Study of molecular orientation and bonding at the polymer–metal interface by surface-enhanced Raman scattering

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The surface geometry and orientation of the first layer of poly(4-vinyl pyridine) on silver foil have been determined by observing the change in relative intensity of the out-of-plane ring deformation and the in-plane ring stretching vibration bands in surface-enhanced Raman scattering spectra. This polymer shows two side group orientations on the silver surface, resulting from different sampling temperatures. At ambient temperature, the pyridine ring lies flat on the metal surface with a π-bonded geometry, while upon heating the ring stands up to form an N-bonded geometry. Infra-red reflection–absorption spectra show no differences related to the bond orientation due to the interference of the bulk film.

(Keywords: molecular orientation; surface geometry; Raman scattering)

Introduction

It is important to gain information about the adsorption and orientation of macromolecular chains at the polymer–metal interface in order to understand the interfacial binding and reactivity. However, general surface analytical techniques are barely able to observe the structure of the polymer adsorbates near the surface. *Figure 1* shows a schematic diagram of a polymer–metal interfacial region. It is very difficult to measure the interfacial region, which is a polymer layer a few to a few tens of angstroms thick adjacent to the metal surface, without the interference of the bulk polymer, which is at least a few hundreds angstroms thick. The discovery and development of surface-enhanced Raman scattering (SERS) spectroscopy makes it possible to probe the interaction between various adsorbates and metal surfaces.

Recently, many SERS investigations have been devoted to the study of surface orientation of molecules adsorbed on metals. Several reports have been concerned with the orientation of polymer molecules on silver sols or island films. Lee and Meisel[1] observed a strong band at 1014 cm^{-1} in the SERS spectra of poly(vinyl pyridine) adsorbed onto silver sol particles. It was concluded that poly(vinyl pyridine) was physisorbed by binding through the π-system with the pyridine rings parallel to the substrate. Roth and Boerio[2] showed that poly(vinyl pyridine) was adsorbed onto silver island films through the nitrogen atoms and that the rings were perpendicular to the surface.

In this paper we will describe SERS measurement of the surface orientation of poly(4-vinyl pyridine) on HNO_3-etched silver foil and its reorientation upon heating. For comparison, i.r. reflection–absorption spectroscopic investigations were performed to elucidate the character of the SERS method in polymer/metal systems.

Experimental

Procedures. Silver foil, 0.025 mm thick, was immersed into vigorously agitated 3.5 M HNO_3 at ambient temperature, for about 2–3 min until the surface of the foil became milky. After etching, the foil was thoroughly rinsed with distilled water and dried in air. The roughened foil was ready for sample doping.

Poly(4-vinyl pyridine) (P(4VP)) was obtained from Aldrich, and was dissolved in dimethylformamide to make a solution with a concentration of 0.03%. A controlled amount of solution was spread uniformly onto 2 cm^2 of HNO_3-etched metal foil, and the foil was placed into a container to evaporate the solvent slowly. The prepared sample was ready for SERS measurement. In addition, P(4VP) was coated onto smooth silver foil, for i.r. analysis.

Instrumentation. Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident excitation wavelength was 647.1 nm from a Kr$^+$ laser source, with output power 20–100 mW. A back-scattering geometry in air was used for all samples. The i.r. reflection–absorption spectra were recorded with a Nicolet 170 SX *FT*i.r. spectrometer.

Results and discussion

Figure 2 illustrates SERS spectra of P(4VP) on HNO_3-etched silver foils before and after heating. Comparing the SERS spectra A and B in *Figure 2*, it is seen that there are remarkable differences between them. The sample that gave SERS spectrum A could be converted to a sample giving SERS spectrum B by heating at 130°C for 6 h. We propose that the spectral differences and their transitions are due to the surface geometry changes of polymer chains. A successful basis for analysing SERS spectra with regard to orientation of adsorbate is from the 'surface selection rules' proposed by Moskovits and co-workers[3–6] and others[7–9]. These rules are based on the electromagnetic theory of SERS intensity which points out that, via resonance interaction

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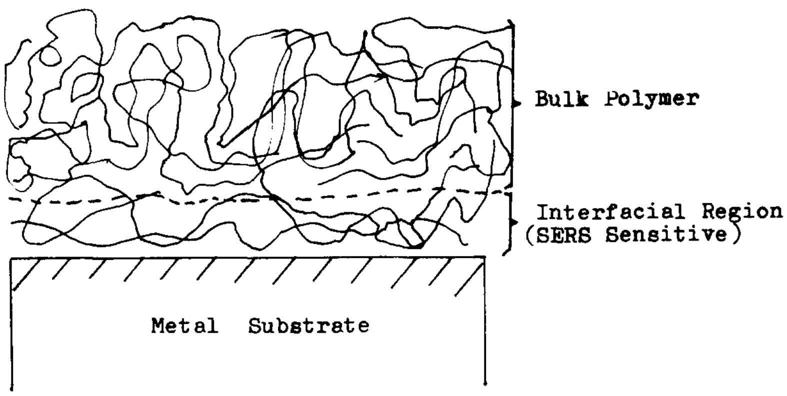

