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Adsorption of Poly(2-vinylpyridine)–Poly(styrene) Block Copolymers from Toluene Solutions

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ABSTRACT: We have studied the adsorption of diblock copolymers of poly(2-vinylpyridine) (PVP)–poly(styrene) (PS) from toluene solutions onto oxidized silicon and mica substrates. Adsorbed amounts for copolymers of various molecular weight and composition were measured by scintillation counting from tritium-labeled adsorbed layers and by X-ray photoemission spectroscopy. We find a dimensionless surface density σ^* to be a unique function of a copolymer block size asymmetry ratio. Within this correlation, we see two regimes of behavior. For copolymers of moderate asymmetry, the surface density σ is influenced more strongly by the molecular weight of the adsorbing PVP block. These results agree well with a model by Marques et al. For copolymers with large PS blocks (high asymmetry), the surface density is determined primarily by the molecular weight of the PS block. Angle-resolved XPS measurements on dry adsorbed layers indicate a layered structure with PS segments preferentially located at the top surface. These results are supported by contact angle measurements on the dry adsorbed layers.

Introduction

Block copolymers show an inherent interfacial activity that makes them useful as large surfactant molecules. Surfactancy of block copolymers is related to their high molecular weight. A small difference in chemical affinity between the blocks on a monomer scale is magnified by their large molecular weight to produce a strong tendency to straddle phase boundaries. Furthermore, the large size of these molecules allows them to penetrate into the individual phases to a depth not possible for small-molecule surfactants, producing special effects on the mechanical properties of polymer interfaces.

One facet of their interfacial activity is adsorption from solution onto an impenetrable substrate. The present work is concerned with selective adsorption from selective solvents. In this case, a preferential adsorption affinity of one of the blocks gives rise to a layer in which the adsorbed block forms a poorly solvated phase in contact with the wall, while the well-solvated, nonadsorbing block, being covalently attached to the adsorbing block, extends to the solution. These adsorbed layers find commercial use in the stabilization of colloidal dispersions, as well as in other situations where one wants to manipulate intersurface interactions.[1]

From the point of view of the fundamental physics of polymer adsorption, block copolymers, or indeed any copolymer, play an interesting role in that the interactions with the surface and those with the solvent can be manipulated independently. In selective block copolymer adsorption, the anchoring blocks compete for surface area on the substrate while the nonadsorbing blocks, tethered by their anchors, can crowd one another in the solution. Surface interactions and polymer–solvent interactions are separated in a way impossible for homopolymers, where adsorption of a segment is always a competition between sticking and solvation. Block copolymers can combine

very strong binding with very good solvation. The question is, how important are the relative influences of competition for surface area and solution interactions in dictating the amount of polymer that becomes adsorbed? This paper presents data to answer this question.

Several models have been proposed for block copolymer adsorption from selective solvents.[2] As we shall demonstrate, the model proposed by Marques et al.[2e] makes some analytical predictions that can be tested with the data we have obtained. Furthermore, by rearrangement of the model of Marques et al., we have uncovered a new prediction for the effect of block size asymmetry on adsorbed amount arising from the physics of their theory. We therefore focus our introductory discussion on this theory.[2e] Detailed comparison with other models, which will require some computational effort, is reserved for future publication.

The model of Marques et al. imagines adsorption to be as depicted in Figure 1. The block copolymer is dissolved in a solvent that is selective for one of the blocks. That is, for single chains in solution, the well-solvated block (B) is assumed to take on the swollen coil configuration ($R_B = aN_B^{3/5}$) while the poorly solvated block (A) is in solution in the form of a collapsed globule, which may be plasticized by the solvent to a polymer A volume fraction c ($R_A = a(3/4\pi N_A/c)^{1/3}$). (We use a here to denote the segment size for both blocks.) Upon adsorption, the A blocks form a thin concentrated film, which completely wets the substrate surface. The thickness of the film d is related to the polymer volume fraction c and surface density σ in chains per unit area by

$$N_A a^3 \sigma = cd \tag{1}$$

where σ is related to the average distance, δ, between adsorbed chains by $\sigma = (1/\delta)^2$. The adsorbed layer is then assumed to be in equilibrium with solution having polymer
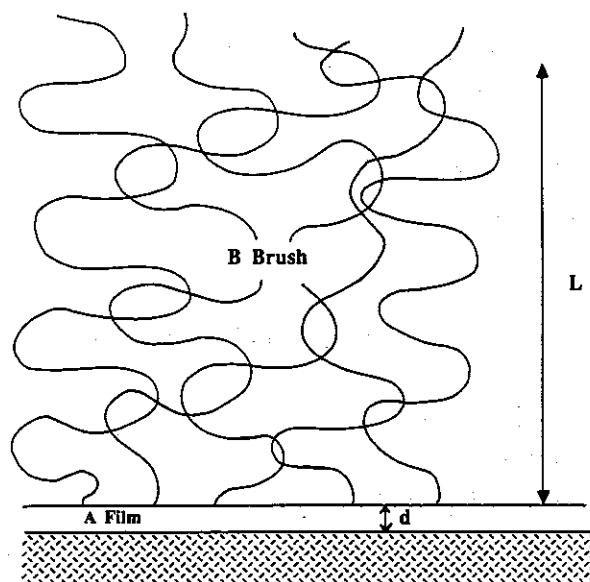
Figure 1. Adsorption of AB block copolymers from a selective solvent. The poorly solvated A block forms a thin adherent wetting film on the substrate while the well-solvated B blocks form a terminally attached brush.

chemical potential μ_{ex}.

The free energy of the well-solvated B block is assumed to be that of terminally attached chains in a good solvent. Grafted brushes in a good solvent have been the subject of considerable theoretical and experimental studies. Initial theoretical treatment of grafted brushes assumed a uniform density of monomers within the brush.[3,4] This situation is anticipated at surface densities sufficiently high to produce overlap among the swollen, grafted coils ($\delta < R_B$ or $\sigma > 1/R_B^2$). Scaling arguments based on the blob picture[4] predict an equilibrium average brush height $L_B = a^{5/3}\sigma^{1/3}N_B$. The corresponding free energy per unit area for the equilibrated brush is given by

$$F_B = a^{5/3}TN_B\sigma^{11/6} \qquad (2)$$

More recently, Milner et al.[5] and Patel[6] have solved the self-consistent mean-field problem for the segment density profile. In the limit of strong stretching, an analytical solution is obtained, which shows the density profile to be parabolic rather than a step function.[5] However, the scaling of brush height and free energy with molecular weight and surface density is unchanged from that predicted by the global energy balance analysis.[4]

Analyses of grafted brushes treat surface density as a parameter,[3-6] but for block copolymers the equilibrium surface density is also dependent on the free energy of the adsorbed anchoring block F_A. In the analysis of Marques et al., energetic contributions to the adsorption of the A block are the dominant factors. Two contributions to the energy of adsorption of the A block are considered. The first contribution is the spreading coefficient S defined as

$$S = \gamma_{WS} - \gamma_{WA} - \gamma_{AS} \qquad (3)$$

where γ_{WS}, γ_{WA}, and γ_{AS} are the surface tensions for the wall and solution, wall and concentrated A film, and A film and the solution, respectively. In essence, S is the free energy gain ($S > 0$) per unit area when a wall/solution interface is replaced by the wall/A film and A film/solution interfaces.

