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Orientation Study of Atactic Poly(methyl methacrylate) Thin Film by SERS and RAIR Spectra

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ABSTRACT: Reflection−absorption infrared (RAIR) and surface-enhanced Raman scattering (SERS) spectroscopy were used to determine the orientation of the bulk and interface of a polymer thin film formed by atactic poly(methyl methacrylate) (a-PMMA) which was dip-coated onto a novel dual-sided substrate. The novel substrate with silver particles deposited on both sides of a glass slide by silver mirror reaction had two sides with different roughness and reflectivity. The top side (rough) and the bottom side (smooth) were suited for the SERS and RAIR analyses, respectively. The experimental results suggested that the molecular chain axis of bulk a-PMMA tended to parallel orientation to the silver substrate a little. However, the polymers at interface obviously oriented parallel to the substrate. A conformation transition of ester groups of a-PMMA after annealing at high temperature was confirmed using SERS and RAIR techniques.

Introduction

Reflection−absorption infrared spectroscopy (RAIR) and surface-enhanced Raman spectroscopy (SERS) are very useful in determining the molecular structure and orientation in the thin films of polymers.[1−3]

There are two important characteristics about SERS. First, SERS can be used as a nondestructive technique for characterizing the interfaces between metals and polymers.[4,5] Venkatachalam et al. have investigated the SERS effect from polymer bilayers deposited onto silver island films.[4] Raman scattering is observed from the first-layer film which is directly adjacent to the silver surface but not from the overlayer as long as the thickness of the first polymer film is more than approximately 10 nm. The other characteristic is that SERS can be used to determine the orientation and structure of adsorbed molecules according to "the surface selective rule" developed by Moskovits.[6] As a result, SERS has emerged as a powerful new technique for nondestructive determination of the orientation and conformation of interfacial molecules between adsorbates and SERS-active substrates.[7−10] Even though many details of the process have yet to be fully understood, it is generally admitted that SERS excitation has a double origin: an electromagnetic one and a chemical one.[1]

On the other hand, RAIR spectroscopy also provides rich information about the thin films of polymers, but mostly from the bulks. RAIR spectroscopy has also two important characteristics.[11−13] First, RAIR spectra will depend on both the real and complex parts of the refractive index of the absorbing species whereas spectra obtained in transmission almost entirely result from the complex part. Certain types of "distortions" may appear in RAIR spectra when compared to transmission spectra of the same compound. The other characteristic of RAIR is that the resultant electric field vector is perpendicular to the metal surface. Therefore, if molecules are adsorbed onto the substrate with a preferred orientation, vibration modes having transition moments perpendicular to the surface will appear with greater intensity than modes having transition moments parallel to the surface. So, RAIR is also a powerful technique for determining the orientation of adsorbed molecular species. We should note that this technique gives us the information about the whole film adsorbed on the substrate including both the interface and the bulk of the film. However, the information on the interface is so weak that we only observe the bulk information on the film when RAIR is used for a thin film.

Therefore, by combining the two techniques, the structural information about the bulks of polymer films and the interfaces between polymer films and metals can be acquired. Unfortunately, the two techniques have different sampling demands. Only molecules adsorbed onto the roughened surfaces of certain metals show the surface-enhanced Raman spectra,[14] but the RAIR test needs the thin film adsorbed on a smooth, reflective metal substrate.[15] Consequently, it is difficult to test the same thin film−metal sample by both RAIR and SERS. Usually, two film−metal samples using different substrates are prepared for SERS and RAIR analyses. In such circumstances, sampling conditions may be changed.

In this work, we get a unique substrate with different roughness and reflectivity on its two sides by the silver mirror reaction, which is suited for both SERS and RAIR analyses. The purpose of this paper is to report the results that we have obtained using SERS and RAIR to investigate the structure of the interface and the bulk of an a-PMMA thin film formed by dip-coating onto the novel dual-sided substrate.

