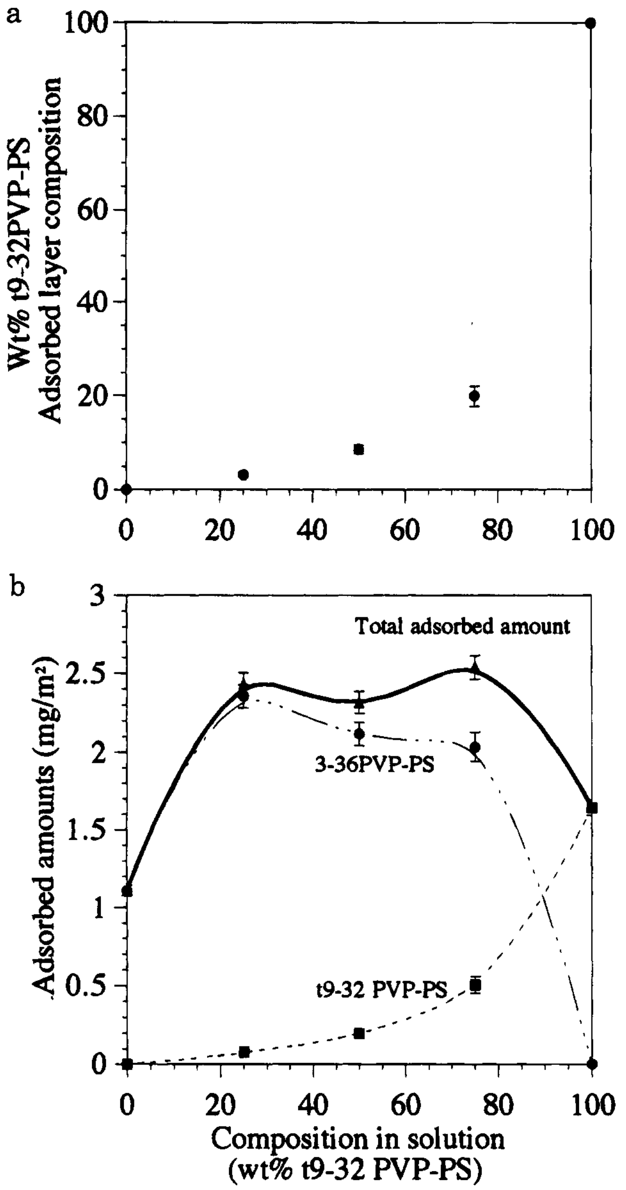

Figure 4. (a) Adsorbed layer composition by weight percentage of t9−32 PVP−PS as a function of the solution composition by weight percentage of t9−32 PVP−PS. (b) Adsorbed layer amounts of the polymers as a function of the solution composition by weight percentage of t9−32 PVP−PS for the t9−32 PVP−PS and 3−36 PVP−PS system. Smooth lines are drawn through the points to guide the eye.

Results

Figures 2a−5a show the weight percentage adsorbed layer composition as a function of the solution composition by weight percentage of the diblock copolymer having a smaller nonadsorbing block. Figures 2b−5b show the adsorbed layer amounts of the polymers as a function of the solution composition by weight percentage.

For the 15−152 PVP−PS and 9−36 PVP−PS system, the total adsorbed amount was determined using XPS. The amount of 9−36 PVP−PS was determined in the following manner. Adsorption was performed onto mica substrates for a mixture of t9−32 PVP−PS and 15−152 PVP−PS from solutions at the same composition as in the 15−152 PVP−PS and 9−36 PVP−PS system. Scintillation counting is used to determine the fractional amount of t9−32 PVP−PS on the mica substrate relative to a mica substrate having a known amount of only t9−32 PVP−PS, determined using XPS. This fraction was then used to determine the amount of 9−36 PVP−PS.

