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Near-infrared SERS Study of the Adsorption of a-PMMA Dip-coated onto Silver Mirror Substrate

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Abstract: The interface between a-PMMA thin film and silver mirror substrate was investigated using surface-enhanced Raman scattering (SERS). It is found that the molecular chain axis of a-PMMA tends to parallel the substrate in the interface. When the sample is annealed at different temperatures, some interesting changes appear in the SERS spectra. The spectra differences and their transition are due to the surface geometry change of the ester group.

Keywords: SERS, polymer-metal interface, a-PMMA.

Near-infrared Fourier transform surface enhanced Raman scattering (NIR-SERS) has become an important technique in the structural studies of adsorbed molecules on the roughened metal surface[1,2,3]. The technique has advantages arising from both the NIR excitation and the SERS effect. By use of the NIR excitation, one can avoid both strong fluorescence and unfavorable photo-reaction of chromophoric groups of the adsorbed molecules at the same time[4].

In this work, by dip-coating the atactic poly(methyl methacrylate) (a-PMMA) solution onto the silver mirror substrate and slowly evaporating the solvent, a well ordered polymer film can be formed on the surface, resulting in a good SERS effect. To our knowledge, this is the first time to report the SERS spectra of PMMA thin film dip-coated onto metal substrate.

All spectra were recorded on Bruker IFS 55/FRA 106 spectrometer. NIR excitation at 1064 nm was provided by a Nd:YAG laser. The SERS spectrum was obtained by averaging 128 scans with a resolution of 4 cm^{-1}. The laser power at the sample point was 200 mW for the films and 100 mW for the solid powder samples.

Figure 1 shows the SERS spectrum of a-PMMA dip-coated onto the top of the substrate from a 1% chloroform solution and the normal Raman spectrum from the solid powder of a-PMMA. It is interesting to note that the intensities of two bands were very strong in the SERS spectra than in the normal Raman spectra. The bands near 1003 cm^{-1} in the infrared and Raman spectra have been assigned to the OCH_3 rock vibration interacting with the stretch vibrations of the COC group[5,6]. Dybal *et al.* confirmed this assignment by the normal coordinate calculations and the potential energy distribution

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(PED) indicated large contributions from the C-O-C stretch vibration[7]. However, it is difficult to assign the band near 1602 cm^{-1}.

A successful basis for the analysis of SERS spectra with regard to orientation of the adsorbate was worked out in the form of "surface selection rule"[8]. These rules are based on the electromagnetic theory of SERS intensity, which indicates that, *via* resonance interaction 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 scattered intensity and the Raman excitation intensity. Since the local fields are the highest normal to the surface, normal modes of the surface molecule, which involve the changes in molecular polarizability with a component normal to the surface, are subject to greatest enhancement. This type of analysis has been applied successfully by many authors[9,10,11].

Figure 1 (A) SERS spectrum from a-PMMA dip-coated onto the top of the substrate from a chloroform solution 1%; (B) normal Raman spectrum of the bulk a-PMMA

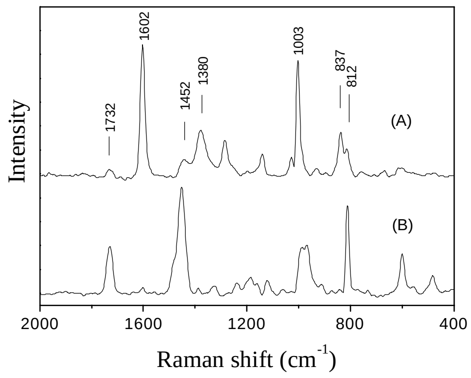
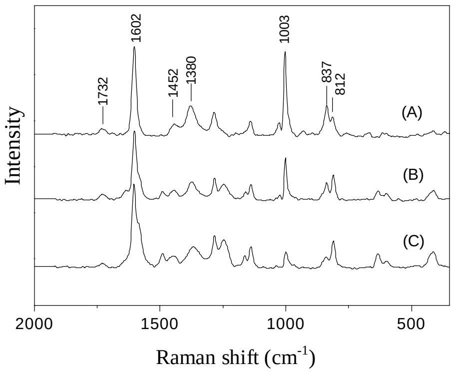


Figure 2 SERS spectra from a-PMMA dip-coated on the top of the substrate from a chloroform solution 1% without annealing (A) and annealing at temperature 120 °C (B) 150 °C (C) for 1 hour respectively