The second component of the A free energy is the long-range van der Waals attraction of the substrate with the A film. A similar problem was first addressed by Hamaker[7] for the interaction between two semiinfinite slabs

separated in vacuo by a distance d. The energy of interaction is given by

$$P(d) = -A_H/12\pi d^2 \qquad (4)$$

where A_H is the Hamaker constant. Lifshitz and co-workers[8] further developed a theory for the interaction between two bodies partitioned by a thin liquid film. For thin films, the energy of interaction has the same form as eq 4. However, with a medium in between, the relative interaction between the two bodies can be either attractive ($A_H > 0$) or repulsive ($A_H < 0$) depending on the nature of the intermediate fluid. (Repulsive here means that the film tends to thicken.) The free energy for a thin wetting A film of thickness d per unit area is thus given by

$$F_A = -S + A/12\pi d^2; \quad A_H = -A \qquad (5)$$

where the negative Hamaker constant reflects the relative attraction of the A film to the substrate.

The grand canonical free energy (G) per unit area contains the solution chemical potential μ_{ex}, brush free energy F_B, and a film free energy F_A

$$G = -\mu_{ex}\sigma - S + A/12\pi d^2 + a^{5/3}TN_B\sigma^{11/6} \qquad (6)$$

where the film thickness d is related to the surface density σ through eq 1. Minimization with respect to σ then gives an expression for the equilibrium surface density:

$$\mu_{ex} = -(A/6\pi)c^2N_A^{-2}(a^2\sigma)^{-3} + (11/6)a^{5/3}TN_B\sigma^{5/6} \qquad (7)$$

This is essentially the result of Marques et al.[2e] for one of the regimes they studied that is most applicable to the present work. It expresses a testable relationship between adsorbed amount and the molecular weights of the two blocks. We develop this relationship further in the discussion of our results.

Experimental work on the adsorption of block copolymers includes the measurement of adsorbed amounts for a variety of systems. We limit our review of other data here to experiments in which adsorbed amounts were measured directly or to surface forces data in which the stretching energy of eq 2 can be probed. The kinetics of adsorption of PVP-PS block copolymers from toluene solutions onto silver substrates has been studied by Tassin et al. using surface plasmon oscillations.[9] Their results indicate the kinetics of assembly to be very slow and dependent on the microstructure in solution. Stouffer and McCarthy[10] have measured adsorbed amounts for the adsorption of PS-poly(propylene sulfide) (PPS) block copolymers onto gold substrates from THF solutions. Adsorbed amounts were measured by scintillation counting from adsorbed layers of tritium-labeled polymers. Their results indicate a decrease in the surface density with increasing molecular weight of the anchoring PPS block. Furthermore, the measured surface densities become less sensitive to PPS molecular weight for polymers having a relatively low PPS content. Dawkins et al.[11] have reported isotherms for the adsorption of PS-poly(dimethylsilox-ane) (PDMS) block copolymers, along with the corresponding homopolymers, from trichloroethylene solutions onto silica particles as measured by infrared spectroscopy from the supernatant. They observe adsorbed amounts for PS and PDMS to bracket those observed for the PS-PDMS block copolymers. Furthermore, adsorbed amounts for the block copolymers showed an apparent insensitivity to solution concentration. This system is nonselective in the sense that both blocks adsorb to the substrate.

Other experimental work on the adsorption of block copolymers has included the measurement of forces

between adsorbed layers[12-17] using the surface force apparatus.[18] The measurement of forces between adsorbed layers has been recently reviewed.[19] The surface force measurements are relevant to the present work in that they provide support for the form of layer thickness and stretching energy embodied in eq 2. Patel et al.[12-14] have made surface force measurements for the adsorption of PVP–PS block copolymers from toluene solutions onto atomically smooth mica substrates. The salient result of these experiments is the long-range character of the forces and a linear variation in the range of the forces with the molecular weight of the well-solvated PS block at fixed PVP molecular weight. Toluene is a preferential solvent for the PS block, and the results can be interpreted as interactions between the PS brushes of the adsorbed layer. The long-range nature of the forces ($\sim 10~R_{PS}$) suggests the PS blocks are taking on extended configurations due to unfavorable segmental interactions in a crowded adsorbed layer. These results are in agreement with the theoretical predictions for overlapping terminally attached chains in a good solvent.[3-5]

Watanabe and Tirrell[15] observe similar results for the adsorption of PVP–poly(isoprene) (PI) block copolymers from toluene solutions. Furthermore, they measured adsorbed amounts for several PVP–PS and PVP–PI block copolymers. The measured surface densities were generally lower than expected from previous models.[12] However, the measured surface densities were sufficiently large such that the PS and PI blocks are overlapping in the adsorbed layers. Thakkar et al. have measured surface forces and adsorbed amounts for adsorption of two PVP anchored polymers from toluene solutions onto Pyrex glass surfaces.[20] The results are in quantitative agreement with those studied by Patel et al. and Watanabe et al., suggesting there is not a large difference between the adsorption properties of these two substrates. Adsorption of PVP–poly(tert-butylstyrene)[21] and PS–poly(ethylene oxide)[22] from toluene solutions onto mica substrates have also been studied by using surface forces. As in the PVP–PS measurements, these systems also exhibit long-range monotonic repulsions between adsorbed layers in solution. However, quantitative interpretation of the surface force measurements requires knowledge of adsorbed amounts, an issue not completely addressed in those experiments. Webber et al.[23] have studied the hydrodynamic layer thickness of a PVP–PS adsorbed layer and obtained values for the extension of the nonadsorbing block normal to the surface that are in fair agreement with those obtained from surface force measurement.

The issue remains of the proper interpretation of how the sizes of the blocks in a copolymer each affect the adsorption process. This understanding is essential to comprehend all other aspects of block copolymer adsorption, such as surface forces or hydrodynamic thickness. The purpose of this work is to elucidate the effect of the molecular weights of each of the blocks on the adsorbed amount for PVP–PS block copolymers adsorbed from toluene solutions onto mica and polished silicon wafers. We study a total of 18 different polymers in order to ascertain the fundamental dependence of surface density on the size of each of the blocks. Scintillation counting (using tritium-labeled polymers) and XPS are used to measure the adsorbed amount for a large set of polymers of varying molecular weight and composition. The results are compared with the predictions of Marques et al.[2e] The effect of solution concentration on the adsorbed amount, kinetics of exchange, and preferential adsorption of PVP are also studied.

