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SERS evidence for existence of a critical concentration for polymer coil shrinking in poly(4-vinyl pyridine) solution

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Summary

The dependence of intensity of surface enhanced Raman scattering on the concentration of poly(4-vinyl pyridine) solutions was investigated. The spectral quality and the Raman scattering intensities of the enhanced spectra of poly(4-vinyl pyridine) adsorbed on nitric acid-roughened silver foil were inversely proportional to the concentration when it changed from semi-dilute to very dilute. The band intensity-concentration plot displays a turning point corresponding to the critical concentration for coil shrinkage. The observed phenomena are in accordance with Qian's proposal for the existence of C_s for coil shrinkage in dilute solution.

Introduction

The studies of polymer solutions have had a long history and played an important role in the development of the early concept of macromolecules. The problem about how macromolecular chain dimension varies with concentration in polymer solution is important both theoretically and practically. Most studies have been concerned with dilute solutions. The introduction of scaling theory by de Gennes to polymers made a strong impetus to the study of polymer solutions over the entire concentration range[1]. By introducing the concept of screening length into the statistical thermodynamic treatment, the mean field theory of Lohse predicts that the coil starts to shrink only as the concentration reached a certain value[2]. Recently Renyuan Qian et al. has put forward the concept of a concentration boundary of the solution from very dilute to semi-dilute region[3,4]. The critical concentration value could be identified clearly, designated as C_s. At and beyond C_s the effect of inter-chain interactions begin to be felt by the chains in solution. On further increase of solution concentration the coils will overlap each other and the spatial segment density distribution will become continuous but undulating. For further increase in concentration the chains in solution will be densely overlapped. The *Cs* value of polystyrene with weight average molecular weight of 3 10^5 in dichloroethane solution was measured to be about 0.05% by the use of excimer fluorescence[3]. Based on this conception it was proposed that the coils of polystyrene chains in a very dilute solution above the Θ temperature are expanded with few entanglements.

The discovery of surface enhanced Raman scattering (SERS) is probably one of the most important developement in the last decade in the area of surface chemistry[5]. Practically attractive silver substrate forms on which the SERS effect is observed most intensely include colloidal silver, silver island films, silver films deposited on quartz or Teflon particles, and chemically reduced silver films on glass slides. However, these substrates are not quite stable for long periods of time or at elevated temperature. It is difficult to obtain reproducible enhancements. This problem hinder widespread acceptance of SERS as a technique for mechanistic investigations. Recently, stable substrate prepared by the nitric acid etching method for SERS study has been developed in this laboratory. Silver foils etched with nitric acid exhibit excellent enhancement factor, show extraordinary stability under various environmental conditions.[6] SERS has been used to characterize thin film of polymer on the etched silver foils where the samples were coated from dilute solutions[7,8]. We have taken the advantage of stability and reproducibility of nitric acid etched silver substrates to do quantitative measurement of polymer coatings. In this paper we report a "dilution effect" on SERS signals of polyvinylpyridine on metal. We found that when the polymer was applied from a very dilute solution (0.015%) the SERS signal improved significantly as compared with that from semidilute solution (0.5%) and that there is a turning point in the plot of Raman signals versus the concentrations. We intend to relate this phenomenon to the critical concentration for coil shrinkage in polymer solution.

Experimental

An atactic poly(4-vinyl pyridine) with weight average molecular weight of 95000 was supplied by Department of Chemistry, Nanjing University, China. The polymer was dissolved in purified DMF to make solutions with concentration of 0.50%, 0.12%, 0.07%, 0.03%, 0.015% and 0.005% respectively. Commercial silver foil (30 mm × 30 mm 0.025 mm) was immersed in a freshly prepared 5 M HNO_3 solution at room temperature. Vigorous agitation was applied. After about a few minutes, a sponge-like surface with much roughness was formed. After etching, the silver foil was thoroughly rinsed with distilled water and dried in air. The etched foil was cut into several species (10 mm× 10 mm). Controlled amount of poly(4-vinyl pyridine) solution was spread on to each silver foil and the solvent was evaporated under vacuum for 24 hours. The thickness of the film was measured with an electrochemical quartz crystal microbalance. The average thickness was 400± 50 Å. Raman spectra were recorded with a Jobin-Yvon U1000 Raman spectrometer. The incident laser excitation was 514.5 nm from a Innova 200 Ar^+ laser source. The laser power reached the silver foils was about 20 mW. The stepsize was 4 cm^{-1} and the integration time was 6 seconds for each spectrum. A back scattering geometry in air was used for all samples. The Raman intensity for each spectrum was labeled as "Counts mW^{-1} Sec^{-1}". In order to ensure that there is no laser-induced change in the SERS spectra, the foil was spun during the measurement. Spining can also average the detecting adsorbate thickness.