Experimental Section

Materials. The average molecular weight of commercial a-PMMA was determined by means of gel permeation chromatography (PL-GP210); MW = 43.3×10^4, $M_w/M_n = 1.34$. The tacticities of a-PMMA were determined by ^{1}H NMR; the proportions of iso, hetero, and syndio triads were 9%, 34%, and 57%, respectively. The 1% (m/v) solution of PMMA in chloroform was prepared and equilibrated stored for 1 week at room temperature to achieve equilibrium.

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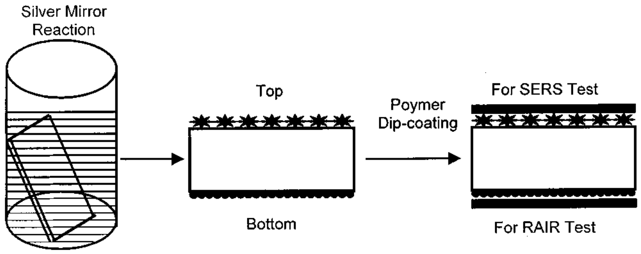
Scheme 1. Model of the Dual Substrate and the Sampling Process



Preparation of the Dual-Sided Substrate. A 20 mm × 10 mm × 1 mm glass slide was successively immersed in 0.1 N NaOH and 0.1 N HCl aqueous solutions for 1 h. After being rinsed in distilled deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and blown dry with nitrogen again, the slide was placed at a tilt angle in a 10 mL beaker, which was previously washed with water and acetone. 5 mL of 10^{-2} M silver ammonia complex and 1 mL of glucose water solution (10%) were mixed in the beaker. A few seconds later, the solution turned to yellow and gray, indicating that the silver ions were reduced and deposited on the glass plate to form fine silver films. 30 min later, the glass plate was withdrawn, thoroughly washed with distilled water, and dried with nitrogen. It was found that the two sides of the slide were obviously different. The substrate's top side was relatively rough surface and had SERS activity, while its bottom side was very smooth and suited for RAIR analyses. A S-250-III scanning electron microscopy (SEM) was used for the measurements of the silver particle size in the silver mirrors. The results showed that the average size of the silver particles on the substrate's top and bottom side were about 250 and 100 nm, respectively, and the silver particles on the bottom side were packed more order than that on the top side.

Sampling Methods. The sampling method was “dip coating”. The substrate was vertical immersed into a polymer solution at 30 °C for 1 min. Then, it was withdrawn at a raising speed of about 2 cm/s, and the solvent was evaporated. The film thickness on the substrate was estimated to be about 200 nm on the basis of the weight of polymer film, the density of the sample, and the area of the metal surface. Scheme 1 shows the model of the dual substrate and the sampling process.

Measurement. A Bruker IFS 100 FT-Raman spectrometer equipped with a Ge detector was used to obtain the FT-Raman spectra. NIR excitation at 1064 nm was provided by a Nd: YAG laser. The spectra were measured by averaging 128 scans at a 4 cm^{-1} resolution, and the laser power at the sample point was 200 mW for the films and 100 mW for the solid samples. To avoid degradation, the laser was defocused (the laser spot diameter of approximately 1 mm) when testing the thin film adsorbed on the silver mirror substrate. The FT-Raman spectra reported in this paper were smoothed and baseline corrected. Infrared measurements were made by a Bruker EQUINOX 55 FT-IR spectrometer equipped with a MCT detector. The reflection−absorption IR (RAIR) measurement were obtained by averaging 512 scans obtained at an angle of incidence equal to 84° and a resolution of 4 cm^{-1}. The polarization of the incoming beam was parallel to the plane of incidence (p-polarized). All RAIR spectra were obtained by subtracting the spectrum of the smooth side of the silver mirror substrate with no film from the spectrum of a film-covered substrate.

Results and Discussion

Infrared and Raman spectra of PMMA have been studied by many authors.[16−20] Robolt et al.[21] have investigated the RAIR spectra of PMMA thin film spin-coated onto Ag-, Cu-, and Cr-coated substrates, and the S/N ratio of RAIR spectra obtained on Ag-coated substrate is relatively good. However, no information has been obtained using Raman spectroscopy to investigate interfaces between PMMA films and metals. To our knowledge, this is the first time that the SERS spectra of PMMA have been reported. Therefore, the RAIR spectra will be discussed first.

