An Investigation of the Adsorption of Polystyrene/Poly(2-vinylpyridine) Diblock Copolymers onto Silver Substrates Using Surface-Enhanced Raman Scattering

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Received May 22, 1992; Revised Manuscript Received November 10, 1992

ABSTRACT: Adsorption of polystyrene/poly(2-vinylpyridine) (PS/P2VP) diblock copolymers having molecular weights of 152K and 15K in the PS and P2VP blocks, respectively, onto silver island films from toluene solutions was investigated using surface-enhanced Raman scattering (SERS). The length of the P2VP blocks was short compared to that of the PS blocks so that only bands characteristic of the PS blocks were observed in the normal Raman spectra of the diblock copolymers. When adsorption was carried out from solutions having concentrations above the critical micelle concentration (cmc), the SERS spectra were a strong function of the adsorption time. For an adsorption time of 2 min, the SERS spectra were similar to the normal Raman spectra of the diblock copolymer and only bands characteristic of the PS blocks were observed. However, for adsorption times of 1 and 5 days, bands related to the PS blocks decreased in intensity and bands related to the P2VP blocks increased. These results indicated that micelles were initially adsorbed from solutions above the cmc. However, the micelles unfolded on the silver surface as a function of time as P2VP was gradually chemisorbed. When the adsorption was carried out at solution concentrations below the cmc, the SERS spectra were similar to the normal Raman spectra of the copolymer and only bands characteristic of the PS blocks were observed regardless of the adsorption time. It was concluded that, in this case, the P2VP blocks were chemisorbed onto the silver surface and that the PS blocks extended into the solution. However, due to repulsive interactions between the PS blocks, the coverage of the surface by the P2VP blocks was very low and many surface sites remained unoccupied. During drying, the PS blocks collapsed onto the surface and occupied those sites.

I. Introduction

Block copolymers exhibit inherent interfacial activity which makes them useful as surfactant molecules. This surfactancy is related to their high molecular weight which magnifies the small differences in chemical affinity between the monomers and produces a strong tendency to straddle phase boundaries. Because of the surface activity of block copolymers, there has been a great deal of recent interest in the kinetics of adsorption and the molecular structure of the interfaces.

Tassin et al.[1] investigated the kinetics of adsorption of polystyrene/poly(2-vinylpyridine) (PS/P2VP) diblock copolymers from toluene solutions onto silver substrates by measuring changes in the surface plasmon resonance. It was found that the kinetics strongly depended on the solution concentration and the composition of the copolymer. Tassin et al. described the interface as a thin layer of P2VP and a brush of extended PS chains. However, their techniques did not provide direct evidence for the proposed interfacial structure.

Munch and Gast[2] determined the kinetics of adsorption of polystyrene/poly(ethylene oxide) (PS/PEO) diblock copolymers having long PS blocks and short PEO blocks onto glass and sapphire substrates. They found that the copolymers adsorbed strongly onto both substrates even though PS homopolymers did not adsorb onto either. The initial rate of adsorption varied linearly with concentration above and below the critical micelle concentration (cmc) but with a weaker dependence above the cmc. Differences in the dependence on concentration suggested two adsorption mechanisms, adsorption of single chains below the cmc and adsorption of micelles above the cmc. Munch and Gast suggested that the micelles adsorbed with an unfolding of the micelles so that the PEO blocks would contact the surface or that the PS blocks screened the attraction between the PEO blocks and the surface. However, their experimental technique did not permit them to determine the molecular structure of the adsorbed films.

Tirrell and co-workers[3] used the surface forces apparatus to measure the forces between cleaved mica cylinders bearing adsorbed PS/P2VP diblock copolymers. When the experiments were carried out in toluene, which is a good solvent for PS but a poor solvent for P2VP, the forces were repulsive. The results showed that the P2VP blocks were adsorbed strongly onto the mica surface and that the PS blocks were forced into an extended configuration away from the surface.

Parsonage et al.[4] used scintillation counting techniques to determine the effect of the relative block length (asymmetry) on the amount of PS/P2VP diblock copolymer adsorbed from toluene solution onto oxidized silicon and mica substrates. For copolymers with moderate asymmetry, the surface density decreased as the chain length of the PVP blocks increased. However, for copolymers with a high degree of asymmetry, the surface density depended more on the size of the PS blocks and less on that of the P2VP blocks. The adsorbed amount decreased as the chain length of the PS blocks increased.

Stouffer et al.[5] used XPS and liquid scintillation counting techniques to investigate the behavior of diblock copolymers of polystyrene and poly(propylene sulfide) (PS/PPS) adsorbed from solution onto gold. Considering the affinity of sulfur for gold, strong adsorption through the PPS blocks was expected. It was observed that the

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amount adsorbed on the surface was a function of the size of the PPS blocks, indicating that the PPS blocks interacted directly with the surface, forcing the PS blocks away from the surface.