Table I
Characterization of Tritium-Labeled PVP–PS Block Copolymers

code	PVP–PS copolymer			precursor PS	
	$10^{-3}M_w$	ϕ_{PVP}, wt %	M_w/M_n	$10^{-3}M_w$	M_w/M_n
PVP–PS t9-32	41	22.0	1.09	32	1.03
PVP–PS t52-63	115	45.2	1.10	63	1.03
PVP–PS t124-60	184	67.4	1.10	60	1.03

^{a} $M_{PVP-PS} = M_{PS}/(1 - \phi_{PVP})$. ^{b} PVP content determined by NMR.

Experimental Section

Materials. Tritium-labeled diblock copolymers of PVP–PS were synthesized anionically with the high-vacuum technique.[24] The results of the characterization for these polymers are given in Table I. The code for the polymers represents the molecular weight of the constituent blocks (PVP–PS) in units of thousands. The prefix "t" indicates the block copolymer contains a tritium label.

Monomers of styrene and 2-vinylpyridine were obtained from Aldrich. Living anionic polymerization requires extensive purification of commercial monomer. The monomers were first washed with concentrated aqueous NaOH solutions to extract inhibitor. After washing, the monomers were dried over NaOH and distilled at low pressure (0.1 mmHg) under a nitrogen atmosphere. The monomers were then subjected to a cascade (~ 6) of high-vacuum (10^{-6} mmHg) distillations over fresh calcium hydride. The final styrene monomer was stored in sec-butylmagnesium as a final purification procedure. The final purified monomer of 2-vinylpyridine was stored over calcium hydride.

The solvents for the polymerization were also subjected to extensive purification. Approximately 1 L of toluene (HPLC Grade, Fisher) was first treated with concentrated sulfuric acid. The treated solvent was then distilled under high vacuum into a 2-L flask coated with elemental sodium. This process was repeated and the final purified toluene stored in the presence of the scavenging diphenylethylene anion (DPE). Approximately 1 L of tetrahydrofuran (HPLC Grade, Fisher) was first treated by refluxing with Na metal in the presence of napthalene. The formation of the scavenging sodium–napthalene complex was signatured by a clear to green color change of the solvent. The THF was then twice distilled under high vacuum into a sodium-coated flask, with the final purified solvent stored in DPE.

Tritiated methyl iodide (specific activity 100 mCi/mmol) was purchased from ICN Radiochemicals. Three samples containing 10 mCi (0.1 mmol) each of CT_3I were received in sealed ampules possessing a breakable glass tip for direct mounting to the polymerization apparatus. No further purification of the methyl iodide was conducted.

The initiator for the polymerization was sec-butyllithium. The initiator was synthesized by the reaction of sec-butyl bromide with Li metal. The details of this synthesis have been given elsewhere.[15]

The styrene block was first polymerized by addition of a desired amount of purified styrene monomer to a solution of initiator (sec-butyllithium) in toluene at 0 °C. (To help insure a narrow molecular weight distribution, a small amount of styrene was first added to seed the reaction. A similar procedure of adding at first a small amount of VP monomer was used for the initiation of the PVP block.[24]) The formation of the living styryl anion was indicated by the yellow color change in the reacting solution, and the polymerization was allowed to proceed for ~ 12 h. Upon complete conversion of the styrene monomer, an aliquot of the PS precursor was removed from the polymerization reactor and terminated with methanol. The solvent was then changed to tetrahydrofuran by vacuum distillation, and the PVP block, initiated at −78 °C by addition of the desired amount of 2-vinylpyridine monomer (red color change). Upon complete conversion of the pyridine monomer (~ 6 h), the final living anions were terminated by introduction of the methyl iodide to affect the tritium labeling. The radioactive CT_3 group is attached to the end of the PVP block in this terminal reaction.

Subsequent to polymerization, the PVP–PS block copolymers were precipitated from heptane, dissolved in benzene, filtered, and freeze dried. The copolymer samples were characterized by

size-exclusion chromatography (SEC) and nuclear magnetic resonance. The PS precursor molecular weights and polydispersity, along with the block copolymer polydispersity, were measured by SEC against PS standards. The elution solvent was THF. The copolymer composition was measured by NMR from 5% solutions in deuterated chloroform. Relative activities of the tritium-labeled polymers checked by scintillation counting from equimolar copolymer solutions. Relative to the PVP–PS t52-63 sample, the measured activities for t9-32 and t124-60 are 0.6 and 2.5, respectively.

Glass-distilled SPEC-grade toluene (EM Science) was used as received for the incubation solutions. The mica used in this study was Grade No. 4 ASTM V-2, clear and slightly stained Muscovite, ruby red mica obtained from Asheville-Schoonmaker Mica Co. Silicon wafers polished on one side and containing a native oxide layer were purchased from Aurel. The wafers were used as received.

Adsorption onto both freshly cleaved mica and polished silicon wafers was studied. However, no measurable difference in the adsorption properties of these two substrates 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. Stock solutions of the desired copolymer were first prepared by the addition of 2.5 mg of polymer to 25 mL of fresh toluene (100 μg/mL). The solutions were warmed for 1 week at 40 °C to ensure dissolution. After thorough cleansing of the ground-glass containers (1.5 × 6 cm) for the adsorption solutions, they were then incubated in a dilute solution of the desired copolymer to coat the walls of the container with an adsorbed layer. After the containers were rinsed with pure solvent, solutions of nominal concentrations were constructed by dilution from the mother.

Substrates were allowed to remain in the incubation solutions for a period of several days. At this time, the substrates containing the adsorbed layer were removed from solution, immediately and thoroughly rinsed with fresh solvent, and dried under vacuum for 24 h. No desorption of the polymer during the rinsing process was observed. Samples were stored under vacuum until the measurements were made.

Measurements. Scintillation Counting. Scintillation cocktails were prepared by mixing in a vial the sample (solution or substrate) 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.

Measurement of absolute values for adsorbed amounts by scintillation counting directly from the immersed substrate is complicated by the necessary assumptions of polymer specific radioactivity and the efficiency of the scintillation experiment.[10] To avoid these assumptions, we used the following technique. An incineration oven (1500 cm³) was connected to a cold trap at –78 °C. The temperature of the oven was maintained at a high level (~2000 °C) for a sufficient period of time (~30 min) to ensure oxidative degradation of the polymer to small-molecule fragments. The radioactive CT₃ group is converted to tritiated water, T₂O, during the incineration procedure. Scintillation measurements were then made on the oxidation products recovered from the trap.