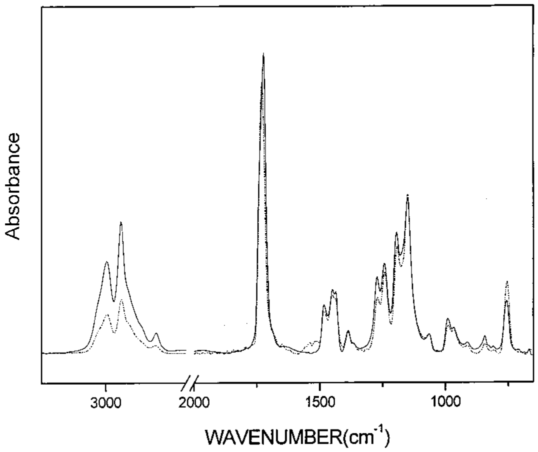


Figure 1. RAIR spectrum of a-PMMA thin film dip-coated on the bottom side of the substrate (—) and IR transmission spectra of a-PMMA thin film dip-coated on the KBr pellet (- - -).

RAIR Spectra of a-PMMA Dip-Coated on the Bottom of the Substrate. Shown in Figure 1 are the transmission spectra of a-PMMA thin film coated on a KBr pellet and the RAIR spectra of a-PMMA thin film dip-coated on the bottom side of the silver mirror substrate. Neither spectrum is smoothed. We can see that the RAIR spectrum is of a good quality. It is known that reflectance spectra clearly show large changes in both peak position and shape compared to transmission spectra.[13,22] The phenomenon is indeed observed from the band shift of C═O. To get the qualitative information about the molecular orientation, we avoid the disturbance of the band distortions by comparing the relative intensity of band in the same spectra.

When comparing with TR spectra, a significant difference appears in the RAIR spectra of the PMMA thin film. The intensities of the C−H stretching bands in the region of 2800−3100 cm^{-1} exhibit a great increase relative to that of the band near 760 cm^{-1}. The bands at 2952 and 2842 cm^{-1} are assigned to the C−H stretch vibration of CH_2, α-CH_3, and O−CH_3, and their transition moments are perpendicular to the backbone of a-PMMA.[23] The band near 760 cm^{-1}, assigned by Nagai to a combination of C−C stretching and −CH_2− rocking, has been shown to exhibit a considerable dichroism in the IR spectra of oriented a-PMMA, and its transition moments are parallel to the main chain of a-PMMA.[17,21] The band near 1730 cm^{-1} which is assigned to the C═O stretch vibration and the band in the range of 1050−1300 cm^{-1} are all perpendicular bands.[17] The ratio of the intensities of these bands relative to that of the parallel band near 760 cm^{-1} is also increased. This indicates that there is a selective orientation for the PMMA backbone.

The p-RAIR selects only the polarization of the incident electric field perpendicular to the metal surface as mentioned. If molecules are adsorbed onto the substrate with a preferred orientation, vibration modes having transition moments perpendicular to the surface will appear greater in intensity than modes having transition moments parallel to the surface.[11] Since the

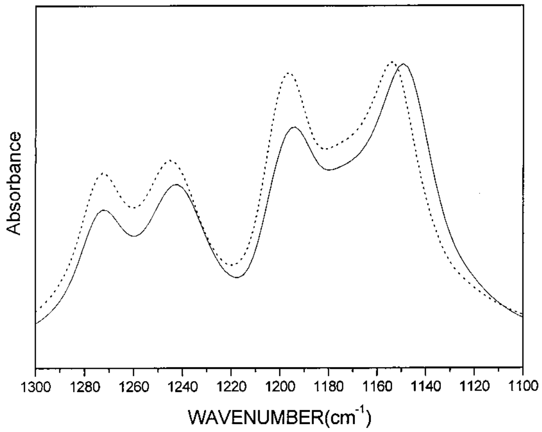


Figure 2. RAIR spectrum of a-PMMA thin film dip-coated on the bottom side of the substrate before (—) and after annealing at 150 °C for 1 h (- - -).

intensities of these perpendicular bands mentioned above are enhanced and the intensity of the parallel band near 760 cm^{-1} is slightly decreased, we can conclude that the main chain of the PMMA in the bulk thin film shows some alignment parallel to the substrate. On the basis of the relative intensity of the 760 cm^{-1} band and C−H stretch vibrations, it is suggested that the orientation extent is small.