Balazs and Gempe[6] developed Monte Carlo techniques to model the adsorption of AB diblock copolymers from solution onto a solid surface. The A moieties were assumed to be attracted to the surface, but the B moieties were not. For the same copolymer composition, different adsorbed structures were obtained depending on whether the copolymers were alternating, random, blocky, or diblock. It was concluded that diblock copolymers had the highest fraction of A moieties bound to the surface among the four different copolymers.

None of the investigations described above provided direct evidence for the molecular structure of the interface between the diblock copolymers and the substrates. However, surface-enhanced Raman scattering (SERS) seems ideal for this purpose. SERS is a process in which the Raman scattering cross section of molecules adsorbed onto the roughed surfaces of certain metals is enhanced by as much as 10^6 compared to the cross section for normal Raman scattering. Two mechanisms appear to be responsible for most of the enhancement. One is associated with the large electric fields that can exist at the surfaces of metal particles with small radii of curvature and is only obtained for metals for which the complex part of the dielectric constant is small. The other mechanism is related to distortions of the polarizability of the adsorbed molecules by formation of charge-transfer complexes with the metal surface. Enhancement due to the charge-transfer mechanism is restricted to molecules immediately adjacent to the substrate, but enhancement due to the electromagnetic mechanism may extend several molecular layers away from the metal surface. The enhancement decreases very quickly as a function of distance, and little enhancement is obtained for molecules that are more than a few monolayers away from the surface. As a result, SERS is surface selective and can be used for in-situ, nondestructive characterization of interfaces between polymers and metals.

Several applications of SERS to polymer systems have been reported. Boerio et al.[7] investigated SERS from poly(α-methylstyrene) (PMS) spin-coated onto silver island films from methyl ethyl ketone solutions having different concentrations. They found that the intensity of the bands due to PMS was constant even though the film thickness varied from 300 to 2000 Å. These results indicated that SERS is an interfacial rather than bulk effect.

Venkatachalam et al.[8] investigated SERS from polymer bilayers deposited onto silver island films. Raman scattering was observed from the polymer film which was directly adjacent to the silver surface but not from the overlayer as long as the thickness of the first polymer film was more than approximately 100 Å. These results again confirmed that SERS is an interfacial effect and that the enhancement extends no more than a few molecular layers from the silver surface.

SERS can also provide direct information regarding the bonding and orientation of adsorbed molecules on metal surfaces. Roth and Boerio[9] investigated poly(4-vinylpyridine) (P4VP) adsorbed onto silver surfaces. Considering the selection rules for Raman scattering by molecules adjacent to metal substrates,[10] Roth and Boerio concluded that P4VP was adsorbed onto the silver surface through the nitrogen atoms with a vertical conformation in which the 2-fold symmetry axes of the pyridine rings were perpendicular to the silver surface. Moreover, the shift of the band assigned to the ring breathing mode $\nu(1)$ from 997 to 1020 cm^{-1} indicated the presence of pyridinium ions or coordinated pyridine at the silver surface due to the adsorption through the nitrogen atoms.

Very recently, Tsai et al. investigated SERS from symmetric PS/P2VP diblock copolymers having molecular weights of 60K in each block adsorbed onto silver island films from 0.05% solutions in toluene.[11] Bands near 1615 and 1041 cm^{-1} related to the PS blocks were only weakly observed in the SERS spectra of PS/P2VP diblock copolymers, but those near 1073 and 1585 cm^{-1} related to P2VP blocks were relatively strong in intensity. Since SERS had previously been shown to be an interfacial rather than a bulk effect, the results obtained indicated that the P2VP blocks were adsorbed onto the silver substrates while the PS blocks were positioned away from the surface.

The purpose of this paper is to report results that we have obtained using surface-enhanced Raman scattering to investigate the adsorption of PS/P2VP diblock copolymers consisting of a long chain of PS and a short chain of P2VP from solution onto silver substrates. Our results show that when these highly asymmetric copolymers were adsorbed from solutions having concentrations above the critical micelle concentration, the molecular structure of the interface depended strongly on adsorption time. For short times, the PS blocks were adsorbed. However, as the adsorption time increased, the P2VP blocks displaced the PS blocks. When adsorption was carried out from solutions having concentrations below the critical micelle concentration, only PS blocks were detected on the silver surface regardless of time. Complementary results were obtained using angle-resolved X-ray photoelectron spectroscopy (XPS) and ellipsometry.

II. Experimental Section

Substrates for SERS were prepared by slow thermal evaporation of silver films onto glass slides. The glass slides were first immersed in a 0.1 N NaOH solution for 1 h and then rinsed in a 0.1 N HCl solution for 1 h. After that the slides were ultrasonically cleaned in deionized water and blown dry using nitrogen. Silver was evaporated onto the cleaned glass slides at a rate of about 1 Å/s to a thickness of about 40 Å using a vacuum chamber equipped with sorption, sublimation, and ion pumps. The evaporation rate and thickness were controlled by a quartz crystal oscillator thickness monitor.

