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Characterization of the Interfacial Interaction between Polyacrylamide and Silicon Substrate by Fourier Transform Infrared Spectroscopy

Xiaolin Lu and Yongli Mi*

Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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ABSTRACT: The formation of the interface between the polyacrylamide (PAL) spin-coated thin films and the silicon (Si) substrates was characterized by Fourier transform infrared spectroscopy (FTIR). The increase in the peak intensity and the decrease in the peak frequency of the Si−O stretching vibration at 1107 cm^{-1} support that the hydrogen bonds are formed between the hydrogen atoms in the PAL amino groups and the oxygen atoms in SiO_2 on the Si substrate. Compared to the PAL casting film on the Teflon surface, the orientation of PAL carbonyl groups parallel to the substrate surface for the spin-coated PAL thin films was found. This side-group orientation is believed due to the interfacial interaction.

1. Introduction

The issue of the interface is always important when the adhesion problem is considered. To increase the surface activity, surface pretreatments, such as plasma modification[1,2] and surface functionalization,[3,4] are generally used, which enables the covalent bonds to be formed in the interface to enhance the interfacial adhesion. However, the noncovalent bonds via van der Waals force or the hydrogen bonds also play a key role in this issue. When large amounts of functional groups with the proton acceptors and the proton donors exist in the interface, such as halogenide, hydroxyl, or amino groups, the hydrogen bonding dominates the interfacial interaction.[5] In view of the interface (the surface can be regarded as the interface between the material and the air) as a different phase from the bulk phase, the molecular structure in the interface should be different from the bulk. The obvious proof is the difference in the glass transition temperatures between the polymer thin film and the corresponding bulk polymer.[6−8] Considering an amorphous polymer thin film on a planar substrate, there is a possibility for the polymer chains to arrange differently from its bulk state; therefore, ordered polymer chain conformations may be found in the interface.[9−12]

A previous study of polyaniline by the diffuse reflectance Vis/UV spectroscopy has shown that the mechanical forces, such as shaking and spin-coating, can help polymer chains to extend on the substrate.[13] The extended main-chain conformation was also suggested for PMMA film dip-coated on the gold surface.[14] When the polymer and the substrate can wet each other, the main-chain extension should be, of course, better enhanced due to the interfacial interaction. This paper studies the interface between the spin-coated polymer, polyacrylamide (PAL), and the Si substrate using Fourier transform infrared spectroscopy (FTIR). FTIR results show that there exist hydrogen bonds between the PAL molecules and the SiO_2 layer on the Si substrate due to the infrared sensitivity to the vibration of the hydrogen-bonded groups.[15] The top SiO_2 layer on the Si substrate surface gives a characteristic peak for the Si−O stretching vibration. On the basis of the spectra difference between the hydrogen-bonded Si−O stretching and the free Si−O stretching, we obtained more information about polymer/substrate interface. And, the different ratios in the peak intensity of the carbonyl stretching to the amino bending vibrations between the spin-coated PAL thin film on the Si substrate and the PAL casting film on the Teflon surface suggest that the side carbonyl groups of the PAL molecules on the Si substrate exhibit the parallel orientation to the substrate surface.

2. Experimental Section

2.1. Sample Preparation. The Si substrates were purchased from Grinm, Inc. (silicon polished wafer, N type). Without any treatment, the thickness of SiO_2 is 2.2 nm on the Si substrate. After treatment by H_2O_2/H_2SO_4 (3:7 volume ratio, 35 wt % H_2O_2 solution, 98 wt % H_2SO_4 solution) for 2 h, the thickness of SiO_2 layer increased to 4.0 nm on the Si substrate. These two different Si substrates were used in the sample preparation. The PAL ($M_w = (5-6) \times 10^6$, Polysciences, Inc.) casting film was prepared on the Teflon surface from 0.5% g/mL deionized water solution. Spin-coated PAL thin films with different thicknesses were prepared on the silicon substrates by a spin-coater (P6700, Speciality Coating Systems Inc.). The thicknesses of the PAL thin films were adjusted by the solution concentration and the rotating speed of the spin-coater.

