Surface enhanced Raman scattering evidence for the existence of a critical concentration for coil shrinkage in polystyrene solutions

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The dependence of surface enhanced Raman scattering intensity on the concentration of polystyrene solution was investigated. The spectral quality and the Raman line intensities of the enhanced scattering of polystyrene deposited on silver foil, roughened with nitric acid, were related to the concentration. The band intensity *versus* 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 a critical concentration for coil shrinkage, based on excimer fluorescence studies of polymer solutions.

(Keywords: critical concentration; coil shrinkage; polystyrene)

Introduction

The study of polymer solutions has a long history and has played an important role in the development of the concept of macromolecules. The variation of macromolecular chain dimensions with concentration in polymer solution is important in both theory and practice. Most studies have been concerned with dilute solutions. The introduction by de Gennes of scaling theory to polymers made a strong impact on 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 when the concentration reaches a certain value[2]. Recently, Qian *et al.* have put forward the concept of a concentration boundary of the solution from very dilute to semidilute[3,4]. The critical concentration value, C_s, could be identified clearly. At and beyond C_s the effect of interchain interactions begins to be felt by the chains in solution. On further increase of solution concentration, the coils overlap each other and the spatial segment density distribution becomes continuous but undulating. With a further increase in concentration, the chains in solution become densely overlapped. The C_s value of polystyrene (weight average molecular weight $= 3 \times 10^5$) in dichloroethane solution was measured by excimer fluorescence[3] to be about 0.057%. Based on this concept 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 developments in the last decade in the area of surface chemistry[5]. The SERS effect is observed most intensely on silver substrates, including colloidal silver, silver island films, silver films deposited on quartz or Teflon particles, and chemically reduced silver films on glass slide. However, these substrates are not stable over long periods of time or at elevated temperatures. It is difficult to obtain reproducible enhancements. This problem hinders the widespread acceptance of SERS as a technique for experimental investigations. Recently, a stable substrate for SERS study has been developed, prepared by the nitric acid etching method. Silver foils etched with nitric acid exhibit an excellent enhancement factor and show extraordinary stability under various environmental conditions[6]. SERS has been used to characterize thin films of polymer on roughened metal surfaces, where the samples were coated from dilute solutions[7,8]. We have taken advantage of the stability and reproducibility of nitric acid etched silver substrates to make quantitative measurements of polymer coatings. In this paper we report a 'dilution effect' on SERS signals of polystyrene on metal. We found that when the polymer was applied from a very dilute solution (near 0.001%), the SERS signal improved significantly compared with that from semidilute solution (0.5%); it was also found that there is a turning point in the plot of Raman signal *versus* concentration. We intend to relate this phenomenon to the critical concentration for coil shrinkage in polymer solution.

Experimental

An atactic polystyrene (molecular weight 3.1×10^5; polydispersity 1.07) was supplied by the Department of Chemistry, Nanjing University, China. The polymer was dissolved in purified toluene to make solutions with concentration of 0.5%, 0.1%, 0.005%, 0.003% and 0.001%. Commercial silver foil, with dimensions of 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 a few minutes, a rough, sponge-like surface was formed. After etching, the silver foil was thoroughly rinsed with distilled water and

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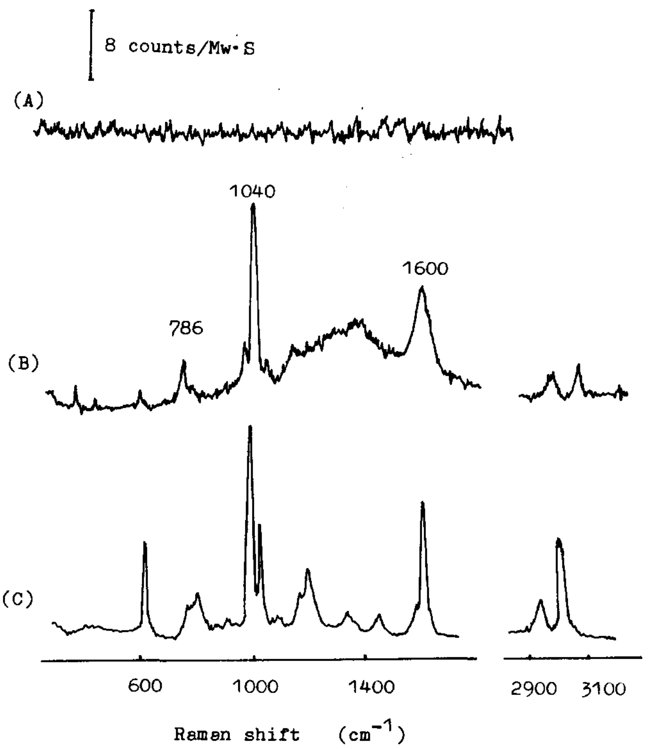