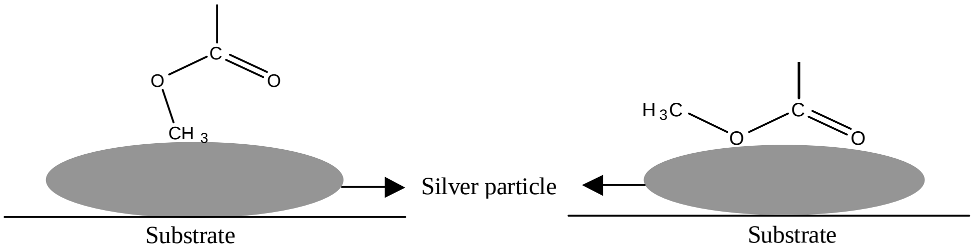
As can be seen from the SERS spectra of a-PMMA, the bands near 1380, and 837 cm^{-1} show great enhancement compared with the normal Raman spectra. So the polarizability changes associated with the band are perpendicular to the interface between polymer and metal. Moreover the bands near 1380 and 837 cm^{-1} are assigned to -CH_3 symmetric bend vibration and CH_2 rocking vibration respectively and both involve considerable motion perpendicular to the long axis of the molecules[7,12]. Assuming that a-PMMA is adsorbed with the molecular axes mostly parallel to the surface, the corresponding bands should appear with considerable intensity and this result was observed. The band near 1452 cm^{-1} is assigned to CH_2 symmetric bend vibration involving motion mostly parallel to the long axis of the molecules[11]. From the SERS spectra of **Figure 1,** it is found that the intensity of the band near 1452 cm^{-1} is largely decreased. So it is rational to assume that the a-PMMA is adsorbed with the molecular axes mostly parallel to the surface

The medium strong band in the normal Raman spectrum, near 1732 cm^{-1}, is very weak in the SERS spectrum. This band was assigned to C=O stretching mode. However the band near 1003 cm^{-1}, which has been assigned to the C-O-C stretch vibration[11,13], is enhanced largely in the SERS spectra. Both of the two bands are connected with the ester group of a-PMMA.

It is believed that in this case the differences are related to a geometry structure caused by the presence of the metal surface. When a-PMMA films are dip-coated on the silver mirror substrate, molecules in the first monolayer have the conformation with one ester group in contact with the surface. According to “SERS selection rules” mentioned above, C=O stretching modes are likely to be parallel to the metal surface and the corresponding Raman lines should be weak, meanwhile the C-O-C stretching modes are likely to be perpendicular to the metal and the corresponding Raman lines should be strong.

The effect of annealing temperature on the configuration of a-PMMA adsorbed onto the silver surface was also investigated. **Figure 2** shows the SERS spectra after annealing at temperature 120°C (B) and 150°C (C) for 1 hour respectively. Compared with the SERS spectra before annealing, it is found that the intensity of the band near 1003 cm^{-1} decreases largely with the increasing annealing temperature. In the RAIR spectra study of s-PMMA, Harvriliak and Roman conclude that there is more than one rotational isomeric state that is possible for the ester group[14]. Based on the above discussion, a model of the conformation transition of ester group adsorbed on the silver particle is proposed (see **Figure 3**). When annealing above the glass transition temperature, the structure of the ester group changes from gauche conformer to *trans* conformer. In such case, the direction of C-O-C stretching mode changes from normal to parallel to the surface of substrate. This is in accordance with the decreasing of the intensity of the strong band near 1003 cm^{-1} in the SERS spectra after annealing.

Figure 3 Possible structures of adsorbed ester group of -PMMA on the silver particle



(a) Gauche conformer

(b) Trans conformer

It is also interesting to note that there is a change in relative intensities of the bands near 837 and 812 cm^{-1} when increasing the annealing temperature. Now there are many debates about the assignment of the band near 812 cm^{-1} in Raman spectrum of a-PMMA. However the band near 837 cm^{-1} has been discussed above and is assigned to CH_2 rocking vibration which involves perpendicular motion to the long axis of the molecule. Its decreasing in intensity indicates that the molecular chain of a-PMMA deviates from the surface after annealing. When annealing at high temperature (above the Tg), the molecular chains begin to relax which is also in accordance with the change of the SERS spectra.

The interface between a-PMMA thin film and silver mirror substrate was investigated using SERS. The experimental results disclose that the molecular chain axis of a-PMMA is tended to be parallel to the substrate in interface. Based on the analysis of the SERS spectra of a-PMMA thin film, a model of the conformation transition of ester group adsorbed on the silver particle after annealing is proposed.

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