Characterization of Adsorbed 2-Vinylpyridine/Styrene Diblock Copolymers on Silver Surfaces Using Surface-Enhanced Raman Scattering

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ABSTRACT: Surface-enhanced Raman scattering (SERS) was used to determine the conformation of 2-vinylpyridine/styrene (2VP/S) block copolymers adsorbed onto silver surfaces. The SERS spectra were also obtained from polystyrene (PS) and poly(2-vinylpyridine) (P2VP) to confirm band assignments of 2VP/S diblock copolymers. The bands near 1615 and 1041 cm^{-1} related to the styrene block were only weakly observed in the SERS spectra of 2VP/S diblock copolymers and the bands due to the 2VP block observed near 1073, 1161, 1336, and 1585 cm^{-1} were relatively strong in intensity in the SERS spectra, indicating that the SERS spectra observed for 2VP/S diblock copolymers were mostly contributed by the 2VP block. Since SERS has previously been shown to be a surface-selective effect, the results obtained here confirmed that the 2VP block preferentially adsorbed to the surfaces while the styrene block was positioned away from the surfaces. The results obtained from angle-resolved X-ray photoelectron spectroscopy (XPS) were consistent with those obtained from SERS. The ratio of nitrogen to carbon (N/C) in the interface region of the adsorbed copolymer was larger than in the bulk copolymer. The N/C ratio was also found to increase with increasing "takeoff" angle in the near-interface region. Since nitrogen is a characteristic element of the 2VP block and the N/C ratio can be used to determine the composition profiles, it was again confirmed that the 2VP block preferentially adsorbed onto the silver surface and that the 2VP layers were enriched in the interface region. Differences in the relative intensities and frequencies of several bands in the normal Raman and SERS spectra of P2VP adsorbed onto the silver surfaces were related to orientation effects. It was concluded that P2VP and the 2VP block of diblock copolymers were adsorbed by σ-bonding through the pyridine nitrogen atoms with a vertical conformation.

I. Introduction

Adsorption of polymer molecules to metal surfaces is of major importance in areas such as adhesive bonding, corrosion protection, and colloid stabilization. Diblock copolymers in which one block adsorbs onto but the other is repelled from the surface may have potential applications in these areas. Several investigations concerned with the configuration of block copolymers adsorbed onto solid surfaces in solution have been reported previously.

One of the major approaches has been to measure the interaction forces between two mica surfaces bearing adsorbed polymers as a function of surface separation. Hadziioannou et al. carried out a series of experiments on forces between mica substrates immersed in solutions of 2-vinylpyridine/styrene (2VP/S) block copolymers.[1] In toluene or in cyclohexane above the Θ temperature, the interaction forces between the adsorbed copolymer layers were monotonic repulsive. It was suggested that the insoluble 2VP blocks adhered strongly to the mica surface and the styrene blocks were forced into an extended configuration away from the surface. Weak attractive forces between the adsorbed copolymer layers were observed when measurements were carried out in cyclohexane below the Θ temperature. This was attributed to attractive osmotic interactions occurring in the poor solvent.

Tirrell and co-workers also measured the forces between mica surfaces bearing adsorbed 2VP/S diblock copolymers having different sizes of the 2VP blocks.[2] It was found that reducing the size of the 2VP blocks further extended the range of repulsive forces in the good solvent toluene. A model was proposed to illustrate the configuration of the adsorbed polymer. The 2VP blocks served as terminal anchors for the styrene blocks, resulting in a grafted layer of polystyrene cilia. It was also suggested that the amount of the styrene blocks attached to the surface was determined by the size of the 2VP blocks.

Similar results were also obtained by Ansarifar and Luckham, who investigated the interaction forces between two mica substrates immersed in solutions of 2-vinylpyridine *tert*-butylstyrene (2VP/BS) diblock copolymer.[3] The force profile obtained from pure toluene was identical with that obtained from solutions of poly(*tert*-butylstyrene) (PBS) homopolymers, indicating that no PBS was adsorbed onto the mica surface. Since PBS did not adsorb onto the mica and P2VP was insoluble in toluene, it was suggested that the diblock copolymers were adsorbed with the 2VP blocks flat on the mica surface and the BS blocks extending away from the surface.

Taunton et al. reported the measurement of interaction forces between two mica substrates bearing adsorbed styrene/ethylene oxide (S/EO) diblock copolymers as a function of surface separation.[4] The styrene blocks were not adsorbed on the mica surface and the repulsive forces were observed between adsorbed layers of S/EO diblock copolymers. It was concluded that this diblock copolymer adhered to the surface through the EO blocks. The force profile obtained was similar to that obtained from polystyrene chains terminally anchored to the mica surface through a single zwitterionic end group.[5] It was suggested that adsorption behavior of diblock copolymers with a

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short length of one adsorbing block on the surface could be quite similar to those of nonadsorbing but end-anchored homopolymers.

Stouffer and McCarthy investigated the adsorption of styrene/propylene sulfide (PS/PPS) block copolymers on gold surfaces from solutions.[6] The amount of the adsorbed copolymers on the gold surfaces was determined by X-ray photoelectron spectroscopy, external reflectance infrared spectroscopy, and liquid scintillation counting techniques. The adsorbed amount on the surface decreased as a function of the size of the PPS blocks, indicating that the PPS blocks strongly adhered and covered the gold surface, thus forcing the PS blocks away from the surface.

Although numerous investigations of the adsorption behavior of polymers on metal surfaces have been carried out, measurements have not been made to test directly the proposed conformation (as opposed to the resulting forces) of adsorbed copolymers. Direct information is particularly sparse on the compact conformations of the adsorbing blocks. Surface-enhanced Raman spectroscopy can be a powerful technique to serve this purpose since surface-enhanced Raman scattering (SERS) has been shown to be an interface rather than bulk effect and can be used for nondestructive characterization of interfaces between polymers and metals.[7,8]

Venkatachalam et al. reported SERS from bilayers of polystyrene (PS), diglycidyl ether of bisphenol A (DGEBA), poly(4-vinylpyridine) (P4VP), and poly(styrenesulfonate) (PSS).[7] Samples were prepared by spin-coating thin films of PS, DGEBA, or PVP onto silver island films from dilute solutions and then overcoating these films with thicker films of PSS. SERS was observed from both films (underlayer of PS, DGEBA, or PVP and overlayer of PSS) when the underlayers were spun from relatively dilute solutions. SERS was not observed from the PSS overlayers when the underlayers were spun from relatively concentrated solutions, even though PSS was a strong Raman scatterer. It was concluded that SERS is an interface effect and that the enhancement extends no more than approximately 100 Å from the silver surfaces.