PS and P2VP homopolymers were purchased from Polyscience, Inc., and used as-received. PS/P2VP diblock copolymers consisting of PS blocks with a molecular weight of 152K and P2VP blocks with a molecular weight of 15K were synthesized by anionic polymerization.

Solutions of homopolymers were made by adding 5 mg of PS and P2VP to 10 g of toluene and methanol, respectively. Stock solutions for PS/P2VP diblock copolymers were made with two different concentrations. One was prepared by the addition of 8 mg of PS/P2VP diblock copolymers to 80 mL of toluene (0.01% solution). The other was prepared by the addition of 5 mg of PS/P2VP diblock copolymers to 100 mL of toluene (0.005% solution). In order to assure that the polymers dissolved completely, both stock solutions were warmed in an oven at 40 °C for 10 days. After removal from the oven, the solutions were clear, indicating that all the polymer had dissolved. The stock solutions were then allowed to cool to room temperature. However, after several hours, a trace of white precipitate appeared at the bottom of the vial containing the 0.01% solution. The solution which had a concentration of 0.005% was always clear after cooling to room temperature.

Several milliliters of the clear, saturated solution was taken from the upper portion of the 0.01% stock solution using a pipette and divided into small vials. Since a small amount of the polymer had precipitated, the concentration of this saturated solution was slightly less than 0.01%. However, this solution will be referred to as having a concentration of 0.01%. The solution

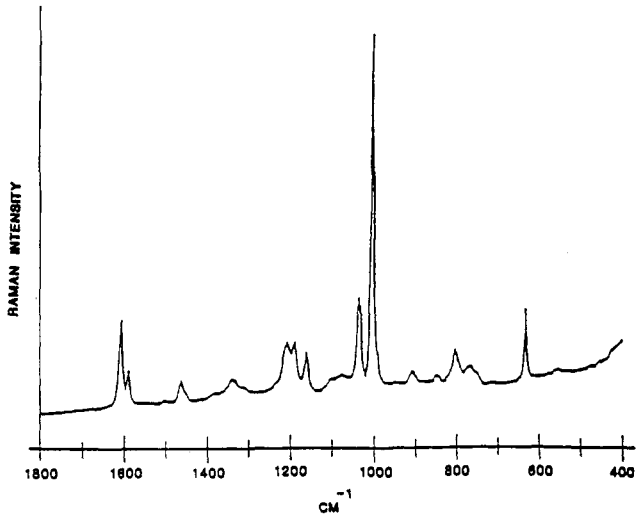

Figure 1. Normal Raman spectrum of polystyrene.

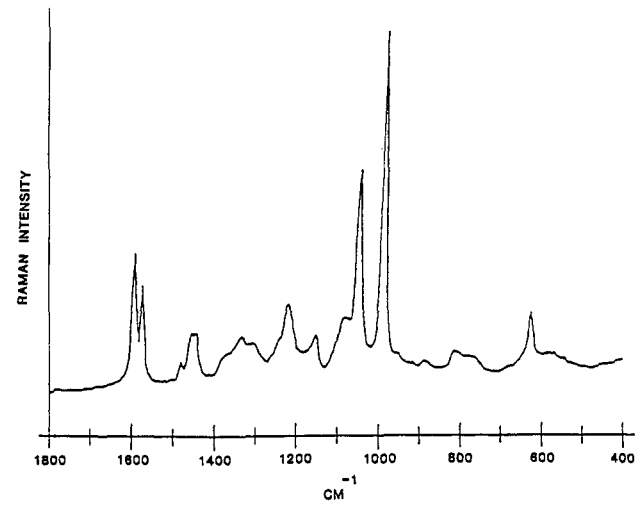

Figure 2. Normal Raman spectrum of poly(2-vinylpyridine).

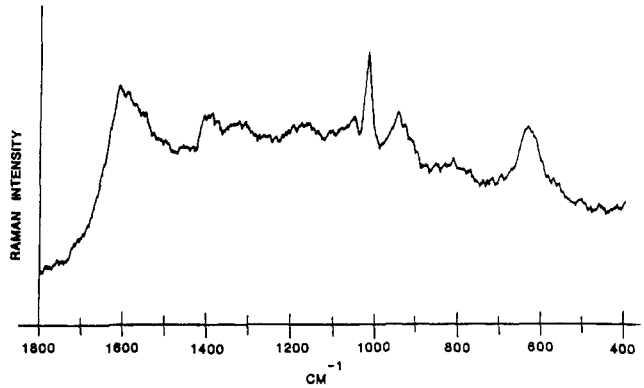

Figure 3. SERS spectrum obtained from a thin film of polystyrene spin-coated onto a silver island film from a 0.05% solution in toluene.

having a concentration of 0.005% was also divided into small vials. SERS substrates were immersed in the copolymer solutions in the vials for several days in order to determine the effect of adsorption time on the configuration of PS/P2VP diblock copolymers adsorbed onto the silver surface. The silver substrates were then removed from the solutions and spun dry, and SERS spectra were obtained.

