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SERS Studies of Polymers on Metal Surfaces. 4. Cyclization and Graphitization of Polyacrylonitrile on Rough Silver Surfaces

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Polyacrylonitrile (PAN) is well-known to undergo structural changes in the presence of oxygen at high temperatures as shown in Scheme I. Recent attention is focused on surface or interfacial reactions between PAN and metals. An ex-situ infrared reflection–absorption study of PAN films obtained by electropolymerization on a nickel substrate showed that cyclization had been completed after 24 h at 200 °C, reticulation had been completed at 300 °C, and dehydrogenation and denitrogenation started well above 300 °C.[2] An XPS and IR study of PAN films on aluminum and copper surfaces illustrated that a double-coupled conjugated system (III in Scheme I) was formed after pyrolysis on Al at 300 °C or on Cu at 200 °C for 2 h.[3] These temperatures are respectively about 100 and 200 °C lower than those previously reported for bulk PAN.[4] Another report revealed that the polymer may undergo facile photodegradation on a smooth silver surface upon ultraviolet irradiation at wavelengths in the region $250 \le \lambda \le 400$ nm. Below 266 nm, the silver-backed PAN turned yellowish brown and increased in electrical conductivity, suggesting the presence of a chromophore system of the type $-(C{=}N)^{-}{}_{n}$.[5] We report here our surface-enhanced Raman scattering (SERS) studies of structural changes of PAN on chemically roughened silver surfaces. Since the electrical conductivity of the double-coupled conjugated system can be increased by about 10 orders of magnitude upon doping,[6] knowledge of such structural changes on metal surfaces should help not only in the preparation of electrically conductive polymeric modifiers on metal electrodes but also in the understanding of the mechanisms of the conduction.

After PAN (molecular weight 9.0×10^4) had been dissolved in dimethylformamide to make a 0.4% solution, 10 μL of the PAN solution was cast on a HNO_3-etched silver foil (Aldrich; 0.025 mm) and evaporated under different conditions. The thickness of the film was about 400 Å, considering that the actual surface area became about 10 times larger after etching. Raman spectra were recorded on a SPEX-1403 spectrometer using a 647.1-nm line of a Kr^+ laser as an exciting source. Great care was taken to prevent any undesirable laser-induced decomposition of the sample.

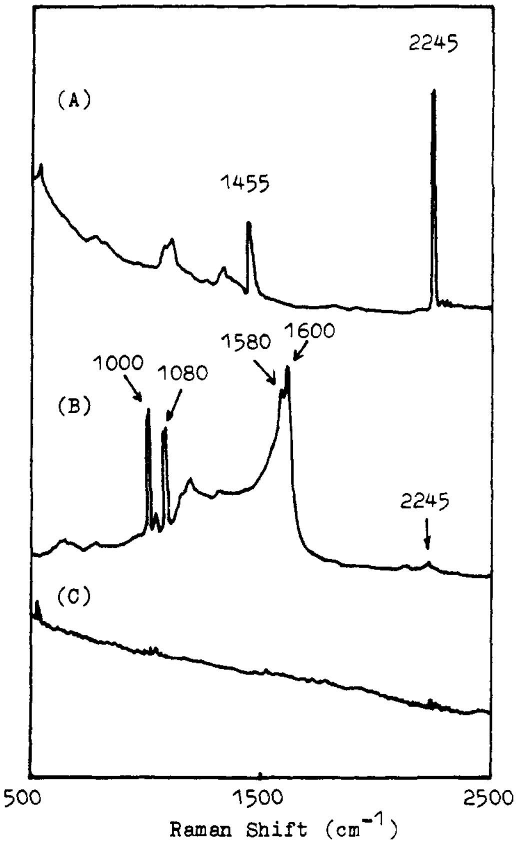
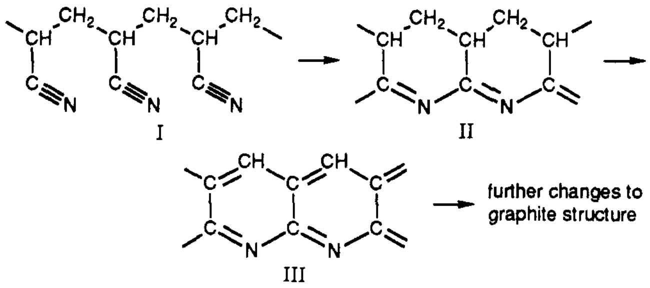


Figure 1. (A) Normal Raman spectrum of polyacrylonitrile (PAN). (B) SERS spectrum of cyclized PAN on roughened Ag foil by slow evaporation of the solvent. (C) SERS spectrum of PAN on smooth Ag foil.