To determine adsorbed amounts for a particular polymer, the experiment was calibrated by the addition of known amounts of the tritium-labeled polymer. Figure 2 shows the calibration curve for the sample PVP–PS t52-63. Once the calibration curve was established, adsorbed amounts were measured by incineration of adsorbed layers from cleaved mica substrates of known surface area (~50 cm²). Using this procedure, for samples with adsorbed amounts of 1–2 mg/m², the scintillation intensity was approximately 1 order of magnitude greater than the background intensity of the pure scintillation liquid. Scintillation counting from the incinerated substrates indicated no adsorbed polymer remaining on the surface. The error in the scintillation experiments was 11% as measured by the standard deviation from the average of replicate runs.
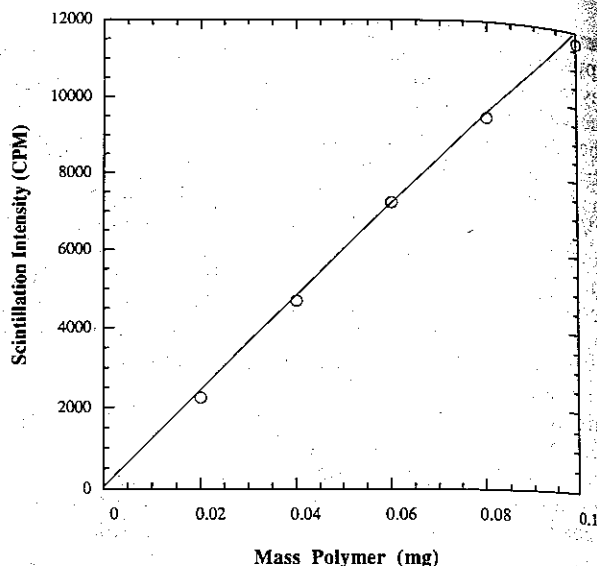

Figure 2. Mass coverage calibration for the tritium-labeled copolymer PVP–PS t52-63.

Adsorption isotherms and exchange kinetics were monitored by scintillation counting directly from the substrate. Substrates of mica or polished silicon wafers possessing an adsorbed layer were placed directly in the scintillation vials, and the intensity of emitted light was measured.

X-ray Photoemission Spectroscopy. X-ray photoemission spectra for dried adsorbed layers on polished silicon substrates were obtained with a Physical Electronics Model 5400 spectrometer with angle-resolved capability and a Mg anode. 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 10° (grazing). Integrated signals were normalized to their 90° values.

Due to the relatively short mean-free path of the photoemitted electrons in the sample, angle-resolved XPS has the capability to determine composition profiles in the near-interface region. Fadley et al.[25] have quantified the technique by assuming an exponential dependence of the escape probability on the escape depth. For a uniform film atop a silicon substrate, the total integrated Si$_{2p}$ intensity should vary as

$$\ln\left[\frac{Si_{2p}(\theta)}{Si_{2p}(90°)}\right] = -\frac{\tau}{\lambda}\left[\frac{1}{\sin\theta}-1\right] \tag{8}$$

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.[26]

Figure 3 shows a semilogarithmic plot of the integrated Si$_{2p}$ intensity against $1/\sin\theta$ for the tritium-labeled polymer t52-63. The linear relationship in the data suggests the dried adsorbed layers are relatively smooth. The values of τ/λ, as measured by a linear least-squares fit to the data, are shown in the accompanying Table II along with the thickness τ of the dried films at bulk density as determined by the adsorbed amounts from the scintillation experiments. From these two quantities the mean-free path λ of the Si$_{2p}$ electrons in the polymer film is calculated. The close agreement in the λ values for the three polymers suggests λ to be fairly insensitive to the composition of this particular polymer. We take it as a constant, $\lambda = 1.57$ nm, for the remainder of this work.

With the relationship between the rate of substrate attenuation and thickness of the dry adsorbed layer established, angle-resolved XPS measurements can also be used to measure adsorbed amounts. Adsorbed amounts for a set of non-tritium-labeled PVP–PS block copolymers of varying molecular weight and composition were determined by the aforementioned technique. (The synthesis and characterization of these polymers have been described elsewhere.[12,27]) That is, the quantity τ/λ was measured and the thickness τ determined by using $\lambda = 1.57 \pm 0.2$ nm. The error in the slope τ/λ measured with XPS was 3% as measured by the standard deviation from the average of replicate runs.

Some comparisons with data in literature are possible. Clark et al. report a value $\lambda = 21$ Å at 1156 eV for electrons attenuated
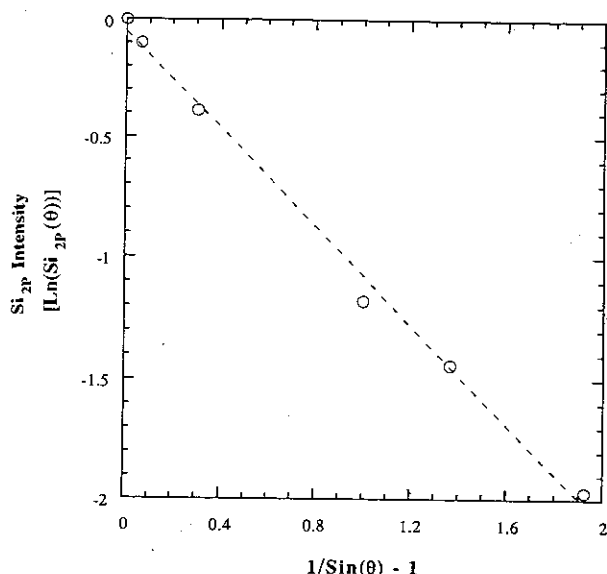
Figure 3. Semilogarithmic plot of the integrated Si_{2p} intensity versus takeoff angle (θ) for the tritium-labeled polymer PVP–PS t52-63. The dashed line represents a linear least-squares fit to the data.

Table II
Si_{2p} Mean-Free Path within Dry Adsorbed Layers

sample	slope τ/λ	thickness τ,[a] nm	mean-free path λ, nm
t52-63	1.0	1.6	1.6
t9-32	1.2	2.0	1.7
t124-60	0.8	1.1	1.4

[a] $\tau = s/\rho$ where s is the mass coverage (M/L^2) and ρ is the copolymer density (M/L^3).

by a poly(p-xylylene) overlayer.[28] This number is considerably less than the value of ~34 Å reported by Bain and Whitesides for this energy range.[29] Their study used a poly(methylene) chain based monolayer system whose structure has been established in detail by vibrational spectroscopy and diffraction techniques. Theoretical calculations based on the method of Penn[30] suggest that a value of ~15 Å is to be expected for carbon. Our belief, based on the suggestions of Penn, is that the mean-free paths of low-energy electrons in attenuating organic overlayers depend sensitively on both the atomic density and electronic structure of the film. It appears that these attenuation lengths are significantly shorter in phases containing aromatic rings, presumably reflecting an increased cross section for inelastic scattering as compared to aliphatic materials.