Thin films of PS and P2VP homopolymers were spin-coated onto SERS substrates from solutions in toluene and methanol, respectively. The solutions were allowed to contact the substrates for 2 min before spinning.

All Raman spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, ITT FW-130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. In the SERS experiments, the slits of the monochromator were set for a spectral resolution of 10 cm^{-1}. The laser beam was incident on the SERS samples at an angle at 65° relative to the normal of the sample surface. Scattered light was collected by an $f/0.95$ lens and focused onto the entrance slit of the monochromator. Spectra were obtained with the 5145-Å line of the laser, a time constant of 10 s, and a scan rate of 50 cm^{-1}/min for the long-range spectra (from 400 to 1800 cm^{-1}) or 25 cm^{-1}/min for the short-range spectra (from 900 to 1100 cm^{-1}). Similar techniques were used for obtaining normal Raman spectra, but the slit width was narrowed to 5 cm^{-1} and the time constant was 2 s.

Similar procedures were used to prepare samples for X-ray photoelectron spectroscopy (XPS). Glass slides coated with thick films of silver were immersed into solutions of PS/P2VP diblock copolymers for 1 day, removed, and rinsed with toluene. Finally, the residual solvent was removed by spinning the coated samples.

XPS spectra were obtained using a Perkin-Elmer 5300 ESCA spectrometer with Mg Kα radiation at a power of 300 W. The pass energy was 44.8 (0.5 eV/step) and 17.9 eV (0.05 eV/step) for the survey and high-resolution spectra, respectively. The pressure in the test chamber was kept between 10^{-8} and 10^{-9} Torr. Take-off angles (angle between the sample surface and the direction of propagation of the ejected electrons) of 15, 45, and 75° were used to obtain XPS spectra.

In order to determine the thickness of the organic films on the substrates, thick (several hundred angstroms) films of silver were evaporated onto glass slides. Polymer films were coated onto the silver mirrors using the same solutions and procedures as were used to prepare SERS and XPS samples. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the silver substrates before and after depositing the organic films.

III. Results and Discussion

The normal Raman spectra of polystyrene (PS) and poly(2-vinylpyridine) (P2VP) homopolymers are shown in Figures 1 and 2, respectively. Most of the observed bands were assigned to vibrations of the benzene or pyridine rings using Wilson's numbering system[12] and have been discussed elsewhere.[11]

Differences in frequency between bands in the normal Raman spectra of PS and P2VP were observed. The very strong band near 1005 cm^{-1} in the normal Raman spectra of P2VP was attributed to $\nu(1)$, the totally symmetric ring breathing mode, while the same vibrational mode was near 1012 cm^{-1} in the normal Raman spectra of PS. The band due to the ring stretching mode $\nu(8a)$ was observed near 1612 cm^{-1} in the PS spectrum and near 1602 cm^{-1} in the P2VP spectrum. The band near 1040 cm^{-1} was assigned to $\nu(18a)$ in the PS spectrum while the band near 1064 cm^{-1} was assigned to $\nu(18b)$ in the P2VP spectrum. As a result of these differences in the spectra, the PS and P2VP blocks in the PS/P2VP diblock copolymer could easily be distinguished.

The SERS spectrum obtained from a thin film of PS spin-coated onto a silver island film from a 0.05% solution in toluene is shown in Figure 3. Only the bands related to $\nu(1)$, $\nu(18a)$, and $\nu(8a)$ were clearly visible in this spectrum, near 1014, 1040, and 1615 cm^{-1}, respectively. The SERS spectrum of P2VP is shown in Figure 4. Only the bands assigned to $\nu(1)$ and $\nu(18b)$ were observed near 1015 and 1073 cm^{-1} in the SERS spectra of P2VP.

The position and relative intensity of the bands observed in the SERS and normal Raman spectra of PS were very similar (see Figures 1 and 3), indicating that PS may be physically adsorbed to the silver surface. However, the SERS and normal Raman spectra of P2VP shown in Figures 2 and 4, respectively, were much different. The strong band assigned to the symmetric ring breathing mode was observed near 1005 cm^{-1} in the normal Raman

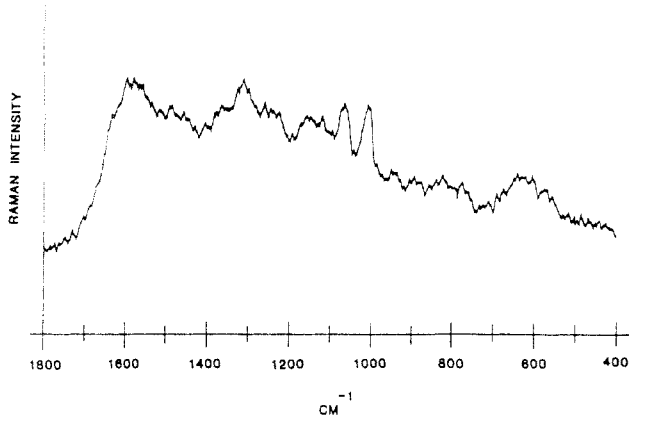

Figure 4. SERS spectrum obtained from a thin film of poly(2-vinylpyridine) spin-coated onto a silver island film from a 0.05% solution in methanol.