Figure 1 (A) SERS spectrum recorded from Ag foil after immersion in pure toluene; (B) SERS spectrum recorded from Ag foil after immersion in polystyrene solution (0.5%); (C) normal Raman spectrum of polystyrene (with integration time 10 s)

dried in air. The etched silver foil was cut into several small pieces (10 mm x 10 mm) to coat polystyrene solutions with different concentrations. A controlled amount of polystyrene solution was spread onto silver foil and the solvent was evaporated slowly. Based on the amount of solution, the concentration and the area of silver foil, the thickness of polystyrene deposited on the surface was calculated to be about 400–500 Å for each sample. Raman spectra were recorded with a Jobin-Yvon U1000 Raman spectrometer. The incident laser excitation was 514.5 nm, from an Innova 200 Ar^+ laser source. The laser power reaching the silver foils was 20 mW. The step size was 2 cm^{-1}. A back-scattering geometry in air was used for all samples. The Raman intensity for each spectrum was recorded in units of 1 counts mW^{-1} s^{-1}. In order to ensure that there was no laser-induced change in the SERS spectra, the foil was spun during the measurement. Spinning also leads to standard thickness of the detecting adsorbate.

The size and morphology of the polystyrene particles prepared from solutions with different concentrations were examined by transmission electron microscopy (TEM). The polymer was dissolved in purified cyclohexane to make dilute solutions. After rapid freezing of the solution in liquid nitrogen, the solvent was sublimed under vacuum at low temperature. The freeze-dried polymer powders were examined directly by TEM.

Results and discussion

Figure 1A shows a SERS spectrum recorded from an etched silver foil after immersion in neat toluene. It does not provide any significant Raman lines except noise, indicating that no observable material was adsorbed on the silver surface. *Figures 1B* and *C* illustrate, respectively, a SERS spectrum and a normal Raman spectrum of polystyrene, recorded with an integration time of 10 s. Both spectra show features of aromatic vibration modes. The shifts in frequencies and disappearance of some bands are due to the SERS effect or to the interaction of silver with the adsorbed material. *Figures 2* and *3* show SERS spectra of the samples prepared from dilute to very dilute solutions, recorded with an integration time of 1 s.

Venkatachalam *et al.* reported SERS spectra of polystyrene from bilayers of polystyrene and poly(4-styrene sulfonate)[9], which showed similar features to the Raman lines in *Figure 1B* (for the sample prepared from a 0.05% solution).

A 'dilution effect' on spectral qualities and the relative intensities between Raman lines in *Figures 2* and *3* can be clearly observed. The signal-to-noise ratio is rather poor in the spectra recorded from the foils prepared from

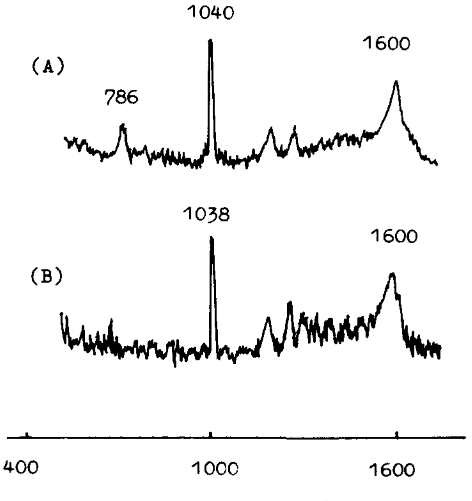

Figure 2 SERS spectra of polystyrene on Ag foil deposited from solutions of 0.1% (A) and 0.5% (B) (the spectra were recorded with integration time 1 s)

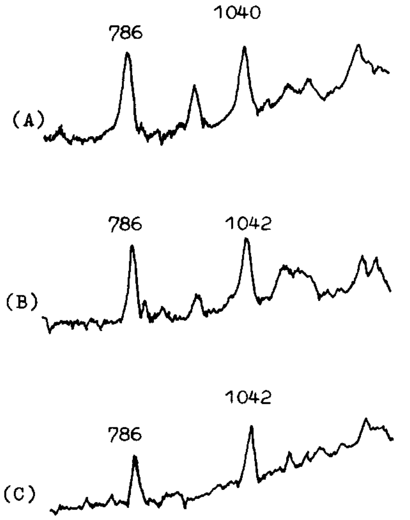

Figure 3 SERS spectra of polystyrene deposited from solutions of 0.001% (A), 0.003% (B) and 0.005% (C) (the spectra were recorded with integration time 1 s)