Boerio et al. investigated SERS from poly(α-methylstyrene) (PMS) spin-coated onto silver island films from methyl ethyl ketone (MEK) solutions having various concentrations.[8] They found that the intensity of the PMS bands near 722, 1012, 1042, and 1613 cm^{-1} was virtually constant even though the thickness of the PMS films was varied from about 300 to 2000 Å. These results again indicated that SERS was an interface rather than bulk effect and that SERS could be used for nondestructive characterization of interfaces between polymers and metals.

SERS has been used to determine the conformation and mechanisms by which polymers were adsorbed onto the surfaces of metals. Roth and Boerio reported SERS from poly(4-vinylpyridine) (P4VP) adsorbed onto silver island films from dilute solutions in ethanol.[9] They found that the relative intensities of the bands in the SERS spectra of P4VP were much different than those in the normal Raman spectra. Weak bands near 1219 and 1613 cm^{-1} in the normal Raman spectra of P4VP were strong in the SERS spectra and the strong band near 1020 cm^{-1} in the Raman spectra was relatively weak in the SERS spectra. Roth and Boerio used Moskovits' theory of Raman scattering by molecules adsorbed onto metal surfaces[10] to determine the orientation of the pyridine moieties. According to that theory, bands associated with vibrational modes belonging to the same symmetry species as α_{zz}, where z is a coordinate perpendicular to the surface, will be most enhanced for molecules adsorbed onto metal substrates with their principal axis parallel to z. Bands associated with modes having eigenvectors that are mostly parallel to z will be especially enhanced. Assuming that 4-vinylpyridine has C_{2v} symmetry and is adsorbed with the 2-fold axis perpendicular to the surface, α_{zz} belongs to the species A1. Therefore, bands corresponding to A1 modes having eigenvectors mostly perpendicular to the surface were predicted to be strongest in the SERS spectra and that is what was observed.

Lippert and Brandt investigated SERS from partially protonated poly(2-vinylpyridine) (P2VP) adsorbed from aqueous solutions at pH 4.9 onto silver electrodes as a function of applied potential.[11] At potentials positive of the point of zero charge (E_z), pyridinium ions were the dominant species on the surface. The SERS spectra were characterized by a band near 1624 cm^{-1} that was attributed to the ν(8a) ring mode of the pyridinium ion. When the applied potentials were near E_z, bands assigned to modes ν(8a) and ν(8b) of neutral pyridine were observed near 1570 and 1600 cm^{-1}, respectively. A band attributed to the CC stretching mode of the polymer backbone was observed near 1084 cm^{-1} in the normal Raman spectra of P2VP. However, the intensity of this band was much weaker in the SERS spectra. It was suggested that the orientation of the backbone was unfavorable for significant enhancement of the CC stretching vibration in SERS.

Lippert and Brandt observed the band related to the symmetric ring breathing mode ν(1) near 998 cm^{-1} in normal Raman spectra of powdered P2VP. The band shifted to near 1010 cm^{-1} in normal Raman spectra of the hydrochloride and to near 1008 cm^{-1} in SERS spectra of partially protonated P2VP adsorbed onto silver electrodes from aqueous salt solutions at potentials between −0.4 and −1.0 V.[11] They also observed a weak band near 760 cm^{-1} in normal Raman spectra of P2VP. The corresponding band was quite strong in the SERS spectra of P2VP adsorbed onto the electrodes, especially at a potential of −1.0 V. Lippert and Brandt suggested that the intensity of this band was indicative of the stereoregularity of P2VP.[11]

Mirkin reported normal Raman spectra of 2-vinylpyridine (2VP) and SERS spectra of 2VP adsorbed onto silver sols.[12] It was observed that the frequency of ν(1) increased from 986 cm^{-1} in normal spectra of neat 2VP to 1005 cm^{-1} in the SERS spectra. σ-Bonding through the nitrogen atom was expected to result in an increase in ν(1), while π-bonding through the ring was expected to result in a decrease in ν(1). As a result, it was concluded that 2VP was adsorbed by σ-bonding through the nitrogen atom. The intensity of the band near 1634 cm^{-1} in the normal spectra, which was assigned to the C=C stretching mode, was not enhanced in the SERS spectra, but the frequency decreased to 1615 cm^{-1}, suggesting that the vinyl group was also perturbed by adsorption. It was concluded that 2VP was adsorbed onto the silver sol particles through the nitrogen atoms with the rings approximately perpendicular to the surface. However, the planarity of the molecules was disrupted by rotation about the C—C bond connecting the vinyl groups to the rings so that the C=C double bonds were oriented approximately parallel to the surface.

Garrell and Beer investigated SERS from P4VP adsorbed onto silver and gold electrodes from acidic aqueous solutions.[13] At applied potentials between −600 and −50 mV versus SCE, neutral P4VP was observed to adsorb onto the surface of the electrodes. When more negative potentials were applied, the surface coverage increased and protonated P4VP was entrained and brought close to the surface. In that case, the spectra were characterized by the appearance of bands near 1445 and 1672 cm^{-1}, which were assigned to a CH_2 deformation mode and a mode of the protonated pyridine ring, respectively. It was concluded that the SERS spectra of P4VP were potential dependent and that the adsorption of P4VP to the surface was through the nitrogen atom of the pyridine ring.