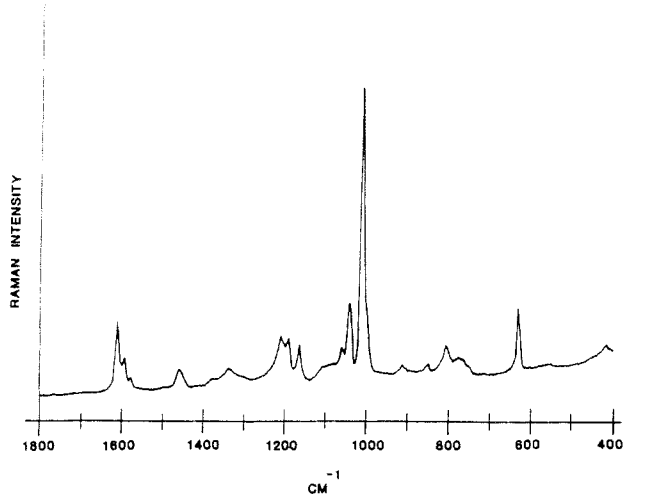

Figure 5. Normal Raman spectrum of a diblock copolymer having polystyrene and poly(2-vinylpyridine) blocks with molecular weights of 152K and 15K, respectively.

spectrum but shifted to near 1015 cm^{-1} in the SERS spectrum and became relatively weak. A medium-intensity band due to the CH bending mode which was observed near 1064 cm^{-1} in the normal Raman spectrum became relatively strong in the SERS spectra and shifted upward to 1073 cm^{-1}. As discussed later, these differences indicate that P2VP interacts with silver substrates through the pyridine nitrogen.

The normal Raman spectrum obtained from a PS/P2VP diblock copolymer consisting of a long chain of PS blocks with molecular weight about 152K and a relatively short chain of P2VP blocks with molecular weight around 15K is shown in Figure 5. Since the chain length of P2VP in this diblock copolymer was relatively small, only bands characteristic of PS were observed.

SERS spectra of PS/P2VP (152K/15K) diblock copolymers adsorbed onto silver island films from 0.01% solutions in toluene were obtained as a function of adsorption time. For a time of 2 min, the SERS spectra of the diblock copolymers (see Figure 6A) were similar to those of PS. The spectra were characterized by a strong band near 1015 cm^{-1} and a weak band near 1040 cm^{-1}. The band near 1015 cm^{-1} was due to both PS and P2VP, while the band near 1040 cm^{-1} was related to PS only. The band near 1072 cm^{-1} due to P2VP blocks was not observed in the SERS spectra of diblock copolymers adsorbed onto silver for 2 min. The appearance of the band near 1040 cm^{-1} due to PS and the lack of a band near 1074 cm^{-1} indicated that the SERS spectra of diblock copolymers

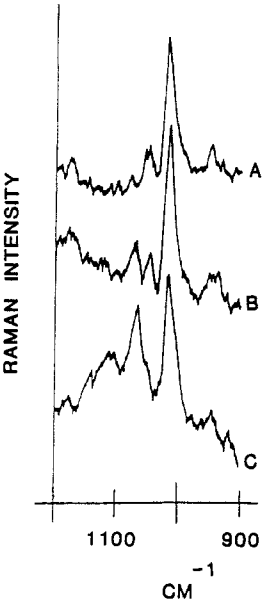

Figure 6. SERS spectra of a diblock copolymer having polystyrene and poly(2-vinylpyridine) blocks with molecular weights 152K and 15K, respectively, adsorbed onto a silver island film from a 0.01% solution in toluene for (A) 2 min, (B) 1 day, and (C) 5 days. The polymer film thicknesses were 20, 45, and 80 Å, respectively.

obtained after an adsorption time of 2 min were dominated by PS blocks.

When the adsorption time was increased, the SERS spectra of the diblock copolymers changed significantly (see parts B and C of Figure 6). After an adsorption time of 1 day, the band characteristic of P2VP appeared near 1074 cm^{-1} and the band near 1040 cm^{-1} related to PS decreased in intensity. When the adsorption time was extended to 5 days, the SERS spectra of the diblock copolymers (see Figure 6C) were dominated by bands near 1015 and 1072 cm^{-1} characteristic of the P2VP blocks. Since SERS is surface selective and the enhancement decreases quickly as a function of distance from the silver surface, it was evident that the PS blocks adsorbed directly to the silver substrate for short times. However, for long adsorption times, a rearrangement occurred and the P2VP blocks were adsorbed onto the silver surface while the PS blocks were directed away from the surface.