We can gain an intuitive feel for the selectivity of the molecules toward adsorption based on the following physical picture. In a noncompetitive situation, for each molecule, the adsorption can be considered to be governed by the balance of the adsorption energy of the PVP block (also termed as the adsorbing block), which wants to adsorb, with the buoy energy of the PS block (also called the solvated block), which wants to remain in solution. The buoy energy scales linearly with the degree of polymerization of the PS block and with the surface density to the two-thirds power.[9,13] A smaller PS block at a fixed surface density results in a lower buoy energy. Consequently, for a given anchoring strength of the PVP block, a diblock copolymer with a smaller PS block can pack itself at a larger surface density. In the competitive scenario, additionally, selectivity of the molecules toward adsorption would

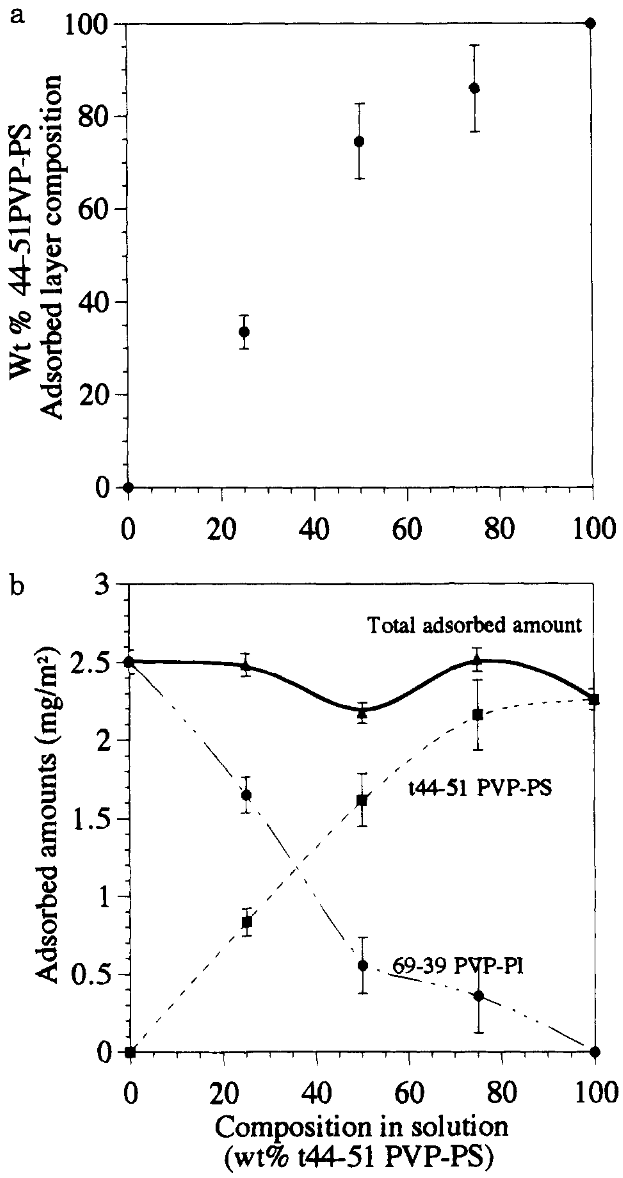

Figure 5. (a) Adsorbed layer composition by weight percentage of t44–51 PVP–PS as a function of the solution composition by weight percentage of t44–51 PVP–PS. (b) Adsorbed layer amounts of the polymers as a function of the solution composition by weight percentage of t44–51 PVP–PS for the t44–51 PVP–PS and 69–39 PVP–PI system. Smooth lines are drawn through the points to guide the eye.

depend upon the relative sizes of the PVP or PS blocks of different molecules. For diblock copolymers with equal-sized PVP anchoring blocks, the molecule with a smaller PS block will be preferentially adsorbed. Similarly, for diblock copolymers with the same-sized PS block, the molecule with a larger PVP anchoring block will be preferentially adsorbed. By comparing the sizes of the PVP and PS blocks, in some cases, we can predict which molecule would be preferentially adsorbed.