It is believed that the chain orientation of the a-PMMA thin film should be caused by the sample preparation method. During the process of sampling by dip-coating method, the flow direction of the solution is parallel to the substrate, and there is a velocity gradient between the substrate/solution interface and solution/air interface because of the effect of the substrate; the molecular chain in the solution is therefore prone to stretching and parallel to the surface to form a thin film.

Figure 2 shows the RAIR spectrum of the same PMMA thin film dip-coated on the bottom side of the silver mirror substrate that is annealed at 150 °C for 1 h. When comparing this spectrum with that before annealing, there appears an interesting difference in the relative intensities of bands in the region of 1050 and 1300 cm^{-1}. The 1240−1270 and 1190−1150 cm^{-1} doublets have been attributed to the stretching vibration of the C−O and C−C bonds of the ester side chain of a-PMMA and have been studied extensively by Havriliak and Roman[19] in syndiotactic PMMA. They interpreted the temperature dependence of bands in the range of 1050−1300 cm^{-1} on changes in the orientation of ester groups of s-PMMA in the solid state. From analysis of the bands in this range, Belopolskaja and Trapeznikova[24] have concluded that conformational changes of ester groups also take place in films of isotactic PMMA; they also considered rotation about the COC bond and determined conformational energy differences. From Figure 2, the relative intensity of the two bands comprising the doublet is obviously different before and after annealing, which illustrates that a conformational transition of ester groups also appears in the a-PMMA thin film. This phenomenon will be discussed further below.

SERS Spectra of a-PMMA Dip-Coated on the Top of the Substrate. The main chain orientation of the bulk of the PMMA thin film dip-coated onto the substrate has been discussed. Now, we will discuss the circumstance on the interface between the PMMA thin film and the substrate.

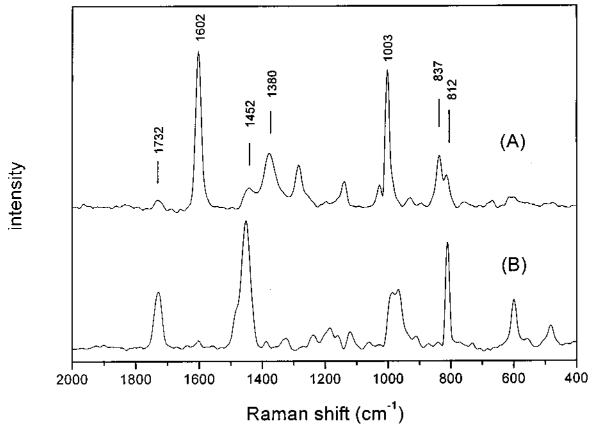


Figure 3. (A) SERS spectrum from a-PMMA dip-coated onto the top side of the substrate. (B) Normal Raman spectrum of the bulk a-PMMA.

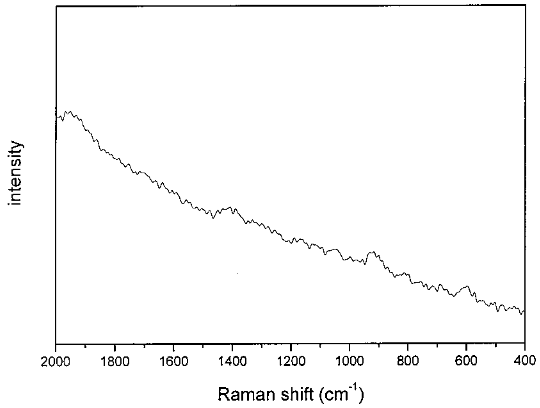


Figure 4. Raman spectrum of the top side of the silver mirror substrate.

