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Surface-Enhanced Raman Scattering Study of Polymer on Metal. 2. Molecular Chain Orientation of Polybenzimidazole and Poly(L-histidine) and Its Transition

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ABSTRACT: The surface geometry of polybenzimidazole on silver foil etched with nitric acid has been determined by observing the relative intensity change of the out-of-plane and the in-plane ring vibration bands in their surface-enhanced Raman scattering spectra. This polymer has been observed to show two orientations of its main chain on the surface of silver, resulting from different sample doping methods. By slow evaporation of the solvent from a dilute solution spread on Ag foil, the aromatic rings are deposited lying down flat on the surface, while dipping silver foil into a warm polymer solution resulted in a perpendicular orientation of the rings. Upon heating, the heteroaromtic rings stand up from the flat orientation to form an N-bonded geometry. Two orientations of side groups of poly(L-histidine) on Ag foil applied from solutions using different solvents were also observed by SERS.

Introduction

The observation of enormously enhanced cross sections (factors up to 10^6) for Raman scattering from molecules adsorbed on metal surfaces is one of the most important discoveries in the field of surface science in the past few years.[1-4] An important aspect of surface-enhanced Raman scattering (SERS) is its potential for probing the interaction between various adsorbates and metallic surfaces. Elucidation of the surface orientation of adsorbed molecules with donor atoms or group of atoms by analysis of the SERS spectrum has been the subject of many investigations.[5-10] SERS is also ideal for the study of the interfacial structure of polymer–metal composites since it enhances almost exclusively the first monolayer adjacent to the surface.

Since the original SERS work involving pyridine adsorbed on silver electrodes and sols,[4] most of the reported SERS spectra of polymers were recorded from electrochemical cells, aqueous environments, or in a vacuum.[11-15] It was reported that spin-casting of a polymer solution onto Ag island films could be characterized by SERS.[16-18] However, we found that the SERS effect of vacuum-deposited Ag island film is not stable at high temperature. This disadvantage limited the application of SERS as a general tool to analyze the polymer–metal interface. Recently, HNO_3-etched metal foils for Raman study of adsorbates were prepared in this laboratory. This new sampling technique exhibits a strong SERS effect on surface adsorbates and better thermal stability.[19] In this work, we report SERS measurements of the surface orientation of polybenzimidazole and poly(L-histidine) on silver foils. We found that different sample doping methods yielded different orientations of polymer chains or side groups on metal. A reorientation transition of the polymer chain was observed upon heating the sample. This work is part of a program of surface chemistry intended to explore the relationships between the microstructure of the interface in polymer–metal composites and the macroscopic properties, such as mechanical strength, corrosion inhibition, etc.

Experimental Section

Preparation of Metal Substrate. Commercial silver foil of 0.025-mm thickness was immersed into a freshly prepared 3.5 M HNO_3 solution at 30 °C. Vigorous agitation was applied. After 2–3 min, a spongy surface with substantial roughness was created. The roughness of the etched silver surface was about 10–100 nm as measured by electron microscopy.[20] After etching, the silver foil was thoroughly rinsed with water and dried in air. The etched silver foil was then ready for polymer doping.

Sample Doping Methods. Polybenzimidazole and poly(L-histidine) were obtained from Aldrich and were dissolved in DMF to make solutions of concentration 0.04%. Two sample doping methods were used to apply the polybenzimidazole onto silver foils. One was "solution spreading": 20 μL of solution was spread onto a 2-cm² foil uniformly, and the foil was put into a cell to evaporate the solvent slowly. The average calculated thickness of polymer film was about 400 Å. Another sampling method was "dip-coating": A nitric acid etched foil was immersed into a polymer solution at 50 °C for 5 min, and, after withdrawal of the sample, the solvent was evaporated. The thickness of the film was measured with an electrochemical quartz crystal microbalance. The average thickness was 400 ± 50 Å. The solvent was evaporated in about 16 h in both methods under nitrogen.

Raman Scattering Measurements. Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident laser excitation was 647.1 nm from a Kr^+ laser source with an output of 20–200 mW. A back-scattering geometry in air was used for all samples. A plasma line at 235 cm^{-1} was used to maintain frequency calibration between the spectra.