PVP–Toluene Solubility Diagram. Samples of homopoly-(2-vinylpyridine) with narrow molecular weight distributions were purchased from Pressure Chemical and used as received. Solutions of PVP in toluene were prepared by the addition of 100 mg of PVP to 1.0 g of toluene (10% PVP by weight). The solutions were allowed to equilibrate for 1 week to ensure equilibrium. The samples were observed to phase separate into a concentrated polymer phase and dilute polymer phase. The volume fraction polymer in the concentrated phase was determined by first pipetting off the dilute phase and weighing the concentrated phase. The toluene solvent was then stripped from the concentrated phase and the amount of remaining PVP weighed. The concentration in the dilute phase was then determined by mass balance from the initial conditions.

Contact Angle Measurements. Hompolymer films of PVP and PS were prepared by spin coating from 10% solutions in chlorobenzene onto polished silicon wafers. The cast films were dried under vacuum for 24 h. Contact angles for the homopolymers and dry adsorbed layers of block copolymer were measured by placing a small drop (~0.05 mL) of distilled water on the desired surface and measuring the angle of contact between the polymer surface and the air/water interface of the drop using a goniometer.

Table III
Summary of Adsorbed Amounts of PVP–PS Diblock Copolymers

sample PVP–PS	mass coverage s, mg/m^2	surface density σ, m$^{-2} \times 10^{-16}$	$1/(\pi R_{PS}^2)$[a] σ_{ol}, m$^{-2} \times 10^{-16}$
3-36	2.16	3.32	0.84
9-36	2.12	2.84	0.84
16-31	1.79	2.30	1.00
18-36	1.83	2.05	0.84
15-92	2.02	1.13	0.27
15-152	1.97	0.71	0.15
31-31	1.66	1.61	1.00
36-36	1.49	1.25	0.84
31-92	1.82	0.89	0.27
30-152	1.89	0.63	0.15
62-31	1.36	0.88	1.00
61-92	1.65	0.65	0.28
61-152	2.05	0.58	0.15
72-36	1.67	0.93	0.84
124-31	1.57	0.61	1.00
t52-63	1.61	0.84	0.43
t9-32	1.95	2.90	0.98
t124-60	1.13	0.37	0.45

[a] The surface density (σ_{ol}) above which the PS buoys will overlap in the adsorbed layer.

Results and Discussion

Table III gives a summary of mass coverages, s (mg/m^2), for both tritium-labeled and nonlabeled diblock copolymers of PVP–PS as measured by scintillation counting and XPS. The code for individual samples represents the molecular weight of the constituent PVP–PS blocks in units of thousands. Also shown in column 3 is the adsorbed amount represented in terms of surface density σ ($\sigma = sN_{Av}/(M_{PVP} + M_{PS})$). The final column gives the surface density σ_{ol} above which the PS blocks are overlapping and form a semidilute solution in the adsorbed layer

$$\sigma_{ol} = 1/\pi R_{PS}^2 \qquad (9)$$

where R_{PS} represents the radius of gyration of the PS blocks in dilute toluene solutions. The data for R_{PS} in toluene has been reported by Higo et al.[31]

$$R_{PS} = aN_{PS}^\nu; \quad a = 1.86 \text{ Å}, \nu = 0.595 \qquad (10)$$

where a and N_{PS} represent the segment length and degree of polymerization of PS, respectively.

The adsorbed amounts are in good agreement with several values reported by Watanabe et al.[15] In those experiments, the thickness of dried adsorbed layers of PVP–PS deposited from toluene onto mica was measured with the surface force apparatus. Furthermore, with only three exceptions where the PVP is much larger than the PS block (PVP–PS 124-31, t124-60, and 62-31), the measured surface densities (σ) are larger than that required for the PS blocks to overlap in the adsorbed layer (σ_{ol}). On comparison of these results with the adsorption conditions in the surface force measurements of Patel et al.[12] and Watanabe et al.,[15] it appears that the osmotic interactions in the crowded brush layer at the measured surface density are sufficient to stretch the PS blocks and to be in the range of validity of eq 2.

Overall, with the range of molecular weights available to us, there is only a modest variation in the mass coverage. The fundamental information to be gleaned from the body of data in Table III is the effect of block molecular weight on the surface density. Figure 4 shows a plot of the experimentally measured surface densities of Table III as a function of both the PS and PVP degrees of polymerization. A reasonable expectation is that the surface
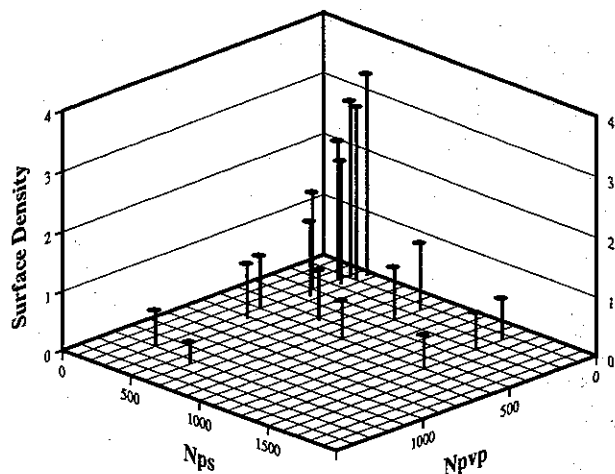
Figure 4. Measured surface densities σ (m^{-2} × 10^{-16}) of Table III as a function of both the PS (N_{PS}) and PVP (N_{PVP}) degrees of polymerization. Vertical lines are used to indicate heights of data points above their coordinates in the N_{PS}–N_{PVP} plane.

density is some function of the relative sizes of the two blocks. One generalization that can be drawn from Figure 4 is that σ generally decreases with the molecular weights of each block. Further information can be gleaned from two-dimensional slices of Figure 4. Parts a and b of Figure 5 illustrate the effect of block molecular weight on the surface density σ using a portion of the data from Table III and Figure 4. Qualitatively, for samples of moderate asymmetry (filled triangles, N_{PVP} = 600 and N_{PS} = 300), σ depends primarily on N_{PVP}, decreasing only slightly with increasing N_{PS}. This is in agreement with suppositions based on surface force measurements between adsorbed layers in solution, where a linear variation in the range of forces with N_{PS} suggests a relatively constant σ.[12,15] Furthermore, σ shows an apparent power law dependence on both N_{PS} and N_{PVP}. It should be noted that the majority of the data in Table III and Figure 4 fall in this regime. However, for samples having relatively large PS blocks, the variation of σ with N_{PVP} and N_{PS} is converse to that of more symmetric blocks. That is, σ decreases significantly with increasing N_{PS} while being less sensitive to N_{PVP}. The apparent power law dependence of σ on N_{PS} and N_{PVP}, and the magnitude of that dependence, can be discussed in the context of the theory by Marques et al.[2e]

To compare our experimental measurements with the theoretical analysis of Marques et al., we cast eq 7 in terms of the dimensionless surface density σ^*.

$$\sigma^* = \sigma/\sigma_{ol} = \pi a^2 \sigma N_{PS}^{6/5} \qquad (11)$$

The resulting rearrangement of eq 7 gives

$$\mu_{ex} = -(A\pi^2/6)c^2\beta^3(1/\sigma^{*3}) + (11/6\pi^{5/6})T\sigma^{*5/6} \qquad (12)$$

where $\beta = N_{PS}^{6/5}/N_{PVP}^{2/3}$ is an asymmetry ratio for the copolymer in solution that arises naturally from this analysis. According to eq 12, the molecular weight dependence of σ^* is principally in β. That is, at fixed μ_{ex} and Hamaker constant A, the theory predicts σ^* to be a unique function of β. Figure 6 shows the collapse in the experimental data of Table III and Figure 4 predicted from eq 12.