Figure 1 Schematic diagram of polymer–metal interfacial region

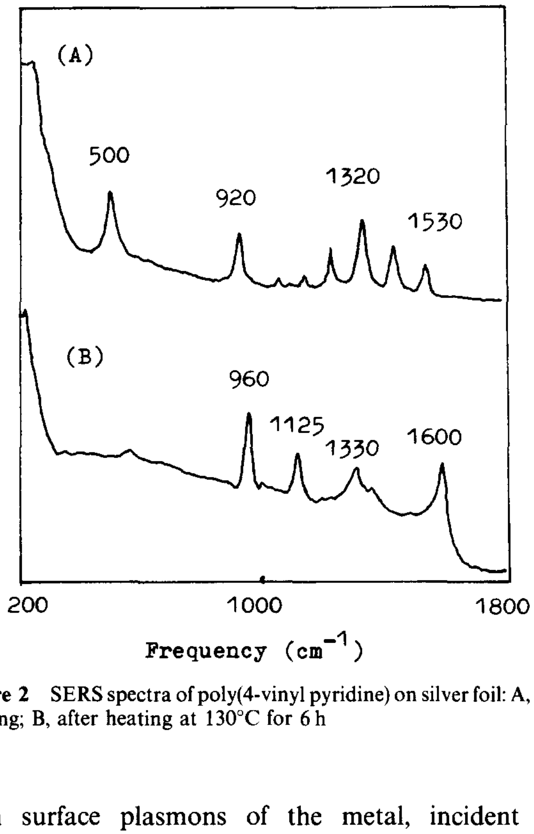

Figure 2 SERS spectra of poly(4-vinyl pyridine) on silver foil: A, before heating; B, after heating at 130°C for 6 h

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 Raman excitation intensity and the scattered intensity. Since the local fields are highest normal to the surface, normal modes of the adsorbed 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 other workers[10–12].

SERS spectrum A of *Figure 2* shows an intensive band at 500 cm^{-1} which is almost absent in spectrum B, while spectrum B shows a strong band at 1600 cm^{-1} which is Raman-inactive in spectrum A. In the Raman spectrum of 4-methyl pyridine, the band near 500 cm^{-1} is due to out-of-plane ring deformation, while the band at 1600 cm^{-1} is due to ring stretching vibration[13,14]. In SERS spectrum A of *Figure 2*, the out-of-plane vibration of the ring at 500 cm^{-1} is enhanced, but the ring stretching vibration is almost absent. On the basis of surface selection rules, we propose that the side groups of P(4VP), pyridine rings, are lying flat on the surface in the form of π-bonding, as shown in *Figure 3*. In SERS spectrum B of *Figure 2*, the ring stretching vibration at 1600 cm^{-1} is intensified, but the out-of-plane vibration at 500 cm^{-1} is absent, indicating that the pyridine rings are standing up on the surface in the form of N-bonding when the silver foil on which P(4VP) was adsorbed was heated at high temperature (130°C) for a prolonged time (6 h), also shown in *Figure 3*. The fact that the flat bonding geometry of the pyridine ring (π-bonded to the surface) could translate to bonding through the nitrogen lone pair (N-bonded through σ-donation) upon heating indicates that the N-bonded geometry is more stable than the π-bonded orientation.

I.r. reflection–absorption spectroscopy can provide much information about the surface film, but mostly from the bulk. This is why spectra A and B in *Figure 4* do not show any differences related to bond orientation for P(4VP) on silver foil before and after heating (at 130°C for 6 h). In fact, these spectra are quite similar to the i.r. spectrum of the polymer. Since the thickness of the polymer film on metal was about 600 Å, the i.r. spectra provided information mainly from the bulk, with little knowledge gained of the interfacial region. It is evident from this that SERS is a source of highly sensitive molecular information, and is more suitable for study of the adsorption state of the polymer chain adjacent to the metal and the interfacial microstructure of polymer–metal composites.

Conclusion

We have demonstrated that HNO_3-etched silver foil shows an excellent SERS effect on adsorbed polymer. The SERS study indicates that the side groups of P(4VP) were adsorbed on roughened silver foil in a flat orientation at ambient temperature. Upon heating, the pyridine rings stands up from the π-bonded geometry to form an N-bonded orientation through the donation of the lone pair of nitrogen electrons, indicating that the N-bonded geometry is more stable than the π-bonded orientation.