Figure 3 shows the SERS spectrum of a-PMMA dip-coated onto the top of the substrate and the normal Raman spectrum from the solid powder of a-PMMA. An obvious difference can be observed. It is interesting to note that the intensities of two bands were much greater in the SERS spectra than that in the normal Raman spectra. The band near 1602 cm^{-1}, which is very weak in the normal Raman spectrum, is the strongest band in the SERS spectrum. Similarly, the band near 1003 cm^{-1} is of medium strength in normal Raman spectra of the a-PMMA but becomes very strong in the SERS 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.[13,22] Dybal et al. have confirmed this assignment by the normal-coordinate calculations, and the potential energy distribution (PED) indicated large contributions from the C−O−C stretch vibration.[23] However, it is difficult for us to assign the band near 1602 cm^{-1}. Figure 4 shows the Raman spectrum of the top of the Ag mirror substrate; only small broad bands near 1400 cm^{-1} could be found, so it is not induced by the substrate.

Hitherto, it is seem that two mechanisms should be responsible for the enhancement.[1,25] The first is electromagnetic in origin and is associated with the large electric fields that can be obtained when the roughened surface of a metal is illuminated with electromagnetic radiation. The other is chemical in nature and is associated with a resonance effect involving charge transfer of metal.

Table 1. Assignment of SERS Spectrum of a-PMMA

wavenumber (cm^{-1})	rel int[a]	tentative assignt of the bands discussed[b]	polarization to interface[c]
1732	vw	ν(C=O)	∥
1602	vs	?	⊥
1452	w	$\delta(CH_2)$	∥
1380	m	$\delta_s(\alpha\text{-}CH_3)$	⊥
1003	vs	ν_s(C−O−C)	⊥
837	m	$r(CH_2)$	⊥

[a] Abbreviations: s = strong, m = medium, w = weak, v = very. [b] Abbreviations: ν_s = symmetric stretching, δ = bending, δ_s = symmetric bending, and r = rocking. [c] The symbol || indicates that the polarizability change associated with the band is parallel to the interface between polymer and metal; ⊥ indicates that the polarizability change is perpendicular to the interface.

The appearance of the strong bands near 1600 cm^{-1} is most likely due to chemical adsorption; in other words, there is some interaction between a-PMMA thin film and silver substrate, although the mechanism of the chemical adsorption is unclear now.

A successful basis for analysis of SERS spectra with regard to orientation of adsorbate was worked out in the form of "surface selection rule".[6] 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 field is highest normal to the surface, normal modes of the surface molecule involving changes in molecular polarizability with a component normal to the surface are subject to the greatest enhancement. This type of analysis has been applied successfully by many authors.[26−28]

The tentative assignment of the SERS spectra of a-PMMA is shown in Table 1. It can be seen from the SERS spectra of a-PMMA that the bands near 1380 and 837 cm^{-1} show great enhancements compared with those in the normal Raman spectra. So the polarizability changes associated with these bands are perpendicular to the interface between polymer and metal. Moreover, the bands near 1380 and 837 cm^{-1} are assigned to α-CH_3 symmetric bend and CH_2 rocking vibration, respectively, and both involve considerable motion perpendicular to the long axis of the molecules.[17,23] Assuming that a-PMMA is adsorbed with the molecular axes mostly parallel to the surface, the corresponding bands should appear with considerable intensity, and that is what has been observed. The band near 1452 cm^{-1} is assigned to CH_2 symmetric bend vibration which involves motion mostly parallel to the long axis of the molecules.[17] From the SERS spectra of Figure 3, we can find that the intensity of the band near 1452 cm^{-1} is decreased largely. So it is rational to assume that the a-PMMA is adsorbed with the molecular axes mostly parallel to the substrate. Moreover, from the relative intensity of perpendicular bands and parallel bands, it is obvious that the molecular chain of a-PMMA is aligned more parallel to the substrate at the interface than in the bulk.