Garrell and Beer observed the band related to $\nu(1)$ near 992 cm^{-1} in normal Raman spectra of solid P4VP. However, they observed that this band shifted to near 1012 cm^{-1} in SERS spectra of partially protonated P4VP adsorbed onto silver and gold electrodes from acidic aqueous solutions.[13]

Since SERS is an interface effect and can be used to determine the conformation of adsorbed polymers on metal surfaces, it is desirable to monitor the adsorption behavior of polymer molecules on metal surfaces by using SERS. The primary purpose of this paper is to describe results obtained by using SERS to determine the conformation of 2VP/S block copolymers adsorbed from solution onto silver island films. SERS spectra were also obtained from P2VP and PS homopolymers adsorbed onto silver island films, so that comparisons could be made with the spectra obtained from the 2VP/S diblock copolymers. It was found that the 2VP block of 2VP/S block copolymers competitively adsorbs to the silver surfaces, while the styrene block lies away from the surfaces. Similar conclusions were reached when angle-resolved X-ray photoelectron spectroscopy (XPS) was used to examine the same copolymers adsorbed onto thick silver films. It was also concluded that the adsorption mechanism involved σ-bonding through the pyridine nitrogen atoms.

II. Experimental Section

Samples were prepared for SERS investigations as described below. Glass slides were immersed in 0.1 N NaOH and in 0.1 N HCl aqueous solution (for 1 h of each), respectively. The slides were then rinsed in distilled deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and blown dry with nitrogen again.

The glass slides were placed in a vacuum chamber (glass bell jar), which was purged with nitrogen and pumped down to 10^{-6} Torr by using sorption, sublimation, and ion pumps. Silver was slowly heated to evaporate the island films onto the glass slides at a rate of about 1 Å/s. The thickness of the silver island films was controlled at about 40 Å by a quartz crystal oscillator thickness monitor.

PS and P2VP homopolymers were obtained from Polyscience, Inc., and used as received. 2VP/S block copolymers were synthesized by using the anionic polymerization technique.[1,14] Thin films of PS homopolymers and 2VP/S block copolymers were spin-coated onto silver island films from solutions in toluene. Films of P2VP were spin-coated from methanol solutions.

Normal and surface-enhanced Raman spectra were obtained by using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon ion laser. The slit settings of the monochromator provided a spectral resolution of 10 cm^{-1} for the SERS spectra and 5 cm^{-1} for the normal Raman spectra. The green line of the laser (5145-Å wavelength) was incident on the sample at an angle of about 65° relative to the normal of the sample surface for SERS experiments and was s-polarized. In obtaining the normal Raman spectra, a glass capillary tube was used to support a small amount of the sample powder.

Plasma lines were removed from the spectra by the placement of a narrow-bandpass filter between the laser and the sample. The scattered light was collected by using an $f/0.95$ collection lens and was focused onto the entrance slits of the monochromator. Most of the spectra were obtained at a scan speed of 50 cm^{-1}/min and a time constant of either 2 or 10 s. In some cases, a scan speed of 25 cm^{-1}/min was used to obtain well-resolved spectra.

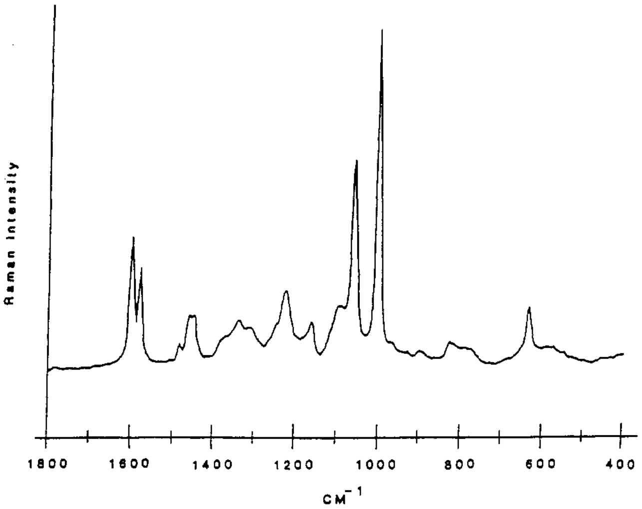

Figure 1. Normal Raman spectrum of poly(2-vinylpyridine) (P2VP).

Samples were prepared for X-ray photoelectron spectroscopy (XPS) by spin-coating films of 2VP/S block copolymers onto thick silver films that had been evaporated onto glass slides, rinsing the films several times in fresh toluene solvent, and then spinning the samples to allow residual solvent to evaporate. Analysis of the samples by ellipsometry indicated that the as-prepared films and the films after rinsing had thicknesses of about 270 and 50 Å, respectively.

XPS spectra were obtained on a Physical Electronics Model 5300 X-ray photoelectron spectrometer with Mg Kα radiation at a power of 300 W. The pass energy was 44.75 and 17.90 eV for the survey and multiplex spectra, respectively. Ellipsometry was carried out with a Rudolph Research Model 436 ellipsometer.

III. Results and Discussion

The normal Raman spectrum of P2VP is shown in Figure 1. Most of the observed bands were assigned to vibrations of the pyridine rings and can be discussed in terms of Wilson's numbering system.[15] The strong band observed near 1005 cm^{-1} was assigned to $\nu(1)$, a totally symmetric ring breathing mode. Medium-intensity bands near 1602 and 1583 cm^{-1} were assigned to the ring stretching modes $\nu(8a)$ and $\nu(8b)$, respectively. Another medium-intensity band near 1064 cm^{-1} was assigned to $\nu(18b)$, a mode related to CH in-plane bending. Medium-intensity bands observed near 1224 and 629 cm^{-1} in the normal Raman spectrum of P2VP were assigned to $\nu(13)$ and $\nu(6b)$, modes related to stretching of the CC bond between the ring and the backbone of the polymer and to in-plane bending of the ring, respectively.

Several weak bands in the Raman spectrum were associated with the pyridine ring modes. The bands near 1482 and 1443 cm^{-1} were assigned to the ring stretching modes $\nu(19a)$ and $\nu(19b)$, respectively. The band near 1160 cm^{-1} was assigned to $\nu(15)$, a CH in-plane bending mode. Another weak band near 828 cm^{-1} was assigned to $\nu(12)$, a ring stretching mode coupled with a stretching mode of the CC bond between the ring and the backbone of the polymer.