2.2. Sample treatment and Characterization. The PAL samples were kept in the vacuum oven (Shel lab 1410, Shalton Mfg Inc.) for 1 day before characterization. The Si substrates and PAL samples were annealed in the vacuum oven at 185 °C for 4 h. The ellipsometer (vase angle spectroscopic ellipsometry, J.A. Woollam Co., Inc.) was used to measure the thicknesses of the SiO_2 layer and the PAL thin films on the Si substrates. The PAL thin film thicknesses were measured after the annealing treatment. The structural characteristics and differences were characterized by the FTIR (FT-IR system, FTS 6000, Bio-Rad Inc., the resolution is 4 cm^{-1}) spectra of the transmission mode in the mid-IR range (4000−700 cm^{-1}). For the PAL casting film, the blank was taken as the background of the spectrum. For the spin-coated PAL thin films on the Si substrates, the Si substrate was taken as the background.

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* Corresponding author: e-mail keymix@ust.hk, tel 00852-2358-7127.

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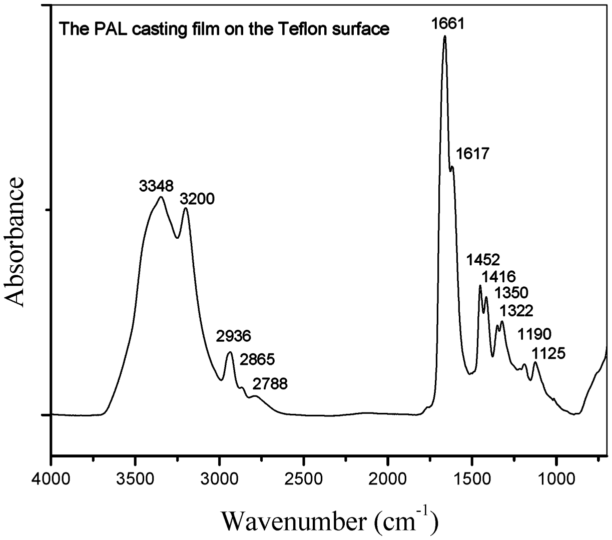

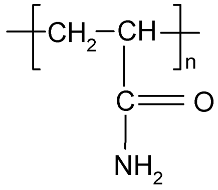

Figure 1. FTIR spectrum for the PAL casting film on the Teflon surface.

Table 1. Peak Assignment of PAL and the Si−O Stretching According to the Spectrum of the PAL Casting Film in Figure 1 and the Spectrum of the Si Substrate in Figure 2

peak position (cm^{-1})	assignment
3348	N−H asym stretching of NH_2 (ν)
3200	N−H sym stretching of NH_2 (ν)
2936	C−H asym stretching of CH_2 (ν)
2866	C−H sym stretching of CH_2 (ν)
2788	C−H stretching of CH (ν)
1661	C═O stretching of CO (ν), amide I band
1617	N−H bending of NH_2 (δ), amide II band
1452	C−H bending of CH_2 (δ)
1416	C−N stretching (ν), amide III band
1350	C−H wagging of CH_2 (wag), out of plane
1322	C−H bending of CH (δ)
1190	N−H wagging of NH_2 (wag)
1125	N−H rocking of NH_2 (r) in plane, C−C skeletal vibration
1107	Si−O stretching (ν)

3. Results and Discussion

3.1. FTIR Peak Assignment of PAL and the Si Substrate. Figure 1 shows the FTIR spectrum of the PAL casting film on the Teflon surface, and Table 1 gives the peak assignment of the FTIR spectrum.[16−19] The peaks at 1661 and 1617 cm^{-1} are the two strong peaks, which are the characteristic bands of the C═O stretching (ν), amide I band and the N−H bending (δ), amide II band, respectively. The C−C skeletal stretching vibration (ν) and the NH_2 rocking vibration (r) may both give the signals in the region of 1100−1150 cm^{-1} in vibration spectroscopy.[15] Since it is difficult to assign this peak to each vibration, we assign the peak at 1125 cm^{-1} as the combined contribution of the vibration of the C−C skeletal stretching vibration (ν) and the NH_2 rocking (r) in the amino group.

