

Notes

STUDY ON THE CONCENTRATION DEPENDENCE OF ORIENTATION OF POLYSTYRENE ON SILVER BY THE SERS TECHNIQUE*

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Abstract Polystyrene films were adsorbed onto a silver surface from dichloromethane solutions with concentrations of 0.1 to 12 wt%, and then studied by the surface enhanced Raman technique. A critical concentration for coil interpenetration was observed.

Keyword Surface enhanced Raman scattering (SERS). Polystyrene. Concentration dependence

INTRODUCTION

It is well known that polymer solutions can be classified into dilute, semi-dilute and concentrated ones, corresponding to the states of separated, overlapped and interpenetrating chains, respectively. If solvent is quickly evaporated, the concentration dependence of interchain interaction of polymer in its solution is reflected in the properties of the aggregated polymer. Our previous work has shown a significant distinction in thermal properties for the polystyrene solution-cast films which are obtained from different concentration regimes by rapid evaporation in vacuum, and a critical concentration for coil interpenetration is observed from DSC^[1]. The difference in properties of the polymers aggregated from different concentration regimes should be accompanied by different condensed structures. In the case of amorphous polystyrene, however, few experimental techniques can directly detect the concentration dependence of condensed structure in a cast film. Therefore, an attempt has been to characterize the dependence of condensed structure on solution concentration, in order to shed some light on the origin of associative variation in properties at a molecular level.

Surface enhanced Raman scattering (SERS) can give some information about the macromolecular orientation of a thin polymeric film on the metal surface, where polymer is adsorbed from its solution. Interestingly, the orientation observed from SERS is usually influenced by solution concentration. Herein, concentration dependence of orientation of atactic polystyrene adsorbed on Ag is studied by SERS spectra, which reflects different interchain interaction of polymer in different concentration regimes.

EXPERIMENTAL

Atactic polystyrene having a viscosity average molecular weight of 1.65×10^5 was dissolved in dichloromethane

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to give solutions with concentration of 0.1 wt%, 1 wt%, 2 wt% and 12 wt%. Chemically etched silver plates ($5 \times 5 \text{ mm}^2$), prepared as described in Ref. [2], were dipped into different concentration solutions for about 20 minutes. The polystyrene films which were estimated to be 50–1000 nm thick, were found to be adsorbed on the activated silver surfaces. After being rapidly dried in vacuum, the polystyrene-adsorbed films were measured on a Perkin-Elmer system 2000 FT-Raman spectrometer, where the excitation wavelength was 1064 nm operating at 300 mW laser power and 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

Figures 1b)–e) illustrate the Raman spectra of the polystyrene films adsorbed from polystyrene/dichloromethane solution with concentrations of 0.1 wt% to 12 wt%. All of these spectra display a clear SERS enhancement effect and a significant difference with varying concentration. As a reference, a typical Raman spectrum of solution-cast polystyrene films is shown in Fig. 1a), which is quite similar to that of commercial atactic polystyrene.

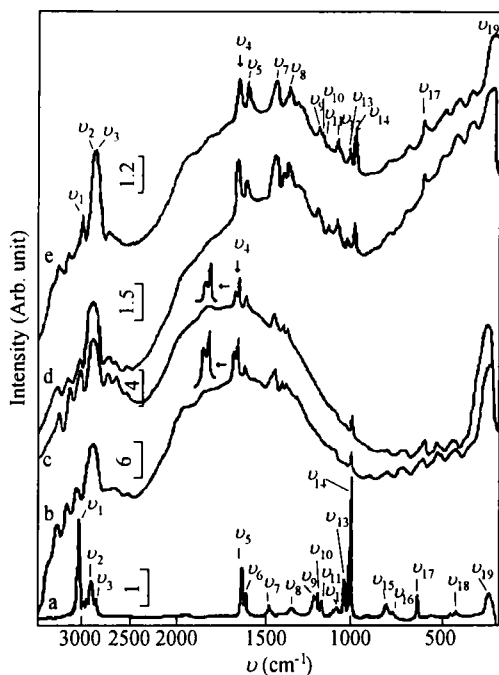


Fig. 1 Raman spectra of a) a solution-cast polystyrene film (with a thickness of a few μm , cast from 2 wt% of polystyrene/dichloromethane solution); b)–e) polystyrene films adsorbed on silver at solution concentration of 0.1, 1, 2 and 12 wt%, respectively

As reported by several authors^[3–5], the overall Raman vibrations assigned to phenyl ring, chain C–H, chain backbone and ring- C_α vibration modes are discussed separately.

Phenyl Ring Mode

The vibrations associated with phenyl ring include ν_1 , ν_4 , ν_5 , ν_6 , ν_{10} , ν_{11} , ν_{13} , ν_{14} , ν_{15} , ν_{16} , ν_{17} and ν_{18} . Among these bands, the band ν_4 at ca. $1640\text{--}1650 \text{ cm}^{-1}$ is of particular interest for the following reasons.

First, the ν_4 band, which is not detected in solution-cast polystyrene films and also was not reported in the literature, appears in the Raman spectra of the polystyrene films adsorbed on Ag. So this band must result from the enhancement of ring stretching vibration.