Several bands related to modes of the polymer backbone were also observed in the normal Raman spectrum of P2VP. The band near 900 cm^{-1} was assigned to a stretching mode of the backbone, while the bands near 1456 and 1332 cm^{-1} were related to methylene deformation and twisting modes, respectively.

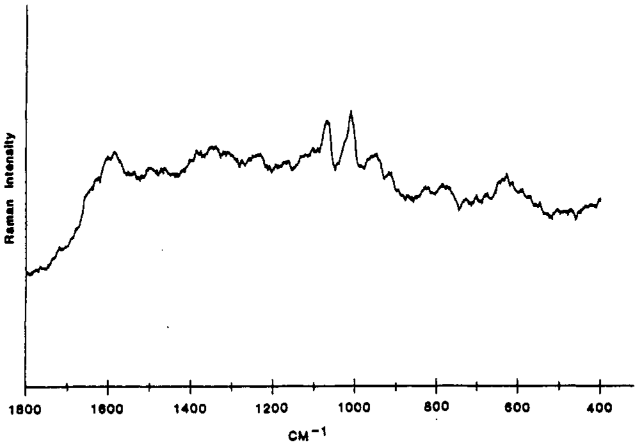

Figure 2. SERS spectrum obtained from poly(2-vinylpyridine) (P2VP) spin-coated onto a silver island film from a 2.5% solution in methanol.

Table I
Tentative Band Assignments of P2VP and PS[a]

P2VP		PS		
NRS, cm^{-1}	SERS, cm^{-1}	NRS, cm^{-1}	SERS, cm^{-1}	assignment
1602 (m)	1603 (w)	1612 (m)	1615 (m)	ν(8a)
1583 (m)	1585 (m)	1596 (w)		ν(8b)
1482 (w)				ν(19a)
1456 (m)	1458 (w)	1458 (w)	1461 (w)	$\delta(CH_2)$
1443 (w)				ν(19b)
1335 (w)	1336 (w)	1330 (w)		$\gamma_t(CH_2)$
1224 (m)	1227 (w)	1210 (m)		ν(13)
		1196 (m)		ν(9a)
1160 (w)	1161 (w)	1170 (m)	1172 (w)	ν(15)
1064 (m)	1073 (s)			ν(18b)
		1040 (m)	1041 (m)	ν(18a)
1005 (s)	1015 (s)	1012 (s)	1015 (s)	ν(1)
		912 (w)		ν(17b)
900 (w)				ν(CC)
		852 (w)		ν(10a)
828 (w)	829 (w)	806 (w)		ν(12)
629 (m)	631 (w)	633 (m)	636 (w)	ν(6b)

[a] NRS = normal Raman spectra; SERS = surface-enhanced Raman spectra; s = strong, m = medium, w = weak.

The SERS spectrum obtained from P2VP adsorbed onto a silver island film is shown in Figure 2. The observed bands are also summarized in Table I. There were some significant differences between the SERS and normal Raman spectra of P2VP. The band assigned to ν(1), the symmetric ring breathing mode, was observed near 1005 cm^{-1} in the normal Raman spectrum but appeared near 1015 cm^{-1} in the SERS spectrum. This band was very strong in the normal Raman spectrum but was relatively weak in the SERS spectrum. The band near 1064 cm^{-1}, which was assigned to an in-plane CH bending mode, had medium intensity in the normal Raman spectrum but was strong in the SERS spectrum.

In the normal Raman spectrum, the band near 1583 cm^{-1}, which was assigned to the ring stretching mode ν(8b), was weaker than the band near 1602 cm^{-1}, which was attributed to ν(8a), another ring stretching mode. However, the relative intensities of these bands were reversed in the SERS spectrum. The bands near 1456, 1224, and 629 cm^{-1} in the normal Raman spectrum had medium intensity but the corresponding bands in the SERS spectrum were weak. The differences between the normal Raman and SERS spectra of P2VP described above were attributed to orientation effects and will be discussed later.

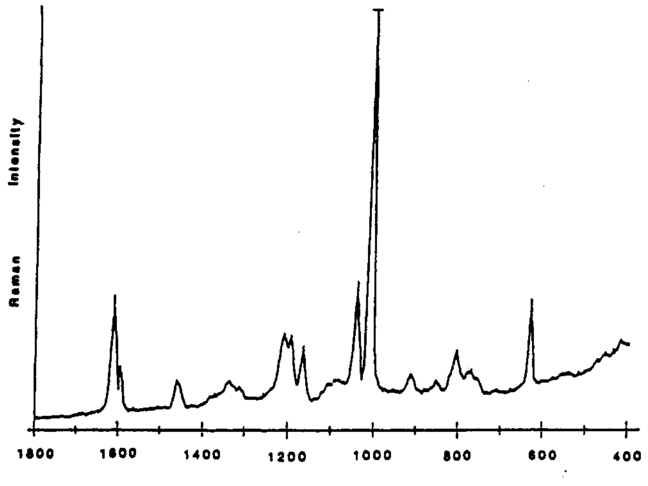

Figure 3. Normal Raman spectrum of polystyrene (PS).

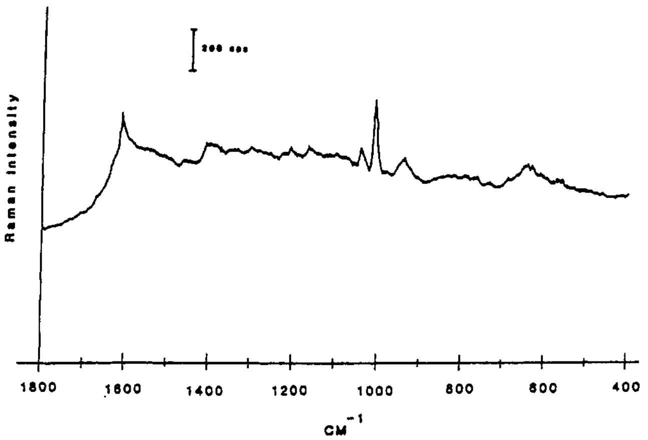

Figure 4. SERS spectrum obtained from polystyrene (PS) spin-coated onto a silver island film from a 2.5% solution in toluene.