Result and Discussion

Figure 1A shows a normal Raman spectrum of DMF and Figure 1B illustrates a SERS apectrum recorded from an etched silver foil after immersion in neat DMF. Figure 1B does not provide any significant Raman lines except noise, indicating that there is no observable material adsorbed on the etched surface after immersion in DMF.

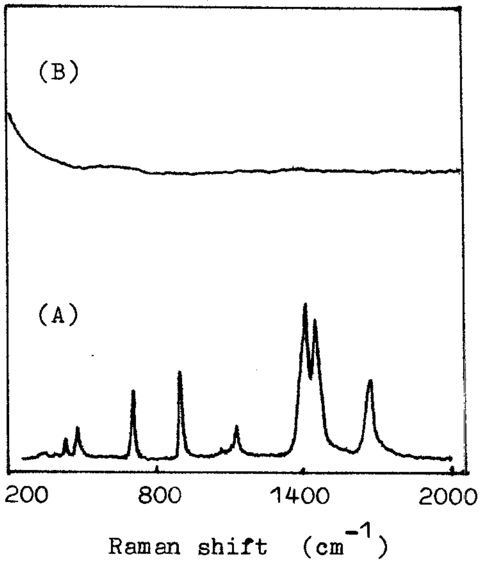

Figure 1. (A) Normal Raman spectrum of DMF; (B) SERS spectrum for an etched foil after immersion in DMF.

Figure 2A, 2B, 2C, 2D, and 2E illustrate SERS spectra of poly(4-vinyl pyridine) applied from 0.50%, 0.12%, 0.07% 0.015% and 0.005% solutions, respectively.

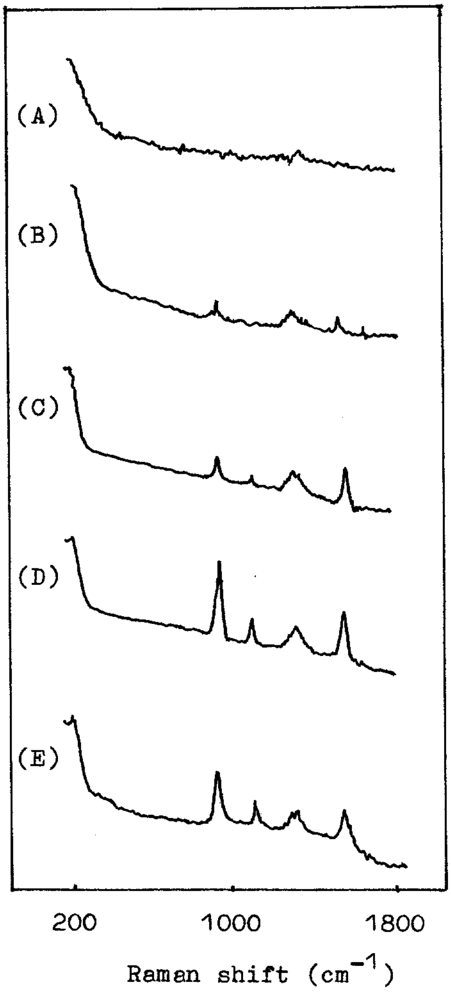

Figure 2. SERS spectra of poly(4-vinyl pyridine) on Ag foils applied from solutions of (A) 0.50%; (B) 0.12%; (C) 0.07%; (D) 0.015%, (E) 0.005%.

Lee and Meisei *et al.* reported SERS spectra of poly(4-vinyl pyridine)[9]. The features of Raman lines of Figure 2, which was recorded for the samples prepared from very dilute solutions, are similar to that reported in literature. The strongest band in Figure 2 is near 960 cm^{-1} that is assigned to the ring-breathing mode, and a medium intensity band near 1600 cm^{-1} that is due to a ring stretching mode.