The effect of solution chemical potential on the adsorption properties can be evaluated by measuring adsorption isotherms. The effect of solution concentration on the adsorbed amount is shown in Figure 7 for the tritium-labeled sample PVP–PS t9-32 as measured by scintillation counting from the substrate. It is observed
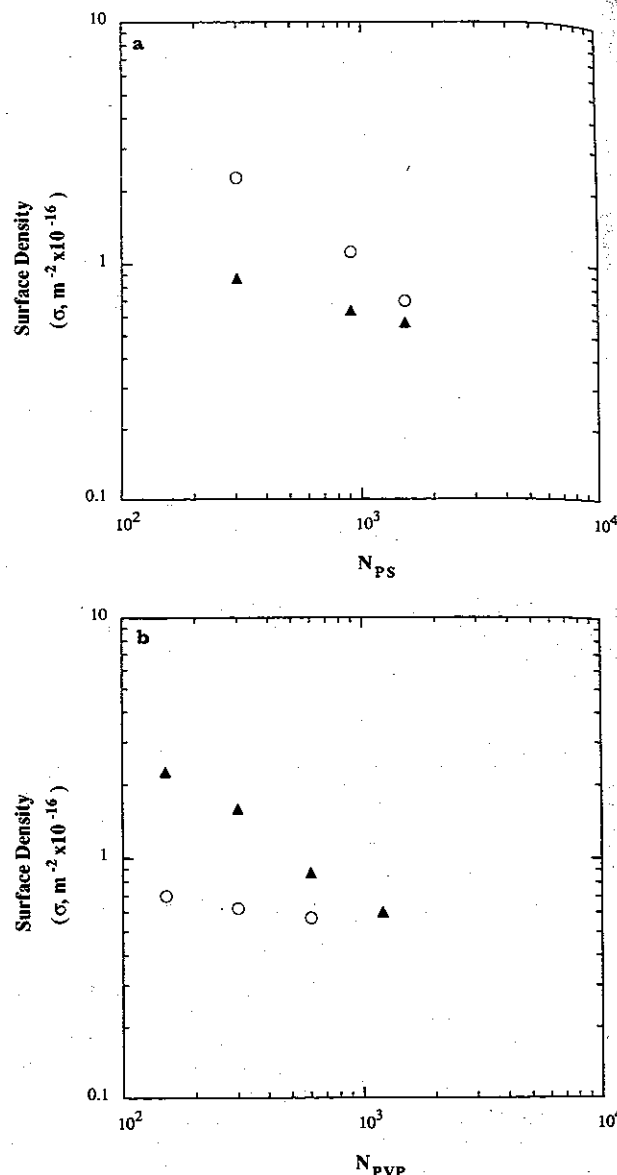

Figure 5. (a) Logarithmic plot of surface density σ versus PS degree of polymerization N_{PS} for N_{PVP} = 150 (circles) and N_{PVP} = 600 (filled triangles). (b) Variation of σ with N_{PVP} for constant N_{PS} = 300 (filled triangles) and N_{PS} = 1500 (circles).

that, over a range of dilute concentrations, σ is fairly insensitive to the concentration of the incubation solution. The chemical potential in the solution phase should change with the concentration c_s. Thus, the measured σ being insensitive to c_s suggests (for the PVP–PS t9-32) that a balance between the van der Waals energy of the PVP film and the free energy of the PS brush (the first and second terms in the right-hand side of eq 12) mainly determines σ and that μ_{ex} can be neglected. This is the behavior expected for the van der Waals–buoy regime discussed by Marques et al.[2e] For such cases, eq 12 predicts

$$\sigma^* = K(A/T)^{6/23}c^{12/23}\beta^{18/23} \qquad (13)$$

where K is a numerical constant of order unity ($K = \pi^{17/23}/11^{6/23}$). As suggested by eq 13, Figure 8 shows a plot of σ^* against $\beta^{18/23}$. The data are in good agreement with the linear predictions of eq 13, although deviations from the theoretical predictions start to appear for the five largest values of β ($\beta > 100$). This corresponds to the break in the curve of Figure 6. If these five values are held out of consideration, a linear least-squares fit to the power law region of a logarithmic plot of σ^* vs β gives a power
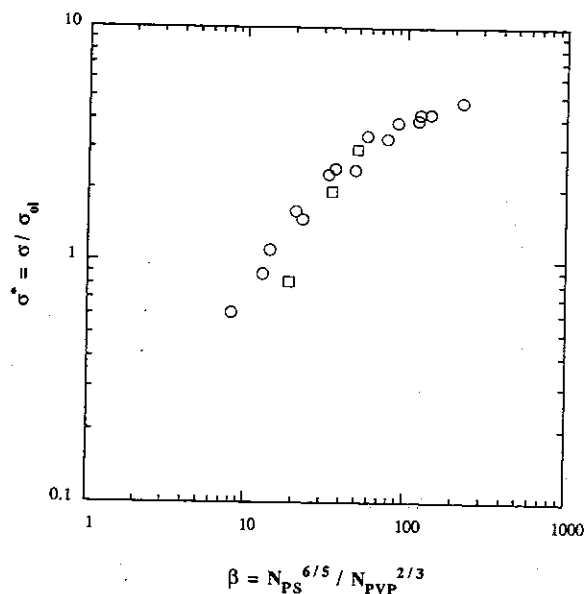
Figure 6. Normalized surface density $\sigma^* = \sigma/\sigma_{ol}$ versus copolymer asymmetry ratio $\beta = N_{PS}^{6/5}/N_{PVP}^{2/3}$ as determined by scintillation counting from tritium-labeled adsorbed layers (squares) and XPS (circles). σ_{ol} represents the surface density above which the PS buoys will overlap in the adsorbed layer ($\sigma_{ol} = 1/\pi R_{PS}^2$).
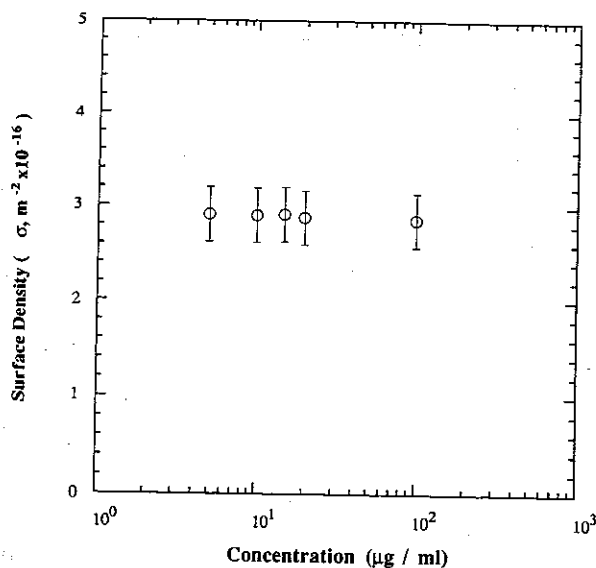

Figure 8. Normalized surface density σ^* versus $\beta^{18/23}$ as measured by scintillation counting from tritium-labeled adsorbed layers (squares) and XPS (circles). The solid line represents a least-squares fit to the linear portion of the data (excluding five data points at highest β values) as predicted from eq 13.