In the collected mid-IR area (4000−700 cm^{-1}), the untreated Si substrate does not give infrared signals, shown as spectrum B in Figure 2, when another untreated Si substrate was used as the background. When the signal of the H_2O_2/H_2SO_4-treated Si substrate was detected with the original (untreated) Si substrate as the background, the thickness difference (untreated: 2.2 nm; H_2O_2/H_2SO_4-treated: 4.0 nm) of the SiO_2 layer gives a strong Si−O stretching (ν) characteristic peak at 1107 cm^{-1}, shown as spectrum A in Figure 2.[17]

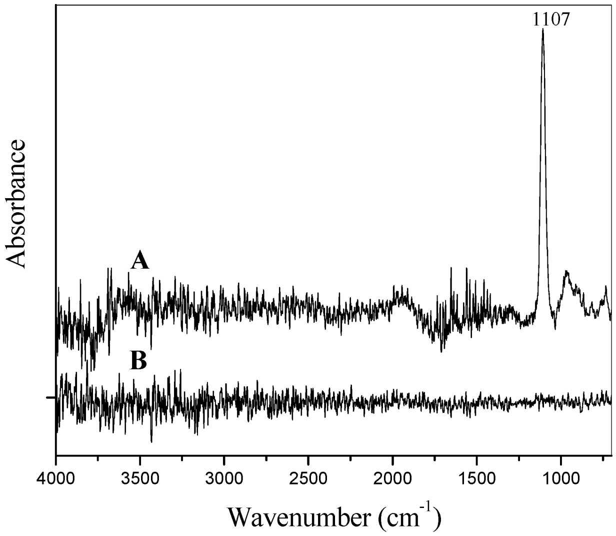

Figure 2. FTIR spectra of the Si substrates with different thicknesses on the H_2O_2/H_2SO_4 and has a SiO_2 layer of 4.0 nm. Substrate B was untreated with a SiO_2 layer of 2.2 nm. The background substrate was the untreated Si substrate.

3.2. FTIR Spectra of the Spin-Coated PAL Thin Film on the Si Substrate. Figure 3 shows two sets of the FTIR spectra of the spin-coated PAL thin films with different thicknesses on the Si substrates before and after annealing. It should be noticed that a Si substrate without any treatment was taken as the background, and the substrates used for the spin-coated PAL thin films were treated by H_2O_2/H_2SO_4. The previous discussion suggests that the thickness difference in the SiO_2 layer (cf. Figure 2) gives a strong Si−O stretching (ν) characteristic peak at 1107 cm^{-1}, and it is concluded that the peaks appearing in the range from 1100 to 1108 cm^{-1} are associated with the Si−O stretching band. The combined NH_2 rocking (r) in plane and C−C skeletal vibration also give a peak near this region (1125 cm^{-1}), which is a weak one judged from the spectrum of the PAL casting film, as shown in Figure 1. Therefore, we speculate that the peak at 1225 cm^{-1} is covered by the stronger Si−O stretching (ν) vibration in the spectra of Figure 3.

The FTIR spectra, showing the annealing effect, can be acquired from Figure 3. The most distinct difference is the enhancement in peak intensity for the Si−O