Scheme I
Chemical Structures of PAN after Different Stages of Pyrolysis



For comparison, the Raman spectrum of a PAN film on an Ag substrate without HNO_3 etching is listed in Figure 1C, which shows that no enhancing effect is observed on a smooth Ag foil. However, a SERS spectrum for a roughened Ag substrate is readily obtained by slow evaporation of the solvent residue in the sample (Figure 1B). The difference between these two spectra may be explained by the general acceptance that surface roughness plays a key role in enhancing Raman scattering cross sections. One can find the dramatic difference between the SERS spectrum of PAN on roughened silver and the normal Raman spectrum of bulk films measured under the same experimental conditions (Figure 1A).[7] The band at 2245 cm^{-1} in Figure 1A attributable to the stretching vibration of the $C{\equiv}N$ side groups becomes rather weak in the SERS spectrum, while strong bands appearing at 1600, 1580, 1080, and 1000 cm^{-1} in Figure 1B are absent in the normal Raman spectrum, indicating that PAN has undergone structural changes on adsorption. It should be emphasized that no Raman shifts attributable to the solvent were detected, therefore eliminating the possibility of any undesirable solvent-induced side reactions. The SERS spectrum is typical of aromatic ring vibrations and correlates well with the FTIR spectra of thermally degraded PAN.[8] The bands at 1600 and 1580 cm^{-1} can be assigned to $-(C{=}C)-$ or $-(C{=}N)-$ conjugation ring-stretching vibrations, implying that the adsorbed PAN has been turned into a fused ring structure (corresponding to III in Scheme I). This is consistent with the great reduction of the signal intensity of the 2245-cm^{-1} band. The bands at 1080 and 1000 cm^{-1} can be ascribed to in-plane ring C–H deformation frequencies. Because of their strong intensity, it is reasonable to propose that the aromatic

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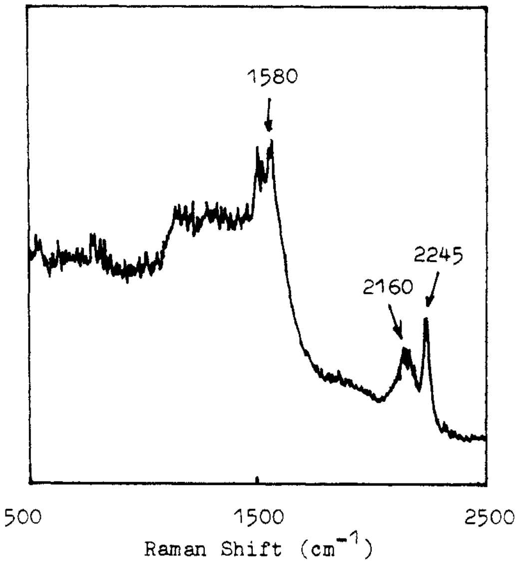
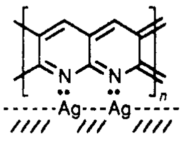


Figure 2. SERS spectrum of PAN on roughened Ag foil. The film was prepared by fast evaporation of the solvent from the surface.

Chart I
Proposed Adsorption Model for PAN on Rough Silver



ring structure is sticking up to the metal surface via its N atoms or at least the fused rings are tilted off the surface as long as the electromagnetic theory on the SERS selection rule is applied (Chart I).[9]

Figure 2 shows the SERS spectrum of PAN adsorbed on Ag prepared by fast evaporation of the solvent in vacuum at room temperature. One can find that the enhancement factor is reduced to some degree and the signal to noise ratio is poorer than that in Figure 1B. Fast evaporation made the formerly solvated polymer chains crash down on the surface and pile up with one another. The side groups had insufficient time to move onto the surface, and the polymer contacts poorly with the Ag surface. In other words, the roughened metal surfaces were less occupied and the enhancement factor is consequently lowered.