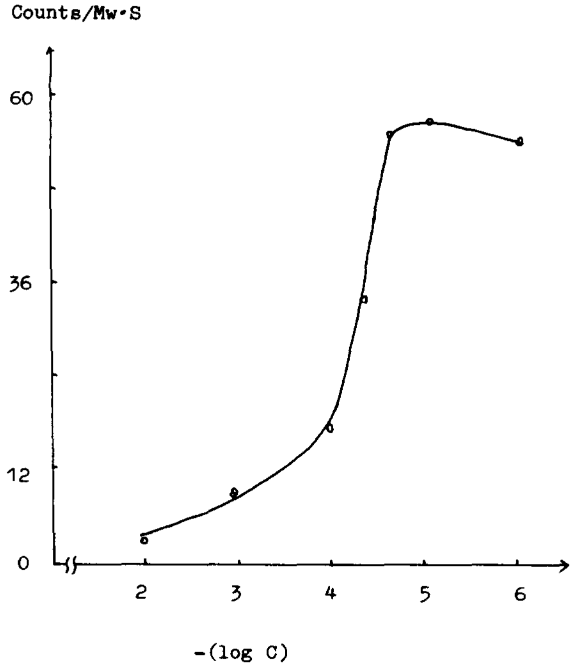

Figure 4 Plot of Raman intensities (786 cm^{-1}) *versus* $-(\log C)$. Note: the units of C are g cm^{-3}

0.5% and 0.1% solutions, as illustrated in *Figure 2*. However, as the applied solution was diluted to 0.005%, 0.003% and 0.001%, excellent SERS spectra were obtained, as shown in *Figure 3*. Furthermore, the strongest band in *Figure 1B* and *Figure 2* is near 1040 cm^{-1}, assigned to the ring-breathing mode, and a medium intensity band appears near 1600 cm^{-1}, due to a ring stretching mode[9]. SERS spectra in *Figure 3*, recorded from the specimen prepared from very dilute solutions, show a strong band near 786 cm^{-1}. However, there are only weak bands in this region in both the normal Raman spectrum and the SERS spectrum for higher concentrations. Jasse *et al.* proposed that the 789 cm^{-1} Raman line was due to the vibration of aromatic rings, and was sensitive to the conformation of the polymer chain[10].

In the polarized Raman study of molecular orientation in uniaxially stretched atactic polystyrene, Jasse and Koenig reported that polarized Raman spectra in four scattering arrangements exhibited bands with different relative intensities[11]. The spectrum for the YY arrangement, by which both incident and scattered radiations were polarized parallel to the stretching direction, showed much stronger Raman lines in this region than those recorded by other arrangements. Based on the relative intensities, the orientation function could be calculated[11]. In analogy to polarization measurement for the oriented polystyrene, we propose that the increase in intensity of the 786 cm^{-1} band in the SERS spectra of *Figure 3* is due to a particular orientation of the aromatic ring of the polymer on the silver surface.

A successful basis for analysing SERS spectra with respect to orientation of adsorbates has been reported in the form of 'surface selection rules' by Moskovits and co-workers[12–16], and others[17,18]. These results are based on the electromagnetic theory of SERS intensity, which states that via resonance interaction with surface plasmons of the metal, normal modes of the adsorbed molecule, involving changes in molecular polarizability with a component perpendicular to the surface, are subject to the greatest enhancement. On the basis of surface selection rules, we may propose that the aromatic rings of polystyrene are basically 'lying down' flat on the surface when the polymer is adsorbed onto the silver surface from a very dilute solution. This adsorption conformation is analogous to a stretched polystyrene from which a strong Raman band near 800 cm^{-1} was reported by a YY polarization measurement[11]. The frequency shift of the band in this region is probably due to the SERS effect or to metal–adsorbate interaction.

The conformation of polymer chains in solution above the θ temperature is highly dependent on the concentration. In a concentrated or a semidilute solution, polymer chains overlap each other. According to Qian's theory, in a very dilute solution, below C_s, the coil is isolated and expanded. As the concentration increases above C_s, the coils start to contact each other and to shrink. As the polymer solution is coated onto the metal surface and the solvent removed, the polymer coils collapse against the surface. If the solution applied is not very dilute, polymer chains have more difficulty arranging themselves, resulting in a more random orientation on the surface. When the solution is very dilute (near 0.001% in the case of polystyrene), polymer chains are isolated and expanded, and have more chance to interact with the metal and arrange themselves by thermodynamic movement. If the solvent is evaporated slowly, the aromatic rings have more chance to bond with the metal through π-system, resulting in a 'lying down flat' orientation. *Figure 3* shows that excellent SERS spectra can be obtained by proper sample doping from very dilute solutions.