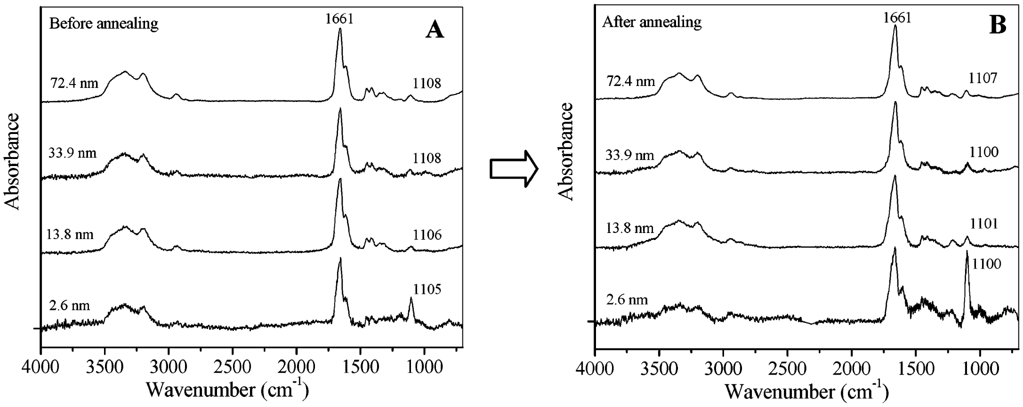

Figure 3. FTIR spectra of the spin-coated PAL thin films with different thicknesses on the H_2O_2/H_2SO_4-treated Si substrates before and after annealing. The samples were annealed at 185 °C for 4 h. The background substrate was the untreated Si substrate.

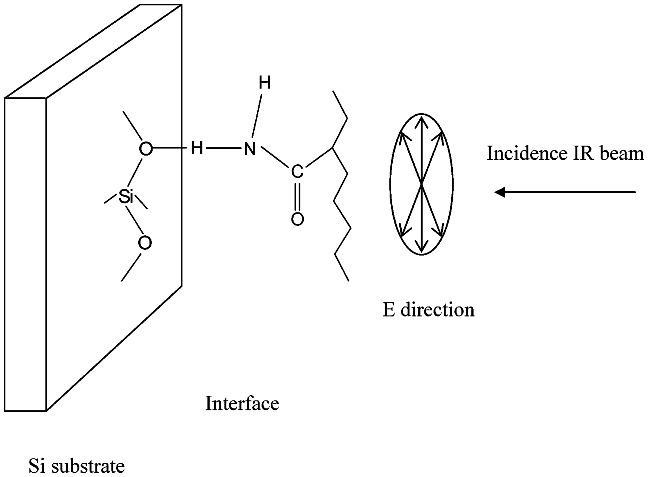

Figure 4. Formation of the interfacial hydrogen bonding between the hydrogen atom in the amino group and the oxygen atom in the SiO_2 layer. The C=O stretching is parallel to the plane of the vectors of the electric field.

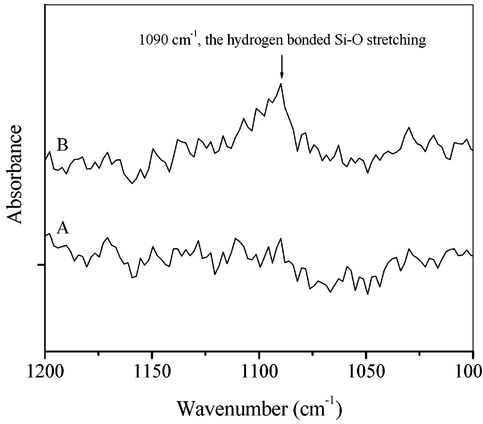

Figure 5. FTIR spectra of the H_2O_2/H_2SO_4-treated Si substrate (spectrum A) and the PAL thin film of 15.0 nm spin-coated on the same H_2O_2/H_2SO_4-treated Si substrate (spectrum B). The background substrate for both spectra was the H_2O_2/H_2SO_4-treated Si substrate.

stretching vibration. In view of the PAL thin film on the Si substrate with a SiO_2 layer, the hydrogen bonds form between the amino groups in the PAL molecules and the oxygen atoms of the SiO_2. The annealing can relax the PAL molecules to a more stable state. The hydrogen bonds, forming between the amino groups and the oxygen atoms, can lower the energy level of the interface. After annealing of the thin films, the peak frequencies of the Si–O stretching vibration in spectra B of Figure 3 decrease by about 1–8 cm^{-1}. The FTIR resolution is 4 cm^{-1}. As a general knowledge in the FTIR analysis, the hydrogen-bonding effect enhances the band intensity and shifts the adjacent stretching vibration to a lower frequency. Figure 3 clearly shows these two effects, particularly for the spectra of the 2.6 and 13.8 nm PAL thin films, which demonstrate the hydrogen bonding effect before and after annealing. We see that the peak at 1105 cm^{-1} decreases to 1100 cm^{-1} with a significant increase in the peak intensity after annealing at 185 °C for 4 h for the PAL thin film of 2.6 nm. The same effect is also found for the PAL thin film of 13.8 nm. A schematic plot of the interface between the PAL molecules and the SiO_2 layer is suggested in Figure 4.