Acknowledgement

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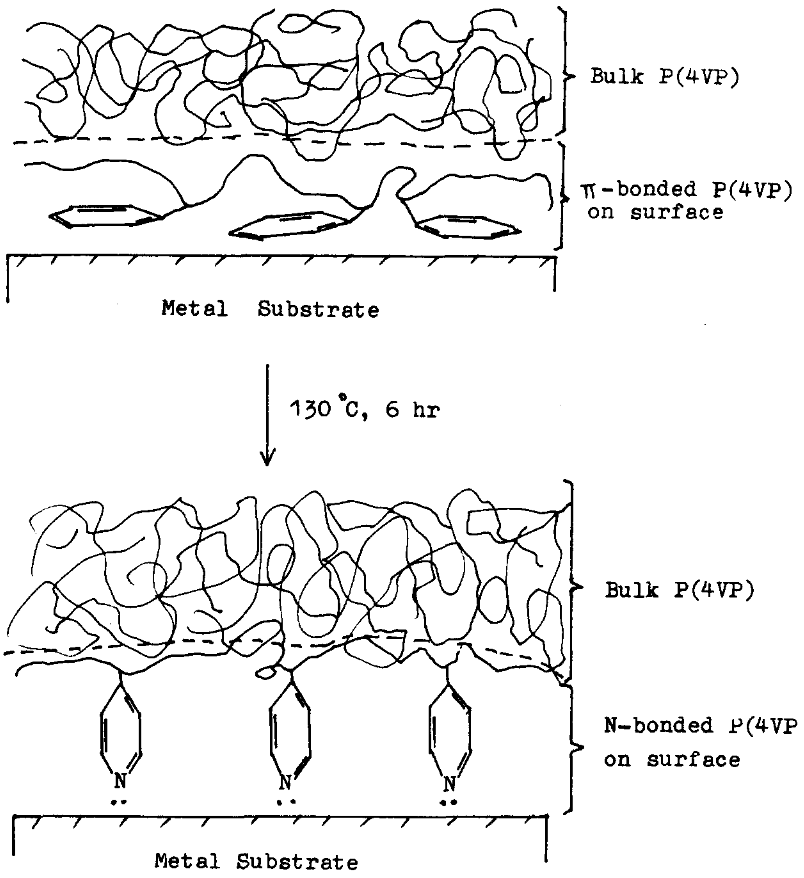

Figure 3 Schematic diagram of orientation and bonding of the first layer of poly(4-vinyl pyridine) on silver foil

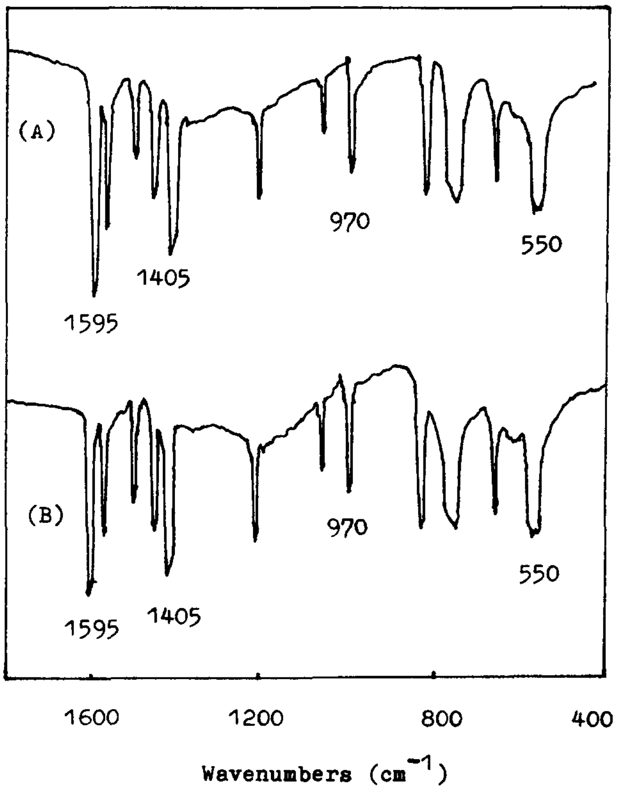

Figure 4 Infra-red reflection–absorption spectra of poly(4-vinyl pyridine) on silver foil: A, before heating; B, after heating under nitrogen at 130°C for 6 h

References

1 Lee, H. and Meisel, D. *Chem. Phys. Lett.* 1983, **99**, 262
2 Roth, P. G. and Boerio, F. J. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1923
3 Moskovits, M. and Suh, J. S. *J. Phys. Chem.* 1988, **92**, 6327
4 Suh, J. S. and Moskovits, M. *J. Am. Chem. Soc.* 1986, **108**, 4711
5 Moskovits, M., Dilella, D. P. and Maynard, K. J. *Langmuir* 1988, **4**, 67
6 Moskovits, M. *J. Chem. Phys.* 1982, **77**, 4408
7 Greenler, R. G., Snider, D. P., Witt, D. and Sorbello, R. S. *Surf. Sci.* 1982, **118**, 415
8 Allen, C. S. and Van Duyne, R. P. *Chem. Phys. Lett.* 1979, **63**, 455
9 Creighton, J. A. *Surf. Sci.* 1983, **124**, 209
10 Ni, F. and Cotton, T. M. *J. Raman Spectrosc.* 1988, **19**, 429
11 Lee, H. I., Suh, S. W. and Kim, M. S. *J. Raman Spectrosc.* 1988, **19**, 491
12 Thomas, C. S. and Panos, S. D. *J. Phys. Chem.* 1990, **94**, 1986
13 Dollish, F. R., Fateley, W. G. and Bentley, F. F. 'Characteristic Raman Frequencies of Organic Compounds', John Wiley, New York, 1973, Ch. 18
14 Green, J. H. S. and Barnard, P. W. B. *J. Chem. Soc.* 1963, 640