Results and Discussion

The chemical formulas of the polymers used for this study are shown in Chart I. These structures seem to be SERS active on a properly roughened metal substrate. Figure 1 illustrates SERS spectra of polybenzimidazole coated on a smooth Ag foil and on a HNO_3-etched Ag foil. Both samples were prepared by dip-coating the foils into a dilute polymer solution at 50 °C. Although the thicknesses of the polymer films on the foils were about the same, the spectroscopic results are quite different. There are no Raman bands in the spectrum recorded from the smooth Ag foil, indicating that the polymer film on the surface was not thick enough to produce a normal Raman spectrum. An excellent Raman spectrum was recorded from the roughened Ag foil by surface enhancement of the polymer–metal interface. However, we were not able to

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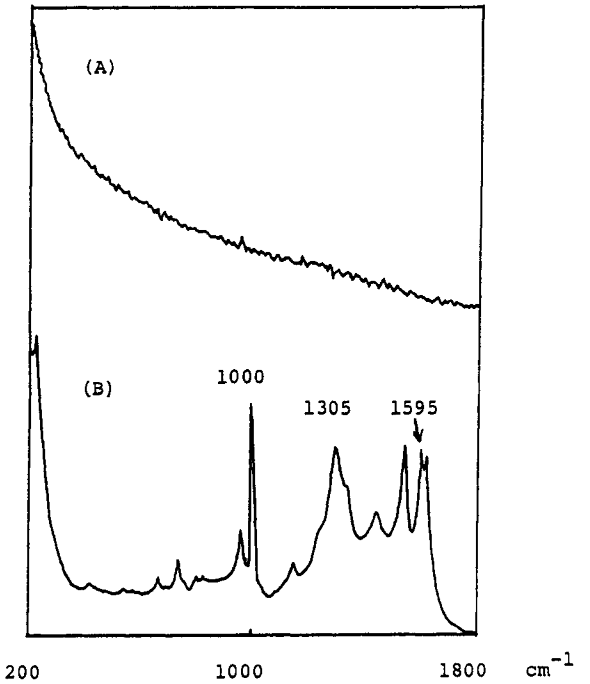
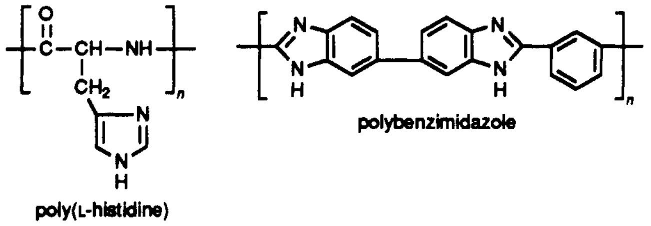


Figure 1. SERS spectra of polybenzimidazole adsorbed from solution by dipping the substrate: (A) adsorbed on a smooth Ag foil; (B) adsorbed on a HNO_3-roughened Ag foil.

Chart I
Chemical Formulas of Polymers Used for the Study



poly(L-histidine)

polybenzimidazole

observe the normal Raman scattering from the polymer because of fluorescence.

Figure 2 shows SERS spectra of the same polymer prepared by spreading the solution onto silver foils and slowly evaporating the solvent. Again, the smooth Ag foil did not give any Raman band, and the HNO_3 roughened Ag foil exhibits a strong SERS effect. However, comparing the SERS spectra of Figures 1B and 2B, one finds observable differences between them. This is an important feature for the SERS phenomenon on the interface of polymer–silver, since these two spectra were recorded from the same polymer solution but with different sample doping methods. More interesting is the observation that the sample that gave the SERS spectrum of Figure 2B could be converted to one that could provide a SERS spectrum similar to Figure 1B. After the sample prepared by the spread-casting method was heated at 130 °C for 6 h, a SERS spectrum was recorded. It showed the same features as that obtained from a sample prepared by the dip-coating method, as shown in Figure 3. We propose that the spectral differences and their transition are due to the surface geometry change of the polymer chains. A successful basis for analysis of SERS spectra with regard to orientation of adsorbate was worked out in the form of "surface selection rules".[21-25] These rules are based on the electromagnetic theory of SERS intensity, which indicates that, via resonance interaction with surface plasmons of the metal, incident light increases the electromagnetic field at the surface of small metallic particles, which in turn amplifies both the scattered intensity and the Raman excitation intesity. Since the local fields are highest normal to the surface, normal modes of the surface molecule involving changes in molecular polarizability with a component normal to the surface are subject to the greatest enhancement. This same type of analysis has been successfully applied by many authors.[26-28] The SERS spectrum of Figure 1B shows strong bands near 1600 and 1000 cm^{-1}, which are very weak in the SERS spectrum of Figure 2B. While Figure 2B shows a band at 510 cm^{-1}, this band is almost absent in Figure 1B. In the Raman spectra of heterocyclic compounds, the bands at 1000 and 1600 cm^{-1} are due to in-plane ring bending and stretching, respectively, and the band at 510 cm^{-1} is due to out-of-