The normal Raman spectrum of PS is shown in Figure 3 and the observed bands are also summarized in Table I. The assignments for bands observed in the normal Raman spectrum of PS were similar to those for P2VP. However, some differences were observed. For example, the band near 1064 cm^{-1} in the spectrum of P2VP was assigned to ν(18b), while the band near 1040 cm^{-1} in the spectrum of PS was assigned to ν(18a).

The medium-intensity band observed near 1196 cm^{-1} in the spectrum of PS was assigned to ν(9a), a CH in-plane bending mode. Weak bands observed near 912 and 852 cm^{-1} were assigned to the CH out-of-plane bending modes ν(17b) and ν(10a), respectively.

The frequencies of some bands were different in the normal Raman spectra of PS and P2VP. For example, the bands near 1602, 1583, and 1005 cm^{-1} in the spectrum of P2VP were shifted to about 1612, 1596, and 1012 cm^{-1} in the PS spectrum, respectively.

The SERS spectrum of PS adsorbed onto a silver island film is shown in Figure 4 and the observed bands are also summarized in Table I. The SERS spectrum of PS was characterized by the bands near 1615, 1461, 1172, 1041, 1015, and 636 cm^{-1} and was similar to the normal Raman spectrum of PS. There were some differences between the SERS spectra of PS and P2VP. For example, the band observed near 1603 cm^{-1} due to ring stretching mode ν(8a) in the SERS spectrum of P2VP was shifted to about 1615 cm^{-1}. The bands due to the in-plane CH bending modes ν(18b) and ν(18a), however, were observed near 1073 and 1041 cm^{-1} in the SERS spectra of P2VP and PS, respectively.

The normal Raman spectrum obtained from a 2VP/S diblock copolymer with each block having a molecular

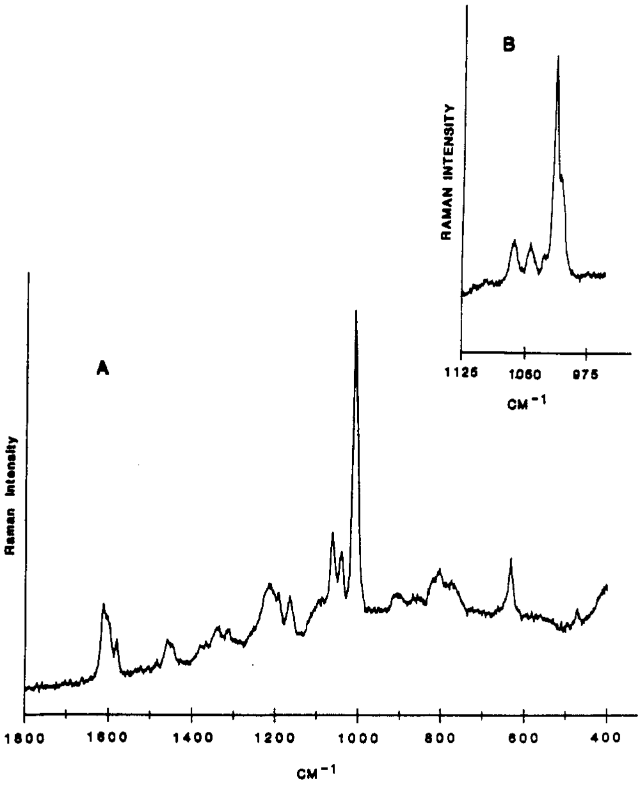

Figure 5. Normal Raman spectra obtained from a 2VP/S diblock copolymer with each block having a molecular weight of 60 000 g/mol (60K/60K). The spectra were taken in the range (A) -400 to 1800 cm^{-1} with a scan speed of 50 cm^{-1}/min and (B) -975 to 1125 cm^{-1} with a scan speed of 25 cm^{-1}/min.

Table II
Bands Observed in the NRS and SERS of 2VP/S[a]

NRS, cm^{-1}	SERS, cm^{-1}	species	NRS, cm^{-1}	SERS, cm^{-1}	species
1612 (m)	1615 (w)	S	1064 (m)	1073 (s)	2VP
1602 (m)		2VP	1040 (m)	1041 (w)	S
1583 (m)	1585 (w)	2VP	1012 (s)	1015 (w)	S
1456 (m)		2VP+S	1005 (s)	1015 (s)	2VP
1335 (w)	1336 (w)	2VP	912 (w)		S
1330 (w)		S	900 (w)		2VP
1224 (m)		2VP	852 (w)		S
1196 (m)		S	828 (w)		2VP
1170 (m)		S	806 (w)		S
1160 (w)	1161 (w)	2VP	633 (m)		2VP+S

[a] NRS = normal Raman spectra; SERS = surface-enhanced Raman spectra; s = strong, m = medium, w = weak.

weight of 60 000 g/mol is shown in Figure 5A. All the observed bands are summarized in Table II. This spectrum was expected to be a combination of the spectra of P2VP and PS and that is what was observed. For example, bands characteristic of 2VP blocks were observed near 1583 and 1064 cm^{-1}, while bands characteristic of styrene blocks appeared near 1612 and 1040 cm^{-1}. It was also observed, that the band near 1015 cm^{-1} consisted of two overlapping bands characteristic of the 2VP and styrene blocks. This was determined by obtaining the normal Raman spectrum of the 2VP/S diblock copolymers with a scan speed of 25 cm^{-1}/min in the range between 975 and 1125 cm^{-1} (see Figure 5B). The band near 1015 cm^{-1} in the spectrum shown in Figure 5A was clearly observed to consist of components near 1005 cm^{-1} due to the 2VP block and near 1015 cm^{-1} due to the styrene block.