SERS enhancement always arises from the vibrations which have depolarizable component perpendicular to the surface, and the magnitude of the enhancement will be proportional to the projection of the dipole moment on the perpendicular to the surface^[6–8]. This selective enhancement of different modes of molecules along with the

appearance of certain new bands gives some insight into the orientation of the molecules on the metal surface. Considering a phenyl ring unit along the polystyrene chain, which has a C_{2v} local symmetry, the ν_4 band belongs to the in-plane vibration. According to the SERS selective rule, only if phenyl ring is perpendicular to silver surface, can the ν_4 band be enhanced.

Second, the ν_4 band appears at a higher frequency compared to the ring stretching vibration of most reported benzene derivatives. The interactions between adjacent oriented rings may be responsible for the shift to high wavenumber, but we have no more experimental evidence to support such a hypothesis.

Third, the shape of ν_4 band changes with changing solution concentration. A double peak for the band at a low concentration gradually changes into a single peak when the solution concentration is more than 1 wt%. Enhancement decreases with the increase of solution concentration. This is in agreement with maximum enhancement of a mono-molecular layer^[9]. Moreover, a double peak is a characteristic for ring stretching vibration, this supports the view that the band is due to enhancement.

As for the other observed ring vibrations, the strong ν_1 , ν_3 and ν_{14} band at 3052, 1603 and 1000 cm^{-1} in the Raman spectra of the solution-cast polystyrene, respectively associated with C—H stretching of ring, C—C stretching of ring and ring breathing, appear at 3080, 1606, 1002 cm^{-1} in SERS spectra. The ν_{10} , ν_{11} and ν_{12} band, which slightly depend on solution concentration, are visible when concentration is more than 1 wt%. The fact that all the observed bands are assigned to in-plane ring vibration supports the orientation of the phenyl plane perpendicular to the silver surface.

Ring- C_α Mode

The vibration of the ring- C_α bond that links the phenyl ring with the backbone is related to the ν_9 and ν_{19} band. Considering a phenyl ring unit, the ν_9 band belongs to the in-plane stretching mode, while the ν_{19} band is comprised of in-plane and out-of-plane bending mode. From the SERS spectra of polystyrene on Ag, it is shown that the ν_9 band at 1195 cm^{-1} is weak while the ν_{19} band at 216 cm^{-1} is enormously enhanced. This suggests that the out-of-plane mode of the ring might be enhanced. From the SERS theory, the ring- C_α bond makes a twisted angle with the linked ring plane. Thus, it is inferred that the phenyl rings stand on the silver surface but make a twisted angle with the silver surface.

Chain C—H Mode

The ν_2 , ν_3 , ν_6 and ν_7 bands attributed to C—H stretching or bending of the chain are greatly enhanced in the spectra of polystyrene films on Ag. Since the SERS selection rule predicts that the vibrations which have a dipolar component perpendicular to the surface are enhanced, the C—H bond of the chain should lie at a significant angle with the silver surface.

Chain Backbone Mode

Based on the publication of Jasse *et al.*^[3], the very weak ν_{12} band at 1080 cm^{-1} in normal Raman spectra of atactic polystyrene is attributed to C—C stretching vibration of the chain. In SERS spectra of polystyrenes adsorbed on Ag, the ν_{12} band is obviously affected by solution concentration. At a low solution concentration, this band is absent. When the solution concentration is higher than 1 wt%, a weak band at 1098 cm^{-1} appears, which is assigned to the C—C stretching of chain. The absence of the ν_{12} band in SERS spectra of polystyrene films formed from a dilute solution suggests that the C—C bond along the polymeric chain lies on the silver surface, leading to the disappearance of the band. When solution concentration increases, the C—C bond becomes twisted and lies at an angle with silver surface, the ν_{12} band thus appears. Disorder begins to occur in the polystyrene films when solution concentration is higher than 1 wt%.

From the foregoing discussion, one conclusion is that these polystyrene films become oriented with respect to the silver surface, the polymeric chain lies on the silver surface with phenyl ring planes and C—H bonds of CH_2 making a significant angle with the silver surface.

Another conclusion is that the orientation of polystyrene on Ag is clearly influenced by the solution concentration. Polystyrene films obtained from a low concentration of 0.1~1 wt% are well oriented on the silver surface. When the solution concentration is higher than 1 wt%, disorder in the polystyrene-adsorbed films starts

to be clearly observed.

The concentration dependence of orientation reflects the concentration dependence of polymer interchain interaction in solution. In a dilute solution, polymer chains are separated. When the non-interpenetrating polymer coils are aggregated, polymer chains have a tendency to adopt a highly ordered conformation. When solution concentration increases to a certain degree, polymer coils begin to interpenetrate, and polymeric chains overlap or entangle with each other. When a polymer film is produced from this kind of solution, it should contain entangled random coils, therefore being more disordered. The concentration for the occurrence of disorder at 1 wt% should correspond to a critical concentration for coil interpenetration, which is in agreement with the results observed by DSC.

Xue and his coworkers have used this technique when estimating the critical concentration of coil shrinkage from the SERS spectra of polystyrene^[10]. They obtained the inconsistent result that phenyl rings lie flat on the silver surface, and they inferred that a significant enhancement occurred at dilute solution concentrations around 0.001%~0.01% mol/L. Without entering into a scientific controversy, the discrepancy means nothing but different experiment conditions. It seems likely that orientation of polystyrene chains could have some effect on the number of adsorbed macromolecules. Ring-standing orientation allows more molecules to be packed on the silver surface than ring-lying orientation. Thus, polystyrenes absorbed from higher solution concentrations of 0.1%~1% show SERS spectra, and have a ring-standing orientation.

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