One can also find that a prominent broad band centered at 2160 cm^{-1} is observed near the sharp C≡N stretching mode in Figure 2. The only attributable vibration mode at this region is the C≡N stretching one. The substantial red shift and band broadening upon surface adsorption indicate the direct interaction between the cyano group and the silver surface. From the studies of the metal–nitrile complexes and the nitriles adsorbed on metal surfaces using EELS, XPS, UPS, and other techniques,[10] it has generally been accepted that the linear coordination (σ bonding) through the nitrogen lone pair electrons results in an increase in the C≡N stretching frequency from that of the free molecule. On the other hand, coordination through the C≡N π system is known to result in a decrease in the C≡N stretching frequency. Loo et al. reported SERS studies of the adsorption of malononitrile and succinonitrile on copper surfaces.[11] They observed the removal of the doubly degenerate ν(C≡N) in the free dinitriles in SERS spectra and concluded that the two C≡N groups in a dinitrile molecule were no longer chemically equivalent, namely, one C≡N group coordinated to the copper surface through the π system, while the other remained free, resulting in a red-shifted C≡N group band and an unshifted one. Adsorption of PAN on metal surfaces necessitates the bonding of cyano groups to metal atoms; thereby it is reasonable to observe the ν(C≡N) band alterations. Wu et al. reported that the C≡N mode of the free ligand was no longer present in the IR spectra of pyrolyzed PAN on a Cu substrate. They observed a band splitting of the ν(C≡N) mode.[3] In our case, the observed phenomenon on a roughened silver surface is very similar to what Loo et al. have reported in the case of aliphatic dinitriles on Cu. Therefore, we propose that the appearance of a ν(CN) band at 2160 cm^{-1} implies side-on type coordination of an Ag atom to a cyano group. Since the peak at 2245 cm^{-1} in Figure 2 has the same Raman frequency and bandwidth as that in Figure 1A, we assign it to the freely dangling groups alongside the chain. Figure 2 also indicates that fast evaporation produced a partially cyclized structure on the surface. The reason for the adsorption-induced cyclization may thus be attributed to the back-donation of electrons from metal to the CN system and the accompanied reduction of the C≡N triple bond energy. Such a favorable configuration and/or orientation on the roughened metal surfaces facilitates the cyclization under room temperature. Similar surface geometry effects on the surface-induced reactions have been found in the case of spontaneous polymerization of vinyl monomers on Ag elucidated by SERS spectroscopy.[12]

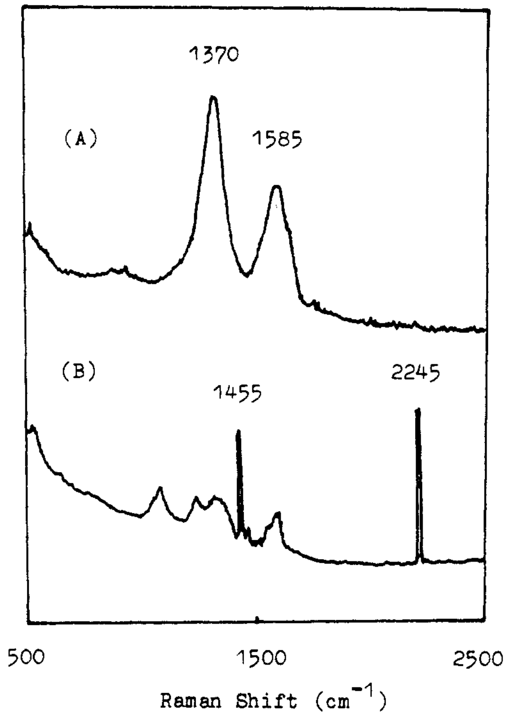


Figure 3. (A) SERS spectrum of graphite produced on an Ag foil by heating the sample at 200 °C for 6 h. (B) Normal Raman spectrum of PAN film degraded 8 h at 200 °C in vacuum.

Figure 3A shows the SERS spectrum of the adsorbed polymer sample on Ag after heating at 200 °C in vacuum for 6 h. The spectrum reveals that PAN on a rough Ag surface has further been converted to a graphite-like structure on heating. This spectrum is exactly identical to the reported SERS spectra obtained by evaporating silver on carbon fiber or graphite fiber[13] as well as the ordinary Raman spectra of graphite or PAN-based graphite fiber.[14] The intensity ratio $R = I(1585)/I(1370)$ and the width (fwhm) of the 1370-cm^{-1} band are sensitive to both the degree of graphitization and the orientation of twodimentionally ordered graphitic planes.[15] In contrast, a bulk PAN film underwent only partial cyclization after it had been treated in the same environment (Figure 3B), let alone graphitization.

Full graphitization of PAN usually needs a temperature of about 2000 °C. On Ni, Al, and Cu surfaces, dehydrogenation did not start until 300 °C. The extremely low carbonization temperature at 200 °C in vacuum on silver implies several responsible mechanisms. The catalytic action of the metal is of course one possible explanation for the observed lowering. Silver in particular is known to function as a catalyst for thermal dehydrogenation of hydrocarbon compounds. Another mechanism for the lowering of the transition temperatures may originate from the induction of laser radiation. This possibility cannot be eliminated although cyclization can be observed only by SERS for PAN chains which are on a rough metal surface and the normal Raman spectrum for bulk PAN shows no signs of structural changes (vide supra). The role of surface roughness is not ascertained directly at present, but it is expected to function in whatever degree if one takes account of the stable PAN films on a smooth Ag mirror surface prior to UV irradiation.[5]

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(7) The band at 1455 cm^{-1} in Figure 1A is attributed to the deformation vibration of the backbone CH_2 groups, whereas the broad bands at 1320 and 1365 cm^{-1} are assigned to CH bending modes.

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