Figure 2a shows that, for the 15–152 PVP–PS and 9–36 PVP–PS system, the smaller 9–36 PVP–PS molecule is preferentially adsorbed. In this case, there is more than a (152/36) 4-fold difference in the buoy block (PS) size while the PVP block size ratio is around 1.7 (15/9). We expect that the PS block size would have a greater influence on the competitive adsorption and that the molecule with the smaller PS block would be favorably adsorbed. Figure 2b shows that the total adsorbed amount for the mixed layers is nearly constant, independent of the solution composition.

Figure 3a shows that, for the 62–31 PVP–PS and t9–32 PVP–PS system, the 62–31 PVP–PS molecule is preferentially adsorbed. In this case, the PS block sizes are close to each other, but the PVP block size for the 62–31 PVP–PS molecule is nearly (62/9) 7 times than that for the t9–32 PVP–PS molecule. We expect that the PVP block size would have a greater influence on the competitive adsorption and that the molecule with the stronger adsorbing PVP block would be favorably adsorbed. Figure 3b shows that the total adsorbed amount for this system is nearly constant.

To summarize, for binary mixtures of diblock copolymer molecules with nearly the same-sized anchoring block, the molecule with the smaller buoy block is preferentially adsorbed while for binary mixtures of diblock copolymer molecules of nearly equal sized buoy blocks, the molecule with the stronger adsorbing block is preferentially adsorbed.

Figure 4a shows that for the 3–36 PVP–PS and t9–32 PVP–PS system, the 3–36 PVP–PS molecule is preferentially adsorbed. If we compare the block sizes, 3–36 PVP–PS has both a larger buoy ($36/32 \approx 1.13$) and smaller adsorbing block ($3/9 \approx 0.33$) as compared to t9–32 PVP–PS. On the basis of the arguments advanced in the preceding paragraphs, we would anticipate that the t9–32 PVP–PS molecule would be favorably adsorbed. However, Figure 4a shows that the adsorbed layer composition favors the 3–36 PVP–PS. Figure 4b also shows that the adsorbed amount for the 3–36 PVP–PS molecule is higher than that for the monodisperse pure component case. Our interpretation of this is the following. In the noncompetitive adsorption case for 3–36 PVP–PS, the surface is not completely covered by the PVP block of the 3–36 PVP–PS molecule; i.e. the amount of PVP polymer available is less than the amount required for a complete uniform layer of monomer thickness on the surface. The amount of polymer required for complete coverage in this case is $a\varrho = 0.1934$ mg/m^2 where ϱ is the density of the dried polymer layer. The amount of PVP available is ($3/39 \times 1.11$) 0.085 mg/m^2, much less than that required for complete coverage. There are bare gaps present on the surface. Parsonage et al.[11] have shown that homopolymer PVP is not completely insoluble in toluene for small blocks of PVP. 3–36 PVP–PS has a small PVP block and it is conceivable that, in the mixed adsorption situation, the larger PVP block of the t9–32 PVP–PS molecule assists the smaller PVP block of 3–36 PVP–PS anchor to the surface, thereby enhancing adsorption. This additional adsorbed amount of the 3–36 PVP–PS and the adsorbed t9–32 PVP–PS can also help fill in the bare gaps.

Figure 5a shows that for the 69–39 PVP–PI and t44–51 PVP–PS system, the t44–51 PVP–PS molecule is preferentially adsorbed. The adsorbing blocks are chemically the same, but the buoy blocks are chemically different. Here the PVP–PI molecule has both a higher anchoring (PVP) block molecular weight as well as a lower buoy (PI vs PS) molecular weight. We find that the adsorption favors the PVP–PS molecule. This can be understood in the following manner. If we look at the contour lengths of the PS and PI blocks, we find that the contour lengths are 151 and 342 nm, respectively. This case is therefore similar to the case in Figure 2a where the adsorption favors the polymer with the smaller buoy block.

When the chemical species are different, we have to consider the following factors for the competitive ad-