Figure 7. Adsorption isotherm over the solution concentration range 5–100 μg/mL for the tritium-labeled polymer PVP–PS t9-32.

Figure 9. Solubility diagram for PVP in toluene. Data on the right indicate the volume fraction PVP in the concentrated swollen polymer phase for a given PVP molecular weight.

law of 0.80, within experimental error of 18/23 (=0.78).

Figure 9 shows the experimentally measured solubility diagram for homo-PVP in toluene. The volume fraction of PVP in the concentrated and dilute phase is shown as a function of PVP molecular weight. The degree of swelling by the toluene of the adsorbed PVP film can be approximated by the volume fraction of PVP in the concentrated phase of the phase diagram.[2e] For higher PVP molecular weight samples (>30 000), the volume fraction polymer in the concentrated phase is approximately 50%. However, PVP becomes increasingly swollen with toluene as the molecular weight decreases. At a total volume fraction of 10%, samples of molecular weight 2000 and 7000 readily dissolved in toluene.

The solid line of Figure 8 represents a least-squares fit to the linear portion of the data. With use of a polymer volume fraction $c = 0.5$ as estimated from the solubility diagram and on application of eq 13, the slope of this line
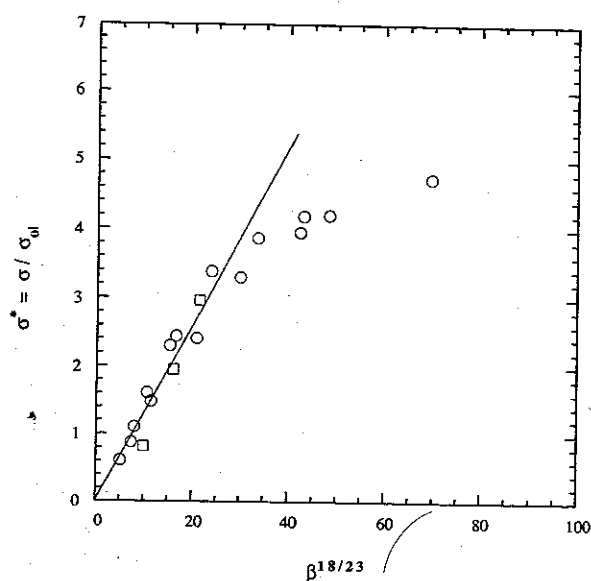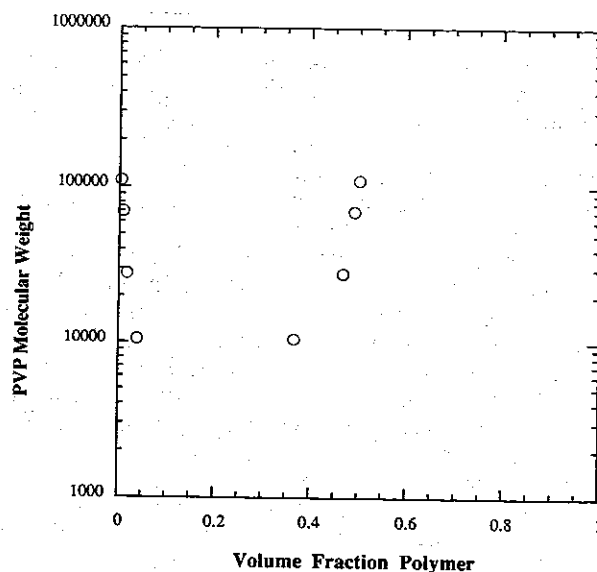
gives an effective Hamaker constant $A = 2.1 \times 10^{-24}$ J.

The deviation from the theoretical predictions in Figure 8 at large β ($\beta > 100$) corresponds to samples that have both high and low molecular weight PVP blocks. Thus it would appear this deviation cannot by entirely attributed to increased swelling of lower molecular weight PVP blocks. One possible explanation may be a contribution of the chemical potential in the solution phase (μ_{ex}) to σ^*, which we had neglected to obtain in eq 13. Another possible explanation may be the breakup of the uniformly wetting PVP film (assumed in the model) due to the relatively large asymmetry of these copolymers. However, theoretical analyses for μ_{ex} and more experiments should be conducted to fully understand this behavior.

Watanabe et al.[15] have published adsorbed amounts for the adsorption of PVP–poly(isoprene) (PI) block copolymers from toluene solutions onto smooth mica substrates. This system is similar to the adsorption of PVP–PS blocks in that toluene is a preferential solvent for the PI blocks.
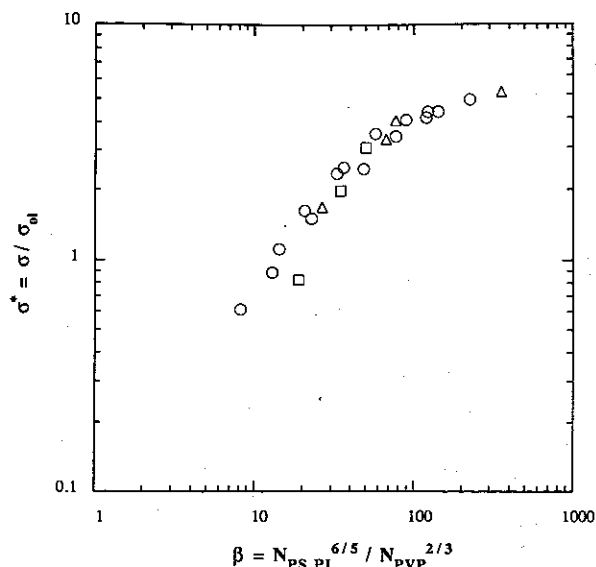
Figure 10. Normalized surface density σ^* versus copolymer asymmetry ratio β for the adsorption of PVP–PS block copolymers as measured by scintillation counting (squares) and XPS (circles) and for the adsorption of PVP–PI block copolymers as measured by Watanabe et al.[16] using the surface force apparatus (triangles).