Since the free Si–O stretching vibration (without hydrogen-bonding effect) brings out the peak at 1107 cm^{-1} (cf. Figure 2, spectrum A) and the hydrogen bonding effect lowers the frequency of the Si–O stretching vibration, the peaks of the Si–O stretching, shown in Figures 3 around 1100–1108 cm^{-1}, are actually from the combination effect of the free and hydrogen-bonded Si–O stretching vibrations. Two Si substrates were prepared with H_2O_2/H_2SO_4 treatment. The ellipsometric measurement showed that the thicknesses of the SiO_2 layers were both of 4.0 nm. Then, one Si substrate was taken for the background collection of FTIR, and a FTIR spectrum for the other substrate was collected which shows no signal in the Si–O stretching region (cf. spectrum A, Figure 5). Next, a 15 nm layer of PAL thin film was spin-coated on the Si substrate with the SiO_2 thickness of 4.0 nm, and the FTIR spectrum was collected as spectrum B in Figure 5. A peak around 1090 cm^{-1} appears. Since we know that the two Si substrates are in the same thickness of SiO_2, it means that the peak at about 1090 cm^{-1} comes mainly from the hydrogen-bonded Si–O stretching vibration, shown as spectrum B in Figure 5.

3.3. Side Carbonyl Group Orientation Induced by the Interface. When the FTIR spectra of the casting film on the Teflon surface and the spin-coated thin films on the Si substrates are compared, we find, in Figures 1 and 3, that the peak intensity ratios of the C=O stretching vibration (ν) at 1661 cm^{-1} to the N–H bending vibration (δ) at 1617 cm^{-1} are different. To obtain the detailed information on amide I and amide II bands, a deconvolution of these two bands was carried out in the spectral range of 1750–1500 cm^{-1}. Figure 6 shows the result of the Lorentzian deconvolution for the spectra of the casting film and the spin-coated PAL thin film of 2.6 nm on the silicon substrate. Table 2 lists the