The film thickness measured by ellipsometry increased from 20 to 80 Å as the adsorption time increased from 2 min to 5 days, indicating that the adsorbed amount also increased. Since the bands characteristic of P2VP were shifted upward from near 995 and 1064 cm^{-1} in the normal Raman spectrum to near 1015 and 1074 cm^{-1}, respectively, in the SERS spectrum of the diblock copolymers, it was concluded that P2VP was chemisorbed to the silver surface through the nitrogen atoms.

The dependence of the SERS spectra on time for adsorption from solutions having concentrations of 0.01% was probably related to unfolding of micelles (see Figure 7). Munch and Gast[2] suggested that, at concentrations above the cmc, micelles adsorbed first followed by single chains.

Since toluene was a good solvent for the PS blocks but a poor solvent for the P2VP blocks, micelles were expected to form in solutions of PS/P2VP block copolymers at concentrations above some critical micelle concentration (cmc). We did not measure the cmc for the copolymers used here, but, as noted above, it was expected to be close to 0.0065% which Tassin et al. determined to be the cmc for PS/P2VP diblock copolymers having molecular weights

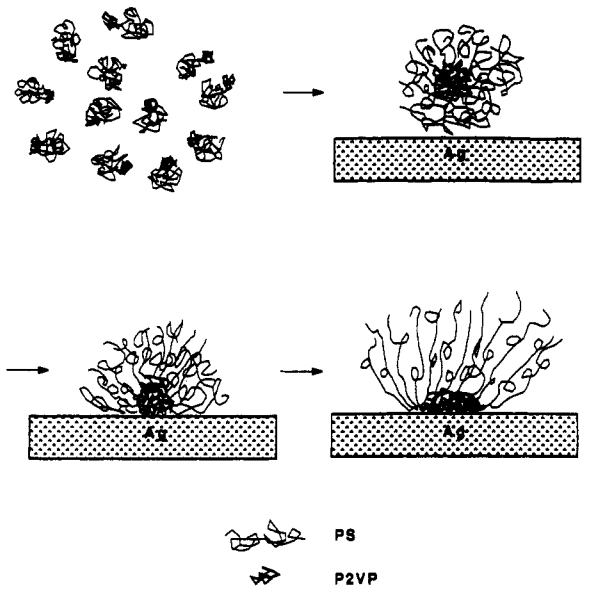

Figure 7. Model for polystyrene/poly(2-vinylpyridine) diblock copolymers adsorbed onto the silver surface from toluene solutions having a concentration above the cmc.

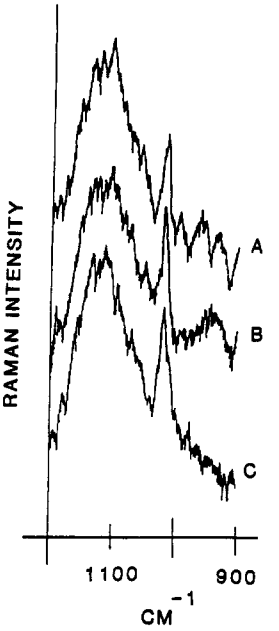

Figure 8. SERS spectra of a diblock copolymer having polystyrene and poly(2-vinylpyridine) blocks with molecular weights 152K and 15K, respectively, adsorbed onto silver island films from a 0.005% solution in toluene for (A) 2 min, (B) 1 day, and (C) 5 days. The polymer film thicknesses were 18, 35, and 45 Å, respectively.

of 60K/5K and 60K/60K.[1] Moreover, the 0.01% PS/P2VP diblock copolymer solutions used here were actually saturated solutions and their concentration was thus above the cmc.

Therefore, the P2VP blocks were initially screened from the silver surface by PS blocks as the micelles adsorbed. In that case, bands due to PS were expected to be strong in SERS spectra and bands due to P2VP were expected to be weak. Reference to Figure 6 shows that this is what was observed.

Since the PS blocks did not chemisorb to the silver surface, the adsorbed micelles may have rearranged their configuration after a long adsorption time,[2] leading to unfolding of micelles and enabling P2VP blocks to adsorb onto the surface because of the strong interaction between silver and pyridine nitrogen. In that case, the intensity of the bands in the SERS spectra due to P2VP was expected to increase. Reference to Figure 6 shows that this was also observed.

Mirkin found that the band assigned to the symmetric ring breathing mode $\nu(1)$ in the normal Raman spectrum of 2-vinylpyridine (2VP) shifted upward by about 19 cm^{-1} in the SERS spectrum of 2VP adsorbed onto silver sols.[13] This upward shift in frequency of the band attributed to $\nu(1)$ was related to σ-bonding between the ring nitrogen atoms and the silver atoms. σ-Bonding of the pyridine ring resulted in a shift of $\nu(1)$ to lower frequencies. Therefore, it was concluded that 2VP was adsorbed through σ-bonding in the nitrogen atom. Lippert and Brandt also found that the band assigned to $\nu(1)$ was shifted from near 998 cm^{-1} in the normal Raman spectrum of P2VP to near 1010 cm^{-1} in the spectrum of $P2VPH^+Cl^-$ and to near 1008 cm^{-1} in the SERS spectrum of protonated P2VP adsorbed onto silver electrodes from aqueous salt solutions at potentials between −0.4 and −1.0 V.[14] We observed similar band shifts in SERS spectra of PS/P2VP diblock copolymers adsorbed onto silver island films, indicating that P2VP was chemically adsorbed through the nitrogen atoms.