PVP–PI adsorbed amounts were determined by measuring the thickness of the dried adsorbed layers using the surface force apparatus. Shown in Figure 10 is a plot of σ^* versus β for the adsorption of both PVP–PS and PVP–PI block copolymers as given in Table III and ref 15. Good agreement is found between the adsorption behavior of these two systems. This is probably in part due to the equivalence of the anchoring PVP block for these two copolymers and the good solvent characteristics of toluene for both PS and PI. Surface force measurements for PVP–PI in solution show similar behavior to the PVP–PS systems.[15] We have also found that the data of Stouffer and McCarthy[10] fit on the correlation of Figure 10; however, we are not sure that the interaction of the adsorbing PPS block in that case is similar to that of PVP in our work.

The question arises as to whether the measured surface densities are the product of a true molecular equilibrium or possibly that the path to equilibrium becomes kinetically blocked by the barriers to adsorption and desorption, which arise during the formation of these layers. The rate of exchange for adsorbed molecules of the tritium-labeled sample PVP–PS t9-32 with a solution of nonlabeled polymer of comparable molecular weight and composition is shown in Figure 11. The results indicate that molecules in the adsorbed layer seem not to readily exchange with those in solution. This observation merits further study.

During the XPS measurements of the dried PVP–PS adsorbed layers, the C_{1s} signal emanating from the PVP and PS blocks and the nitrogen signal of the PVP block were also monitored. Figure 12 shows the C_{1s}/N_{1s} ratio as a function of the takeoff angle θ. Data are shown for several samples of comparable PVP molecular weight. The increase in C/N with decreasing θ indicates a layered-type structure in the dry adsorbed films, with the PVP blocks being preferentially located at the substrate surface. The increase in C/N at lower takeoff angle with increasing PS molecular weight reflects the increased thickness of the PS layer as its molecular weight is increased. These data are supported by the contact angle measurements given in Table IV. The data represent recently advanced contact angles for a drop of water placed on the dry adsorbed layer. Also shown are the contact angles for a
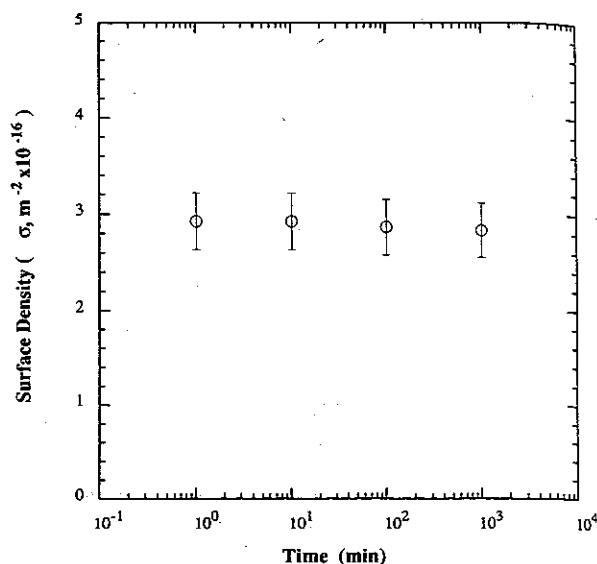

Figure 11. Surface density of tritium-labeled molecules versus exchange time for an adsorbed layer of the tritium-labeled polymer PVP–PS t9-32 in a solution of non-tritium-labeled PVP–PS 3-36.
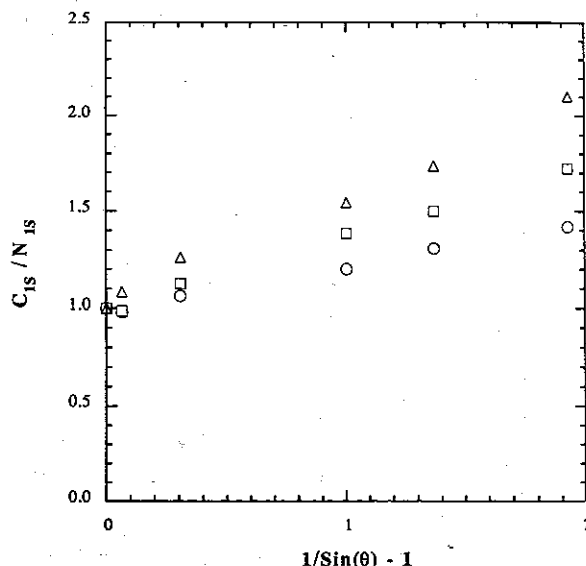

Figure 12. Variation of the carbon to nitrogen ratio C/N with takeoff angle θ as measured by XPS for the copolymers PVP–PS 62-31 (circles), t52-63 (squares), and 61-92 (triangles).

Table IV
Contact Angles for Water on Substrate, Homopolymer Films, and Dry Adsorbed Layers

sample	contact angle, deg	sample	contact angle, deg
polished silicon	25	31-92	87
homo-PVP	50	61-92	85
homo-PS	88	61-152	90
31-31	83		

polished silicon wafer containing a native oxide layer and spin-coated films of homo-PS and PVP. The contact angles for the dried adsorbed layers were very close to those for the homo-PS, reflecting the absence of PVP segments at the very outskirts of the dry adsorbed layer.

Conclusions

The effect of block molecular weight on the adsorbed amount is summarized by the experimental correlation of the normalized surface density σ^* with the asymmetry ratio β. Within this correlation we see two regimes of

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behavior. For polymers of moderate asymmetry $(10 < \beta < 100)$, σ^* varies with β in such a way that the actual surface density σ is determined primarily by the molecular weight of the anchoring block. The results in this range of β are in good agreement with the theory of Marques et al.[2e] where the surface density is determined by a balance between the van der Waals energy of the anchoring PVP film and the free energy of the PS brush. The correlation of σ^* with β is also in good agreement with adsorbed amounts for PVP–poly(isoprene) block copolymers deposited from toluene solutions as measured by Watanabe et al.[15] using the surface forces apparatus. The agreement between the data may be partly attributed to the identity of the anchoring block and the fact that toluene is a very good solvent for both PS and PI.

For samples of large asymmetry $(\beta > 100)$, we see behavior that is somewhat the converse of that described above. That is, for samples of very large PS blocks (relative to PVP), the surface density σ is determined primarily by the molecular weight of the well-solvated PS block, being somewhat insensitive to the molecular weight of the PVP block. An explanation of this regime will require future work, although it may be due to the effect of solution chemical potential or possibly breakup of the wetting PVP film as a result of the large asymmetry of these samples.

The dominance of the nonadsorbing block in determining the adsorbed amounts in this high size asymmetry situation is consistent with the observations made by Munch and Gast[32] and by Taunton et al.[33] in explaining the adsorption of end-anchored polymers. In those cases, one block is reduced essentially to monomeric size.

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