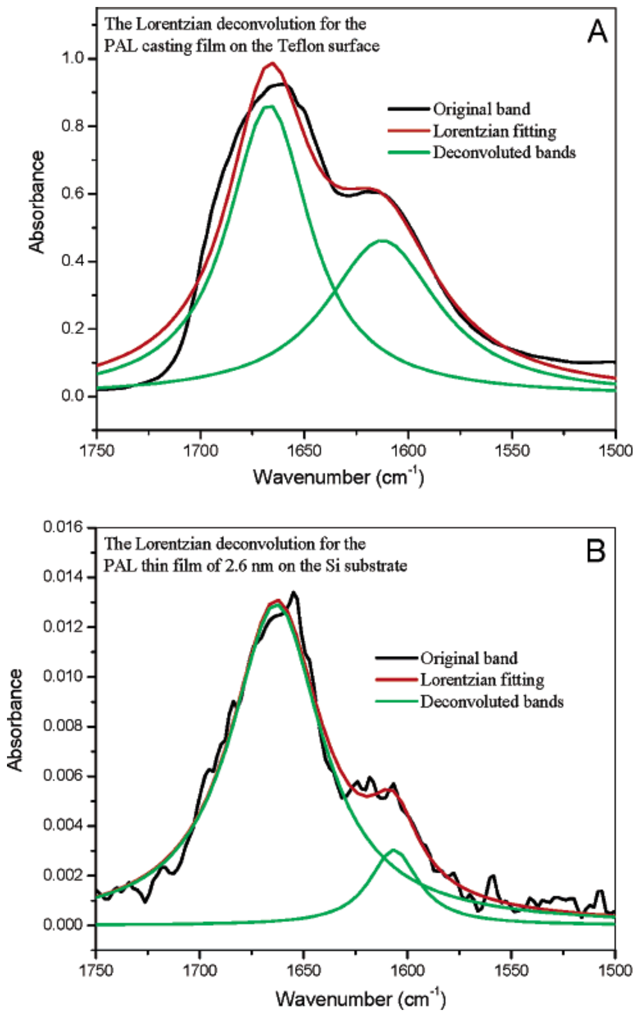

Figure 6. Lorentzian deconvolution for the spectral range from 1750 to 1500 cm^{-1} for the casting film in Figure 1 and the 2.6 nm PAL thin film in Figure 3A.

Table 2. Lorentzian Deconvolution Results for the Amide I and Amide II Bands in the Spectral Range from 1750 to 1500 cm^{-1} for the Spectrum of the PAL Casting film in Figure 1 and for the Spectra of the Spin-Coated PAL Thin Films in Figure 3A

PAL sample	peak position (cm^{-1}) amide I	peak position (cm^{-1}) amide II	amide I peak area	amide II peak area	peak area ratio
casting film (3 μm)	1667	1612	65.0	47.8	1.36
thin film (2.6 nm)	1663	1607	1.09	0.136	8.01
thin film (13.8 nm)	1664	1606	1.76	0.381	4.62
thin film (33.9 nm)	1662	1607	2.80	0.692	4.05
thin film (72.4 nm)	1663	1608	7.89	1.42	5.56

deconvolution results of these two bands from the Lorentzian function. The ratios of the peak-area of amide I band to that of amide II band, for the PAL thin films on the Si substrates, are much larger than that for the casting film on the Teflon surface. We believe that the ratio difference comes from the different orientations of the side groups. For the spin-coated PAL thin films on the silicon substrates, the PAL backbones would extend along the substrate surface due to the spin-coating and wettability effects. Figure 4 shows that, when the FTIR spectrum is collected, the incidence infrared beam is perpendicular to the sample surface. Although the unpolarized light is used, the electric field vectors (E) for the incidence beam are always parallel to the Si surface. From Figure 4, it is seen that the orientation of the carbonyl groups is always in the plane parallel to the E vector plane when there is the interfacial hydrogen bonding between the NH_2 groups and the SiO_2 layer. The side-group orientation of PAL explains the enhancement of the peak intensity of the amide I band for the spin-coated thin films on the Si substrates. For the case when there is no interfacial interaction, such as the PAL casting film on the Teflon surface, the orientation of the side carbonyl groups of PAL must be rather random, considering the random coil state of the PAL long chain molecules. Table 2 confirms the above argument by the fact that the ratios of the peak area of the amide I band to that of the amide II band for the PAL thin films on the silicon substrates are much larger than that for the PAL casting film on the Teflon surface.

4. Conclusions

In this paper, the FTIR spectra of the PAL casting film on the Teflon surface and the spin-coated PAL thin films on the Si substrates are discussed. The FTIR spectra of the Si substrates with the different thicknesses of SiO_2 layers were studied. The Si−O stretching vibration results in a characteristic band at about 1107 cm^{-1}, which is comparable to the PAL characteristic bands when the thickness of the PAL layer is in the same thickness range as that of the SiO_2 layer. The hydrogen-bonding effect on the Si−O stretching vibration enhances the peak intensity and shifts the peak to the low frequency. The peak at about 1090 cm^{-1} attributed to the hydrogen-bonded Si−O stretching vibration. The FTIR spectra of the spin-coated PAL thin films on Si Substrates show certain extent of the C═O orientation parallel to the substrate surface. The C═O orientation is believed to be due to the chain extension and the interfacial effect. This study has direct application of studying polymer thin films for the chain confinement effect on the chain configuration, glass transition, and chain relaxation.

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