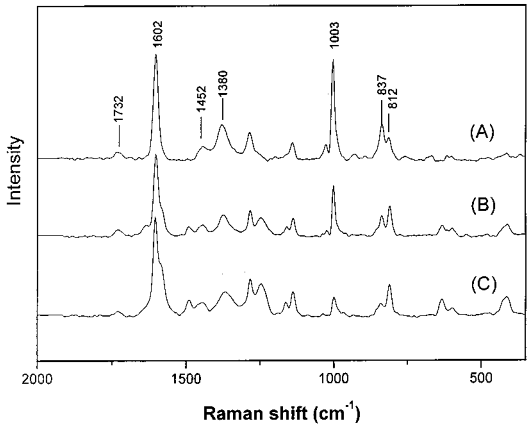


Figure 5. SERS spectra from a-PMMA dip-coated on the top of the substrate (A) without annealing, (B) after annealing at temperature 120 °C/1 h, and (C) after annealing at 150 °C/1 h.

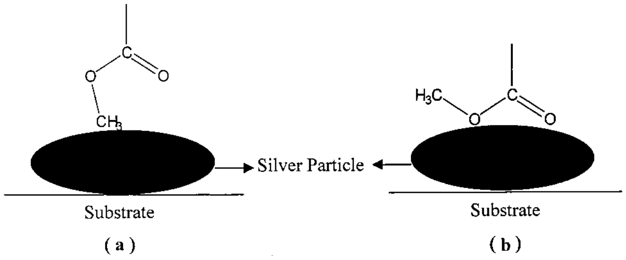


Figure 6. Possible structures of adsorbed ester group of a-PMMA on a silver particle: (a) gauche conformer; (b) trans conformer.

The relatively strong band in the normal Raman spectrum, near 1732 cm^{-1}, is very weak in the SERS spectrum. This band was assigned to the C=O stretching mode.[23,29] However, the band near 1003 cm^{-1}, which has been assigned to the C−O−C stretch vibration,[23,29] is enhanced 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 a 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 is also investigated. Figure 5 shows the SERS spectra after annealing at temperature 120 °C (B) and 150 °C (C) for 1 h. 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 previous discussion of RAIR spectra of a-PMMA, we have concluded that there is a conformational transition of ester groups in the a-PMMA thin film. On the basis of the above discussion, the model of the conformation transition of ester group adsorbed on the silver particles is proposed (see Figure 6). Upon annealing above the glass transition temperature, the structure of the ester groups changes from gauche conformer into trans conformer. In such case, the direction of C−O−C stretching mode changes from normal into parallel to the surface of substrate. This is in accordance with a decrease in the intensity of the strong band near 1003 cm^{-1} in the SERS spectra after annealing.

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 the Raman spectrum of a-PMMA. However, the band near 837, as discussed above, is assigned to a CH$_2$ rocking vibration which involves motion perpendicular to the long axis of the molecules. Its decrease in intensity indicates that the molecular chains of a-PMMA deviate from the surface after annealing. When annealing at a higher temperature (above the T_g), the molecular chains begin to relax, which is also in accordance with the change of the SERS spectra.

Conclusions

RAIR and SERS techniques are very useful in determining the molecular orientation and conformation in the thin films of polymers. In this work, a novel dual-sided substrate, on which silver particles are deposited, is prepared. Its two sides have different roughness and reflectivity, and they were suited for both SERS and RAIR analyses. The experimental results disclose that the molecular chain axis of a-PMMA tended to parallel to the substrate in bulk; however, it is obviously parallel to the substrate at the interface. It is considered that the orientation of the molecular chain should be caused by the sample preparation method and surface effect. Meanwhile, a conformation transition of ester group of a-PMMA after annealing at a higher temperature above T_g is confirmed using both SERS and RAIR techniques. On the basis of the SERS spectra of a-PMMA thin film, a model of the conformation transition of ester group adsorbed on the silver particles has been proposed.

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