The normal Raman spectrum of a 2VP/S diblock copolymer with a large 2VP block (molecular weight 120 000 g/mol) and a relatively small styrene block (molecular weight 30 000 g/mol) was also obtained to confirm the band assignments (see Figure 6A). The intensity of bands observed near 1602, 1583, and 1064 cm^{-1} increased with increasing length of the 2VP block, confirming that these bands were characteristic of the 2VP block. When the spectrum was obtained in the range between 975 and 1125 cm^{-1} with a scan rate of 25 cm^{-1}/min, it was again observed that the band near 1015 cm^{-1} consisted of components near 1005 and 1015 cm^{-1} that were characteristic of the P2VP and PS blocks, respectively. However, the intensity of the component near 1005 cm^{-1} was stronger than that of the component near 1015 cm^{-1} because of the large size of the P2VP block (see Figure 6B).

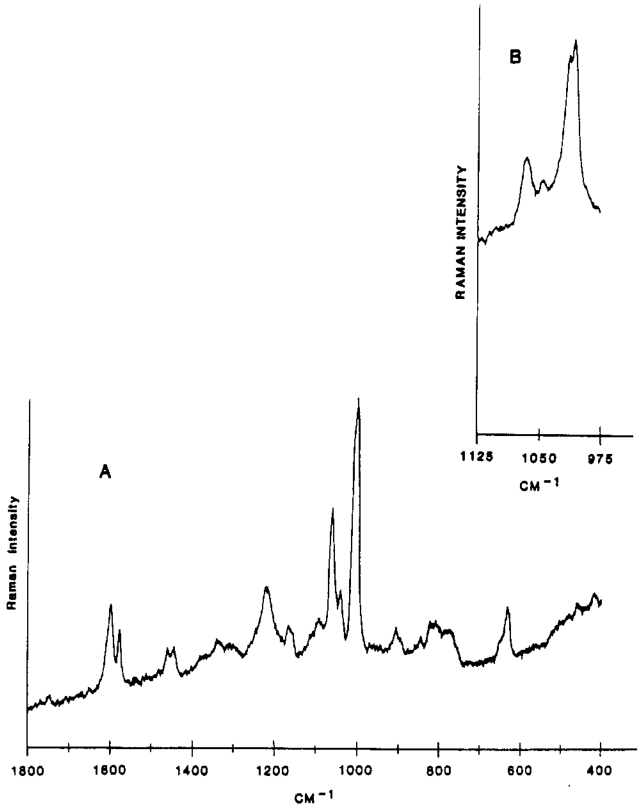

Figure 6. Normal Raman spectra obtained from a 2VP/S diblock copolymer with the 2VP block having a molecular weight of 120 000 g/mol and with the styrene block having a molecular weight of 30 000 g/mol. The spectra were taken in the range (A) -400 to 1800 cm^{-1} with a scan speed of 50 cm^{-1}/min and (B) -975 to 1125 cm^{-1} with a scan speed of 25 cm^{-1}/min.

The SERS spectrum shown in Figure 7A was obtained from a 2VP/S diblock copolymer with each block having a molecular weight of 60 000 g/mol. The observed bands are also summarized in Table II. This spectrum was characterized by a strong band near 1015 cm^{-1}, a medium band near 1073 cm^{-1}, and several weak bands near 1161, 1336, 1585, and 1615 cm^{-1}, respectively. When a well-resolved spectrum of 2VP/S was obtained in the range between 975 and 1125 cm^{-1} with a scan rate of 25 cm^{-1}/min, a weak band was observed near 1041 cm^{-1} in the SERS spectra (see Figure 7B).

The band near 1615 cm^{-1} was always strongly observed in the SERS spectrum of PS (see Figure 4) and the Raman scattering cross section of the styrene block was usually larger than that of the 2VP block (see the normal Raman spectra shown in Figure 5A). However, the bands near 1615 and 1041 cm^{-1} related to the styrene block were only weakly observed in the SERS spectra of 2VP/S diblock copolymers and the bands due to the 2VP block observed near 1073, 1161, 1336, and 1585 cm^{-1} were relatively strong in intensity in the SERS spectra. Thus, it was concluded

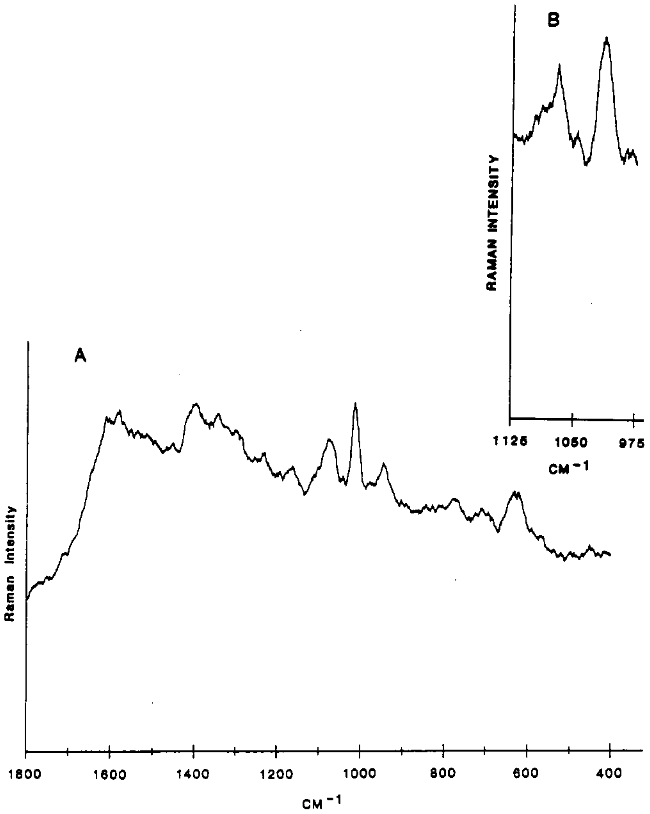

Figure 7. SERS spectra obtained from a 2VP/S (60K/60K) diblock copolymer spin-coated onto a silver island film from a 0.05% solution in toluene. The spectra were taken in the range (A) -400 to 1800 cm^{-1} with a scan speed of 50 cm^{-1}/min and (B) -975 to 1125 cm^{-1} with a scan speed of 25 cm^{-1}/min.

that the SERS spectra of 2VP/S diblock copolymers shown in Figure 7 were mostly characteristic of the 2VP block. Since SERS has been demonstrated to be a surface-selective effect, the results obtained from 2VP/S diblock copolymers adsorbed onto the silver surfaces indicate that the 2VP block preferentially adsorbed to the surfaces, while the styrene block is positioned farther away from the surfaces.