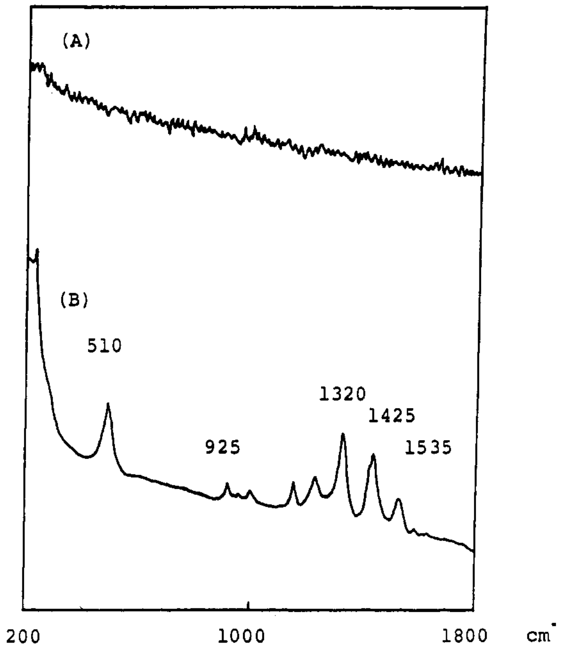


Figure 2. SERS spectra of polybenzimidazole deposited on substrates by applying the solution on them and slowly evaporating the solvent: (A) on a smooth Ag foil; (B) on a HNO_3-roughened Ag foil.

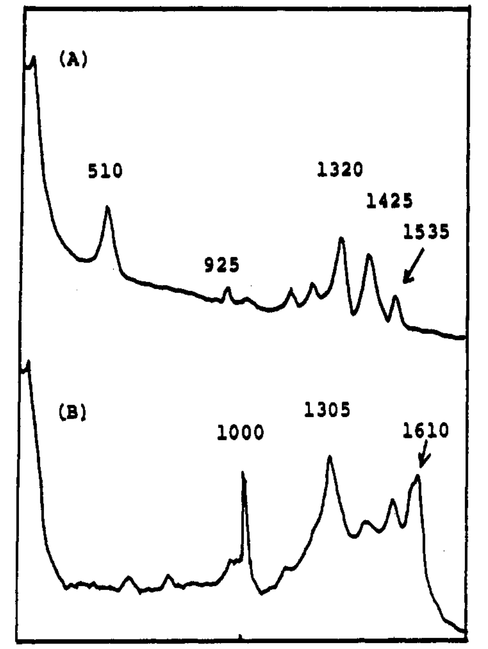


Figure 3. SERS study of the orientation transition of polybenzimidazole on silver: (A) before heating; (B) after heating at 130 °C for 6 h.

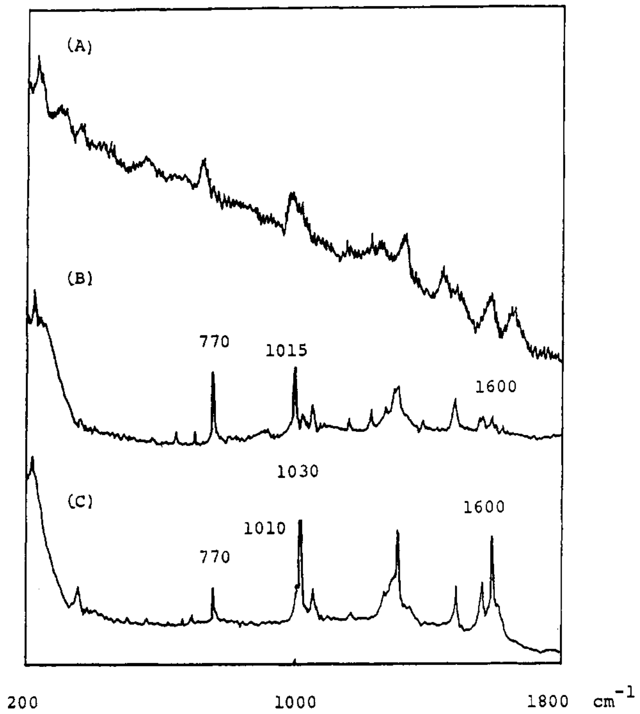


Figure 4. (A) Normal Raman spectrum of neat poly(L-histidine); (B) SERS spectrum of poly(L-histidine) applied from ethanol solution; (C) SERS spectrum of poly(L-histidine) applied from DMF solution.