A "dilution effect" on spectral quality and the relative intensities between Raman lines in Figure 2 can be clearly observed. The signal-to-noise ratio is rather poor in the spectra recorded from the foils subjected from 0.50% and 0.12% solutions. However, as the applied solution was diluted to 0.015%, an excellent SERS spectrum was obtained, as shown in Figure 2D.

A plot of intensities of the Raman band at 960 cm^{-1} (Counts mW^{-1} Sec^{-1}) versus concentrations (-Log *C*) is shown in Figure 3.

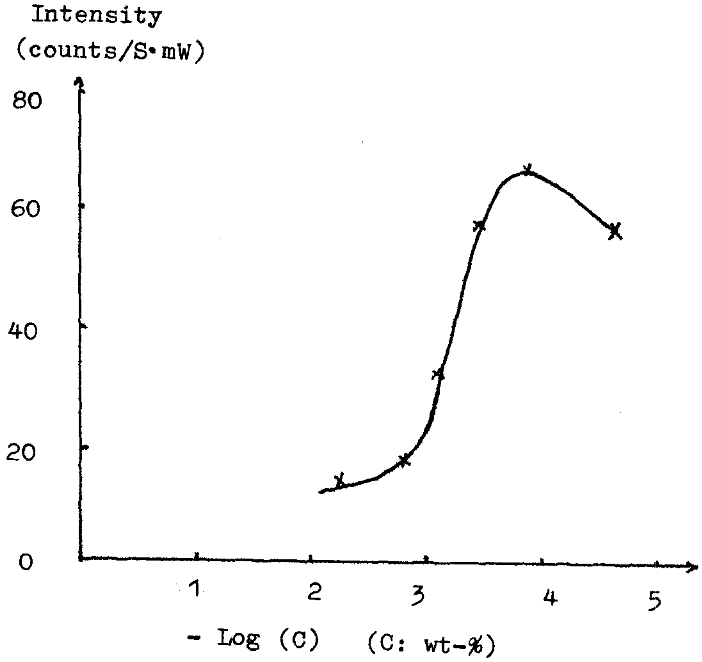

Figure 3. A plot of Raman intensity *versus* concentrations.

One can easily see that the Raman intensity is inversely proportional to the concentration in the range under investigation. A turning point which is about 0.015% in concentration, can be found in the plot. Near the concentration, excellent SERS spectra of poly(4-vinyl pyridine) could be recorded; above the concentration, the spectral quality gradually become poor. The observed evidence for critical concentration for coil shrinkage in this experiment is in accordance with Lohse's mean field theory which predicts that the coil starts to shrink only as the concentration reached a certain value[2], and is in good agreement with Qian's proposal about C_s.

The Raman intensity could be calculated based on the band heights, band height times band width, or the area covered by the band. One should be kept in mind that more than one mechanism may be responsible for the enhancement phenomenon of Raman intensity on roughened surface and that the observed enhancement factors resulted from a combination of several contributions. One may not exclude the possibility that surface interactions, e.g. formation of charge transfer states of the metal-adsorbed molecular complex, are active at close range[10].

The conformation of macromolecular chains in solution above *i* temperature depends highly on the concentration. In a concentrated or a semidilute solution, macromolecular chains overlap each other. According to Qian's theory, in a very dilute solution, below C_s, the coils were isolated and expanded. As the concentration increased above C_s, the coils start to feel each other and to shrink. As the solution was coated on to metal surface and then the solvent was removed, the macromolecular coils collapsed against the surface. If the solution applied was not very dilute, macromolecular chains would have more difficulty arranging themselves, resulting in a more random orientation on the surface. When the solution was very dilute (near 0.015% in case of polyvinylpyridine) and above *i* temperature, macromolecular chains were isolated and expanded, and they would have more chance to interact with the metal and arrange themselves by thermodynamic movement, if the solvent was evaporated slowly, resulting in more contact points along the chain bonded to the surface and thus a stronger enhancement factor. Figure 2 shows that excellent SERS spectra could be obtained by proper sample doping method from very dilute solutions.

Conclusion

We have demonstrated the "dilution effect" on spectral quality of surface enhanced Raman scattering of polyvinylpyridine. The results verified the prior conjecture and expection, i.e., the existence of a theoretical concentration for coil shrinking is confirmed. In other words, Lohe's theoretical considerations and the physical picture proposed by Qian et al. have been proved by SERS experiments.

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