A series of XPS experiments was also carried out to complement the SERS results obtained from 2VP/S diblock copolymers adsorbed onto the silver surfaces. The results are summarized in Table III. Bands characteristic of silver were observed when XPS spectra were obtained from copolymer films having a thickness of about 50 Å deposited onto thick silver substrates. Moreover, the intensity of these bands increased with increasing takeoff angle, indicating that the copolymer films were characteristic of the "interface" region.

No nitrogen was observed in the XPS spectra of as-prepared silver substrates. Nitrogen was a characteristic element of the 2VP block and the N/C ratio could be used to determine composition profiles in the near interface region. The nitrogen to carbon (N/C) ratio was calculated to be 0.067 for a 2VP/S copolymer having a molecular weight of 60 000 g/mol in each block. It was observed that the N/C ratio was somewhat higher, increasing from about 0.077 to about 0.101 as the takeoff angle was increased from 15° to 75°. The increase in the N/C ratio with increasing takeoff angle for thin films of copolymers further confirmed that the 2VP block of the 2VP/S diblock copolymers preferentially adsorbed onto the silver surface and induced the enriched layers of 2VP at the surface. The results obtained from XPS were thus consistent with those obtained by SERS.

Table III
Atomic Concentration as a Function of Electron Takeoff Angle for 2VP/S (60K/60K) Adsorbed on Silver[a]

takeoff angle	element	atomic concentration, %
15°	Ag3d	3.6
	O1s	3.9
	N1s	6.6
	C1s	85.9
	N/C	7.7
45°	Ag3d	5.8
	O1s	4.0
	N1s	7.2
	C1s	83.0
	N/C	8.7
75°	Ag3d	9.9
	O1s	3.0
	N1s	8.0
	C1s	79.1
	N/C	10.1

[a] 2VP/S = 2-vinylpyridine/styrene diblock copolymers.

Similar results have been reported by Parsonage et al.[14] They reported the C/N ratio as a function of takeoff angle when dried 2VP/S-adsorbed layers on polished silicon substrates were investigated by angle-resolved XPS. The C/N ratio was found to decrease with increasing takeoff angle, indicating a layered structure in the dry adsorbed films with the 2VP block being preferentially located at the surface.

It would be very interesting to determine the conformation of adsorbed 2VP units on the surface, since the results obtained from SERS and angle-resolved XPS show that the 2VP block of the 2VP/S block copolymer strongly adsorbed to the silver surface. In fact, there is considerable evidence in the SERS spectra to indicate that the 2VP units are adsorbed with a vertical orientation.

As mentioned above, differences in band intensities between the normal Raman and SERS spectra of P2VP may be related to an orientation effect. Moskovits et al. investigated SERS from several aromatic molecules adsorbed onto silver surfaces.[16] They found that the intensity of in-plane modes of the rings was enhanced more strongly than that of out-of-plane modes when the rings had a vertical orientation. However, if the molecules were adsorbed parallel to the surface, the out-of-plane modes were more strongly enhanced. In the SERS spectra of P2VP, bands corresponding to the in-plane modes $\nu(18b)$ and $\nu(1)$ were strongly observed near 1073 and 1015 cm^{-1}, but no strong bands related to out-of-plane modes were observed. These results imply that P2VP was adsorbed onto the silver surface with a conformation in which the rings were perpendicular to the surface, somewhat similar to the conformation previously observed for P4VP. The intensity of the in-plane modes of the rings was also relatively enhanced in the SERS spectra of 2VP/S block copolymers, implying that the pyridine rings of the 2VP blocks were also oriented perpendicular to the silver surface.

There were some significant differences between the SERS spectra of P2VP and P4VP, even though it seems that in both cases the pyridine rings were oriented perpendicular to the surface. For example, the band near 1613 cm^{-1} due to the in-plane mode $\nu(8a)$ was strongly observed in the SERS spectra of P4VP, while the corresponding band observed near 1603 cm^{-1} was very weak in the SERS spectra of P2VP. However, the band near 1585 cm^{-1} due to the in-plane mode $\nu(8b)$ was relatively strong in the SERS spectra of P2VP. The in-plane mode $\nu(9a)$

was strongly observed near 1219 cm^{-1} in the SERS spectra of P4VP but was weakly observed near 1227 cm^{-1} in the SERS spectra of P2VP. The band near 1073 cm^{-1} due to the in-plane mode ν(18b) was strongly observed in the SERS spectra of P2VP, but no corresponding band was observed in the SERS spectra of P4VP. These results indicate that the orientation of the rings is somewhat different for adsorbed P2VP and P4VP even though the rings are perpendicular to the surface in both cases.

As discussed above, vibrations involving motions directed normal to the surface may be strongly enhanced in the SERS spectra. The in-plane modes ν(18b) and ν(8b) observed near 1073 and 1585 cm^{-1} in the SERS spectra of P2VP, respectively, could involve motions normal to the surface if P2VP is adsorbed with a vertical (edge-on) conformation. As a result, the intensity of bands observed near 1073 and 1585 cm^{-1} in the SERS spectra of P2VP was expected to be relatively strong and that is what was observed. The vibrations of in-plane modes ν(8a) and ν(9a) observed near 1602 and 1224 cm^{-1} in the normal Raman spectra of P2VP would not involve atomic motions normal to the surface if P2VP is adsorbed with a vertical (edge-on) conformation. Thus, the corresponding bands were expected to be weak in the SERS spectra and that is also what was observed. The results obtained here were different from those obtained from P4VP. As mentioned above, Roth and Boerio have shown that P4VP was adsorbed onto the silver surface through the ring nitrogen atoms with a vertical (end-on) conformation.[9]

Further evidence of P2VP oriented with a vertical conformation was obtained by comparing the relative intensity of bands observed in the normal Raman and SERS spectra of P2VP. As shown in Figures 1 and 2, the in-plane mode ν(8b) observed near 1583 cm^{-1} was weaker than another in-plane band ν(8a) observed near 1602 cm^{-1} in the normal Raman spectra. However, the relative intensity of these corresponding bands was reversed in the SERS spectra. Similar results were also obtained from 2VP/S block copolymers. The intensity of the bands related to in-plane modes ν(18b) and ν(8b) was weak in the normal Raman spectra of copolymers, but their corresponding bands observed near 1073 and 1585 cm^{-1} were relatively strong in intensity in the SERS spectra (see Figures 5 and 7, respectively). The bands near 1227 and 1603 cm^{-1} related to in-plane modes ν(9a) and ν(8a) were relatively weak in intensity in the SERS spectra. Thus, results obtained here indicate that P2VP and the 2VP block of 2VP/S block copolymers are adsorbed onto the silver surfaces with a vertical conformation.