It is interesting to note that the band near 1073 cm^{-1} which was assigned to $\nu(18b)$ was strong relative to the band near 1015 cm^{-1} in the SERS spectra of P2VP (see Figure 4). The intensity of this band may be related to an orientation effect. If P2VP was adsorbed through the nitrogen atoms with an edge-on configuration, the eigenvector for the band near 1073 cm^{-1} would involve atomic motions perpendicular to the silver surface and the band would be relatively strong in the SERS spectra.[10]

We also investigated the effect of solution concentration on the configuration of PS/P2VP diblock copolymers adsorbed onto the silver surface. The thickness of the films adsorbed from solutions having concentrations of 0.005%, which was assumed to be below the critical micelle concentration, was about 18, 35, and 45 Å after 2 min, 2 days, and 5 days adsorption time, respectively, and was thus less than that of films adsorbed from solutions having concentrations of 0.01%. As discussed above, films adsorbed from 0.01% solutions had thicknesses that varied from 20 to 80 Å for adsorption times of 2 min and 5 days, respectively. The signal-to-noise ratio in the SERS spectra was much lower for the thinner films adsorbed from solutions having concentrations of 0.005% than for the thicker films adsorbed from solutions having concentrations of 0.01% and was consistent with the lower adsorbed amounts from the more dilute solutions.

SERS spectra of PS/P2VP diblock copolymers adsorbed from solutions having a concentration of 0.005% for times between 2 min and 5 days are shown in Figure 8. Since the concentration of these solutions was below the cmc, single chains but no micelles were expected to be present in the solutions. Only bands characteristic of PS were observed near 1015 and 1040 cm^{-1} in the SERS spectra regardless of the adsorption time (see Figure 8). No bands characteristic of P2VP were observed in the spectrum even when the adsorption time extended to 5 days.

Two explanations for these observations were considered. One was that the P2VP blocks were adsorbed onto the silver surface and the PS blocks extended away from the surface into the solution. However, due to the repulsive interaction between PS blocks in the diblock copolymer solutions, the amount of PS/P2VP diblock copolymers adsorbed onto the silver surface would reach saturation soon. Furthermore, it was expected that P2VP blocks adsorbed with a dense globule configuration on the silver

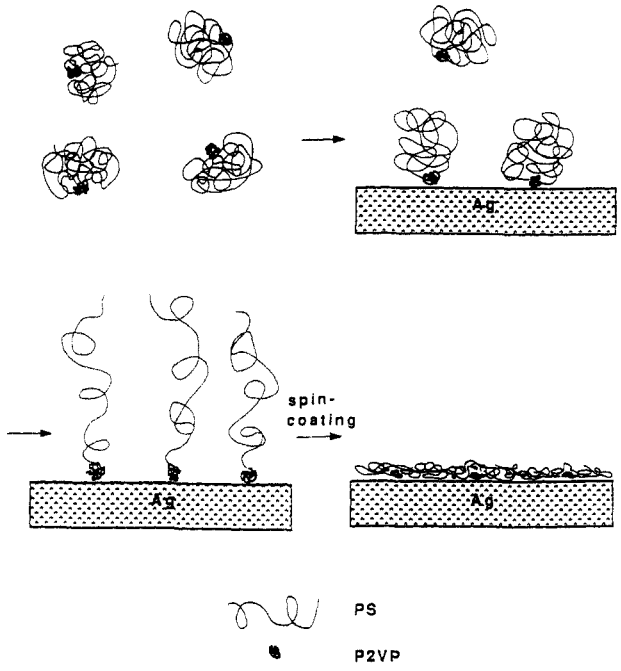

Figure 9. Model for polystyrene/poly(2-vinylpyridine) diblock copolymers adsorbed onto the silver surface from toluene solutions having a concentration below the cmc.

surface. In that regard, only a few segments of 2VP were directly attached to the silver-active sites and hence the coverage of the surface by P2VP was very low (see Figure 9). Therefore, the PS blocks, which extended into solution during adsorption, collapsed onto the surface when the samples were spun dry and occupied vacant sites. In this case, only bands characteristic of PS would be observed in the SERS spectrum.

The other explanation which was considered was that both PS and P2VP blocks adsorbed onto the silver substrates in a flattened configuration. However, the strong interaction between PS and toluene would be unfavorable for strong adsorption of PS onto the silver surface. Therefore, the first explanation was considered most likely.