A plot of the intensity of the Raman band at 786 cm^{-1} (counts mW^{-1} s^{-1}) *versus* concentration ($-\log C$) is shown in *Figure 4*. One can easily see that the Raman intensity is related to concentration in the range under investigation. A turning point is seen in the plot at about 0.001% concentration. Near this concentration, excellent SERS spectra of polystyrene are recorded; above this concentration, the spectral quality gradually becomes poorer. The observed evidence for a 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 reaches a certain value[2], and is in good agreement with Qian's proposal about C_s. By the use of excimer fluorescence study[3], C_s is found to be about 0.057% for polystyrene with a molecular weight of 3×10^5. The critical concentration for coil shrinkage based on the turning point of the plot of *Figure 4* is about 0.001%.

The size and shape of particles prepared from the expanded coils in very dilute solutions can be observed directly by TEM. As the solution is rapidly frozen in liquid nitrogen, the expanded shape is maintained in the frozen solution. After the solvent is removed by subliming, expanded coils in the condensed state are obtained. We previously reported that polystyrene with expanded coils shows a much lower glass transition temperature than ordinary polystyrene, owing to fewer chain entanglements existing in the sample[19]. The TEM photograph in *Figure 5a* shows that the polymer powder prepared from 0.04% solution is a chain-like material, while that in *Figure 5b* illustrates that the powder prepared from 0.004% solution is composed mainly of separated particles, each consisting of one to three molecules

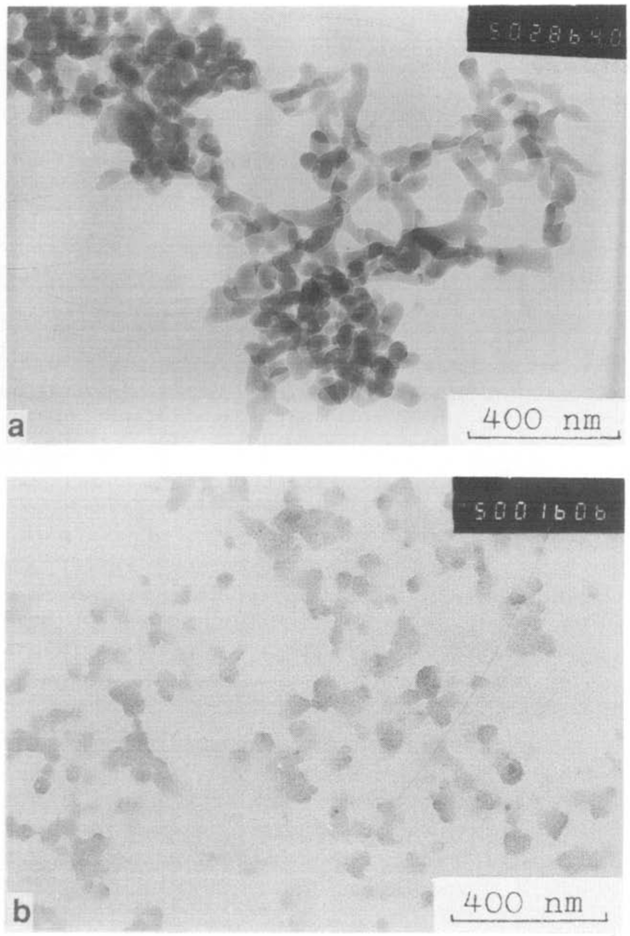

Figure 5 TEM micrographs of polystyrene prepared by freeze-drying (a) 0.04% solution; (b) 0.004% solution

with irregular shapes. Schulz obtained monomolecular particles by freeze-drying a more dilute solution (less than 0.001%), but the experiment was not easy to conduct since the polymer tended to coat the apparatus walls and was difficult to handle in a controllable manner[20]. SERS and TEM results, as well as the literature report[20], indicate that the critical concentration for coil isolation and shrinkage of polystyrene in toluene above the θ temperature is near 0.001%.

Conclusion

We have demonstrated the 'dilution effect' on the spectral quality of surface enhanced Raman scattering of polystyrene. The results verify the prediction that a theoretical concentration for coil shrinkage exists. In other words, Lohse's theoretical considerations and the physical picture proposed by Qian *et al.* are supported by SERS experiments.

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