plane ring vibration.[29,30] The normal mode of out-of-plane vibration involves a changing dipole moment which is perpendicular to the plane of the molecule. In contrast, the change of dipole moment accompanying an in-plane vibration is parallel to the plane of the molecule. In the SERS spectrum of Figure 1B, the in-plane vibrations of the ring at 1000 and 1600 cm^{-1} are intensified, but the out-of-plane vibration at 510 cm^{-1} is absent. On the basis of surface selection rules, we propose that the rings of the polybenzimidazole chain are standing up on the surface when the polymer was applied onto silver by the dip-coating method. In the SERS spectrum of Figure 2B, the out-of-plane vibration of the ring at 510 cm^{-1} is enhanced, but the in-plane vibrations are very weak, indicating that the rings of the polymer chain are lying down flat on the surface. By slow evaporation of the polymer solution spread on Ag foil, a flat orientation of the polymer chain was obtained. Upon heating, these chains are standing up as evidenced by the spectral change in Figure 3. The flat bonding geometry of the aromatic ring (π-bonded to the surface) could translate to a bonding through the nitrogen lone pair (N-bonded through σ-donation); as a result, the rings are standing up. However, our SERS study did not find any evidence that the "standing" ring could translate to the flat bonding geometry, indicating that the N-bonded geometry is more stable than the π-bonded orientation. Since we have found by XPS that polybenzimidazole cannot react with metallic silver chemically under nitrogen, we think that the spectral changes are due to geometric differences rather than the chemical reaction.

Figure 4 shows the orientation of the poly(L-histidine) side groups. The normal Raman scattering from bulk poly(L-histidine) did not provide a good spectrum, as shown in Figure 4A. By slow evaporation from ethanol or DMF solutions of the polymer spread on Ag foils, good SERS spectra were obtained, as shown in Figure 4B,C. However, the relative intensities of bands in these two SERS spectra are different. We propose that these differences are due to a geometry change of the imidazole side groups on Ag. The most intense bands in the SERS spectrum of poly(L-histidine) applied from ethanol solution are at 770 and 1015 cm^{-1}, while the enhanced bands in the spectrum of the polymer applied from DMF solution are those at 1030 and 1600 cm^{-1}. Several reports are concerned with the orientation of the side group of poly(4-vinylpyridine) on silver sols or island films. Lee and Meisel observed a strong band at 1014 cm^{-1} in the SERS spectra of poly(vinylpyridine) adsorbed onto silver sol practicles.[31] It was concluded that poly(vinylpyridine) was physisorbed by bonding through the π-system with the pyridine rings parallel to the substrate. Roth and Boerio showed that poly(vinylpyridine) was adsorbed onto silver island film through the nitrogen atoms and that the rings were perpendicular to the surface.[32] In the Raman spectrum of monosubstituted imidazole, the band near 760 cm^{-1} is due to out-of-plane C–H deformation, and the bands at 1015 and 1600 cm^{-1} are due to symmetric ring-breathing and ring-stretching modes, respectively.[29] The SERS spectrum of Figure 4B shows an enhanced and shifted band at 770 cm^{-1} and a very weak band at 1600 cm^{-1}, indicating that the imidazole rings are "lying down" flat on the surface. In this spectrum there is a strong symmetric ring-breathing vibration at 1015 cm^{-1} but there is only a weak band at 1030 cm^{-1}, which is usually attributed to a heterocyclic ring chemisorbed at the Lewis acid sites.[31],[32] It seems that most side groups were physisorbed by bonding through the π-system. In the SERS spectrum of Figure 4C, there are strongly enhanced bands at 1030 and 1600 cm^{-1}, indicating that the rings were perpendicular to the surface and coordinated through the nitrogen atoms, whereas those at lower frequencies are attributed to rings that were physisorbed or not adsorbed. We conclude that when poly(L-histidine) was applied from ethanol solution, most side groups were lying down on the surface and that when the polymer was applied from DMF solution, most side groups were standing up on the surface. Solvent will interact with polymer chains in polymer solution owing to solvation. The interaction that is determined by the polarity of the solvent and polymer affects the conformation of the polymer chains. It is obvious that the polarity of DMF is stronger than that of ethanol, and it can strongly interact with the imino and carbonyl groups in poly(L-histidine) chains. Since Loeb has found that the conformation of the polypeptide in the surface film was related to its conformation in the spreading solution,[33] we attribute the different orientations of poly(L-histidine) on silver surface from DMF and ethanol to its different conformation in the solutions.

Conclusion

We have demonstrated that HNO_3-etched silver foil shows an excellent SERS effect on adsorbed polymers. SERS study indicates that spreading the polymer solution onto a Ag foil and then slowly evaporating the solvent could result in a flat orientation of the chain of polybenzimidazole and that dipping Ag foil into a warm polymer solution produces a perpendicular orientation on the surface. Upon heating, the aromatic rings stand up from the π-bonded geometry to form an N-bonded orientation through the donation of the lone pair of electrons of nitrogen. Applying poly(L-histidine) from solutions in different solvents resulted in different surface orientations of the side groups.

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Registry No. DMF, 68-12-2; Ag, 7440-22-4; EtOH, 64-17-5; poly(L-histidine) (homopolymer), 26062-48-6; poly(L-histidine) (SRU), 26854-81-9; polybenzimidazole (copolymer), 27288-38-6; polybenzimidazole (SRU), 25734-65-0.