There is considerable support for our interpretation of the SERS spectra of the diblock copolymer adsorbed onto silver from solutions having concentrations below the cmc. As discussed above, Tirrell et al.[3] measured the surface forces between cleaved mica cylinders bearing PS/P2VP diblock copolymers which were adsorbed from toluene solutions at concentrations below the cmc. They found that the forces were repulsive and that the distance between mica cylinders at which the forces became significant increased as the chain length of the PS block increased. This distance was approximately 10 times the radius of gyration of PS, indicating that the PS blocks adopted an extended conformation in the solution.

Motschmann et al.[15] determined the conformation of PS/PEO diblock copolymers adsorbed onto substrates from solutions having concentrations below the cmc by measuring surface concentration and adsorbed film thickness.[2,15] They suggested that the diblock copolymer initially adsorbed via a mushroom conformation on the surface and that the surface coverage was very low. As the adsorption time increased, more chains arrived at the surface through diffusion and the polymer molecules began to overlap. As a result, in order to allow more chains to continuously adsorb to the surface, the PEO blocks remained attached to the surface while the PS blocks were forced away from the surface. At this point, the configuration of the adsorbed polymer changed from "mushroom" to "brush" and the surface coverage became larger. However, the surface coverage soon reached saturation due to repulsive interactions between the PS blocks in the solutions.

Table I. Atomic Concentrations in Films of Polystyrene/Poly(2-vinylpyridine) Diblock Copolymers Adsorbed from Toluene Solutions onto Silver Substrates

take-off angle (deg)	element	concn (%)	N/C (%)
15	N	0.9	0.9
	C	97.0	
	O	1.2	
	Ag	0.9	
45	N	1.5	1.7
	C	91.8	
	O	2.6	
	Ag	4.1	
75	N	2.4	2.7
	C	86.0	
	O	4.2	
	Ag	7.4	

Munch and Gast[2] showed that surface coverage increased with increasing size of the anchor blocks and decreased with increasing size of the tail blocks. So, diblock copolymers consisting of large PS (152K) and small P2VP (15K) blocks adsorbed onto the silver surface would result in small final surface coverage in our experiments. The P2VP blocks did not form a dense layer at the surface region, and many surface sites were still available. After removing these samples from solution and spinning them, the dangling PS blocks collapsed onto the surface and occupied the remaining surface sites.

A series of XPS experiments was carried out to complement the SERS results obtained from PS/P2VP diblock copolymers adsorbed onto the silver surfaces. The results are summarized in Table I. Substrates consisting of glass slides coated with thick silver films were first examined by XPS. No peaks characteristic of nitrogen were observed, indicating that there was no nitrogen on the as-prepared silver substrates. The silver substrates were immersed into the PS/P2VP solution having a concentration of 0.01%, which was above the cmc, for 2 days, removed, and rinsed with toluene. The thickness of the polymer film was determined to be around 40 Å by using ellipsometry to examine the substrates before and after adsorption of the copolymer films. Since nitrogen was characteristic of P2VP, the ratio of the atomic concentrations of nitrogen and carbon (N/C) could be used to determine the composition of the copolymers in the near interface region. The N/C ratio was expected to be 1.1% for the bulk PS/P2VP (152K/15K) diblock copolymer. However, the observed N/C ratios increased from 0.9% to 2.7% as the take-off angle was increased from 15° to 75°. At the same time, the atomic concentration of silver increased from 0.9% to 7.4%, indicating that the copolymer films were approximately 1 electron mean free path in thickness. Therefore, the increase in the N/C ratio with increasing take-off angle or sampling depth for the thin films of PS/P2VP (152K/15K) diblock copolymer suggested that the P2VP block of the PS/P2VP diblock copolymer was enriched at the silver surface. These results were consistent with the SERS observations.

IV. Conclusions

Adsorption of highly asymmetric polystyrene/poly(2-vinylpyridine) diblock copolymers having long polystyrene blocks and short poly(2-vinylpyridine) blocks onto silver island films from toluene solutions was investigated using surface-enhanced Raman scattering (SERS). When ad-

sorption was carried out from solutions having concentrations above the critical micelle concentration, the SERS spectra were a strong function of the adsorption time. For short adsorption times, only bands characteristic of the polystyrene blocks were observed in the SERS spectra. For long adsorption times, the bands related to polystyrene blocks decreased in intensity and those related to poly(2-vinylpyridine) increased in intensity. It was concluded that micelles were initially adsorbed from solutions having concentrations above the cmc, but the micelles unfolded on the silver surface as a function of time as poly(2-vinylpyridine) was gradually chemisorbed.

When the adsorption was carried from solutions having concentrations below the cmc, the SERS spectra were always similar to the normal Raman spectra and only bands characteristic of the polystyrene blocks were observed. It was concluded that the poly(2-vinylpyridine) blocks were adsorbed onto the silver surface from solutions having concentrations below the cmc while the polystyrene blocks extended into solution. However, coverage of the surface by the P2VP blocks was low due to the repulsive interactions between the polystyrene blocks, and many surface sites remained unoccupied. During drying, the polystyrene blocks collapsed onto the surface and occupied those sites.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation. The assistance of Dr. E. Parsonage in preparing the diblock copolymers is also acknowledged.

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