There is also considerable evidence to indicate that P2VP and the block copolymers were adsorbed through the nitrogen atoms. When Roth et al. investigated SERS from P4VP adsorbed onto a silver island film, it was found that the symmetric ring mode ν(1) near 1000 cm^{-1} was shifted to about 1020 cm^{-1} in the SERS spectra.[9] The shift was attributed to the pyridine moieties adsorbed through the nitrogen atoms with a vertical configuration. As indicated above, Mirkin[12] observed that ν(1) was at a higher frequency in SERS spectra of 2VP adsorbed onto silver sol particles than in normal Raman spectra, indicating adsorption of 2VP by σ-bonding through the nitrogen. Lippert and Brandt[11] and Garrell and Beer[13] observed similar shifts in ν(1) for partially protonated P2VP and P4VP, respectively. We observed that the symmetric ring stretching mode ν(1) was near 1005 cm^{-1} in the normal Raman spectra of P2VP but was shifted to about 1015 cm^{-1} in the SERS spectra. A similar shift of ν(1) from 1005 to 1015 cm^{-1} was also observed in SERS spectra of the 2VP/S copolymers. These results imply that the 2VP moieties were adsorbed through the nitrogen atoms.

The P2VP that was used here was a commercial material and no information was available regarding its stereoregularity. Natta has investigated the crystal structure of isotactic P2VP and reported that the repeat period was 6.5 Å.[17] A similar result has been obtained for isotactic polystyrene (IPS), which has a 3_1 helical structure in which the phenyl rings make an angle of approximately 108° with the helix axis.[18] Assuming that the P2VP used here had a structure similar to that of IPS, it would be possible for every third 2VP repeat unit to be adsorbed by σ-bonding through the nitrogen atoms.

It was not possible to provide an accurate estimate of the angle between the plane of the pyridine rings and the normal to the surface. To do so would require knowledge of the enhancement factors and the polarizability tensor for at least two different modes. However, that information is not generally available.

No effort was made to determine the morphology of the SERS substrates used here. However, Venkatachalam used transmission electron microscopy (TEM) to characterize silver island films that were deposited on glass substrates using a very similar procedure.[19] He found that the films consisted of large islands having average diameters of about 225 Å and numerous small islands about 30–40 Å in diameter distributed on the glass substrate. From the number of islands per unit area and the diameter of the islands, the fraction of the glass slide covered by the silver was approximately 31%.

Murray examined SERS from polystyrene spin-coated from chlorobenzene solution onto silver island films having a mass thickness of about 100 Å.[20] According to results obtained from scanning electron microscopy (SEM), the islands were oblate ellipsoids about 300 Å in diameter with a separation of about a diameter between their centers. Considering the sizes of the islands and the length of the adsorbed PS chains, Murray concluded that some polystyrene chains could adsorb onto more than one island. Similar behavior can be expected for the diblock copolymers considered here.

It is reasonable to ask if the roughness of the substrates has any effect on the orientation of the adsorbed species and if SERS provides information on the average surface species or only species adsorbed at certain types of defects. This issue has been addressed in several investigations. Sobocinski et al. reported SERS from an alkanethiol and a series of alcohols adsorbed at roughened silver electrodes.[21] The SERS spectra were very similar to normal Raman spectra of the same compounds adsorbed onto smooth electrode surfaces. As a result, it was concluded that roughness of the SERS substrates has little effect on the orientation of the adsorbed species and that SERS spectra provide information about the average surface species, not just species adsorbed at defect sites. Tsai and co-workers[22] investigated the adsorption of imides onto silver island films using SERS and onto thick silver films using reflection–absorption infrared (RAIR) spectroscopy. The conclusions they reached regarding adsorption mechanisms and the orientation of adsorbed species from the SERS spectra were substantiated by the RAIR results. Since RAIR definitely probes the average surface species, it can be concluded that SERS does also.

IV. Conclusions

Surface-enhanced Raman scattering (SERS) has been reported from 2-vinylpyridine/styrene (2VP/S) diblock copolymers adsorbed onto the silver surface. The SERS intensity from the styrene block of 2VP/S block copolymers was found to be much weaker than that observed from the 2VP block, indicating that the 2VP block of 2VP/S block copolymers competitively adsorbs to the silver surfaces, while the styrene block is positioned away from the surfaces. The results of angle-resolved X-ray photoelectron spectroscopy (XPS) were quite consistent with those obtained from SERS. The ratio of nitrogen to carbon (N/C) in the interface region of the adsorbed copolymer was larger than for the bulk copolymer. The N/C ratio was also found to increase with increasing takeoff angle in the near-interface region. Since nitrogen was a characteristic element of the 2VP block and the N/C ratio could be used to determine the composition profiles, it was again confirmed that the 2VP block preferentially adsorbed onto the silver surface and the 2VP layers were enriched at the interface region.

The results obtained here indicated that SERS can be also used to determine the conformation of adsorbed polymers on the silver surfaces. P2VP and the 2VP block of 2VP/S block copolymers were adsorbed onto the silver surfaces through the pyridine nitrogen atoms with a vertical conformation.

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Registry No. (2VP)(S) (block copolymer), 108614-86-4; P2VP (homopolymer), 25014-15-7; PS (homopolymer), 9003-53-6; Ag, 7440-22-4.