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Discovery of the bi-layered structure in spin-coated polyacrylamide films on the gold surface

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Abstract

The reflection–absorption Fourier transform infrared spectroscopy (RA-FTIR) with the polarized lights was used to characterize polyacrylamide (PAL) films spin-coated on the gold (Au) surfaces. The PAL films spin-coated on the Au surface show the characteristics of a bi-layered structure. The first layer attached to the Au surface with a thickness of around 70 nm shows no chain orientation due to the dewetting effect of the Au surface. The upper layer is composed of the PAL molecules oriented parallel to the Au surface as the film thickness increases, which is believed to be due to the spin-coating effect. The bottom and the top layers are optically isotropic and anisotropic, respectively, as confirmed by the analysis of the RA-FTIR spectra. The thickness-threshold is of the order of the end-to-end distance (R_{ee}, 67 nm) of PAL molecules ($M_w \sim 10^6$) indicating the dewetting distance through which the Au surface functions.

Keywords: Bi-layer structure; Polyacrylamide; RA-FTIR

1. Introduction

Polymer, as a kind of soft matter [1], can easily be fabricated into films of thickness from nanometers to microns on substrates. The interfacial properties are dependent on the chemical compositions of both polymers and substrates [2,3]. It is generally accepted that a polymer film on a substrate is not a homogeneous system. The influence of the interface and the surface on the deviation of the glass transition temperature of polymer thin films provides the evidence [4–7]. Over the past decades, the properties of the polymer–substrate interface have been investigated and significant progress has been achieved in understanding the formation mechanism of the interface by spectroscopic probes, such as Fourier transform infrared spectroscopy, surface enhanced Raman scattering, ultraviolet photoelectron spectroscopy, and X-ray photoelectron spectroscopy in a non-destructive fashion [8–19]; and it is still of great interest to investigate the interfacial properties concerning the wettability of substrates. In this communication, we report the results of reflection–absorption Fourier transform infrared spectroscopy (RA-FTIR) of polyacrylamide (PAL) films spin-coated on the gold (Au) surface. The RA-FTIR spectra of PAL films spin-coated on the Au surface exhibit special characteristics different from those of PAL solution-casting films.

2. Experimental section

An Au layer of 200 nm was prepared by the high vacuum evaporation (High Vacuum Evaporator, DV-502A, Denton Inc.) on the top of the silicon wafer (Silicon polished wafer, N-type, Grinm, Inc.). The PAL films were prepared by spin-coating PAL ($M_w = 5 \times 10^6$–6×10^6; Polysciences, Inc.) deionized solutions on the Au surfaces (Spin Coater, P6700, Specialty Coating Systems Inc.). The thicknesses of the PAL films were adjusted by solution concentrations and spinning speeds. The spin-coated PAL films on the Au surfaces were put in vacuum oven (Shel lab 1410, Shalton Mfg Inc.) at 60 °C for 24 h and then put in the desiccator.

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The thickness of the Au layer was measured by the surface profiler (Surface Profile System, α-step 200, Tencor Inc.). The thicknesses of the PAL films were detected by an ellipsometer (Variable Angle Spectroscopic Ellipsometry, J. A. Woollam Co., Inc.). The RA-FTIR spectra of the PAL films on the Au surfaces were collected by the Fourier transform infrared spectroscopy (FTIR system, FTS-6000, Bio-Rad Inc., diffuse reflection mode). The source lights with different polarization were used in order to detect the molecular orientation. The sample chamber of the FTIR was vacuumed at least for 1 h before the collection of the background and the sample spectra in order to eliminate the signal noises of the humidity and carbon dioxide.

3. Results and discussion

Fig. 1 demonstrates the optics of polarization with the incidence plane defined by the normal line and the incidence beam. Both the incidence beam and the reflection beam can be disintegrated into the p-polarized components (E_p^i and E_p^r) and the s-polarized components (E_s^i and E_s^r), as indicated in Fig. 1. Fig. 2 shows the un-polarized and the polarized RA-FTIR spectra of the amide I band for PAL films with different thicknesses. For transmission mode FTIR study, in the spectral range from 1900 cm^{-1} to 1400 cm^{-1}, there are two characteristic bands for a PAL film, which are the amide I band at 1661 cm^{-1} and the amide II band at 1617 cm^{-1} [20]. For RA-FTIR study, when the film thickness is less than 73 nm, the position of the amide I band is shifted to 1685 cm^{-1} with respect to both the p-polarized light (E_p) and the s-polarized light (E_s) due to the reflection effect [21,22]. When the film thickness is about several hundred nanometers, the amide I band splits into a doublet with one at 1700 cm^{-1} and another at 1650 cm^{-1}. Fig. 2 further shows that, for E_s, the band at 1650 cm^{-1} first appears at the film thickness of 104 nm, whereas, for E_p, it appears at the film thickness of 375 nm. Moreover, as the film thickness increases, the relative band intensity at 1650 cm^{-1} compared to the band intensity at 1700 cm^{-1} for E_s is always stronger than that for E_p. Since E_s is parallel and E_p is perpendicular to the Au surface, as shown in Fig. 1, it can be reasoned that the stretching of the carbonyl

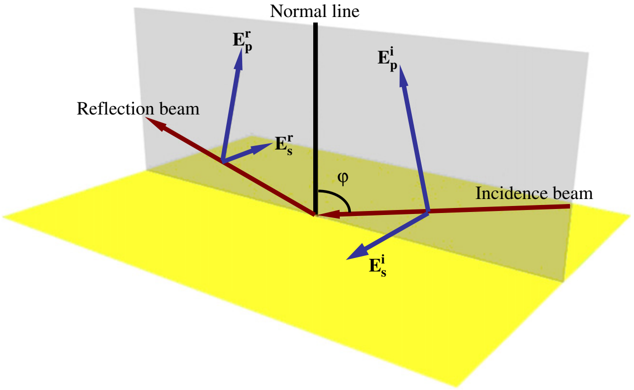

Fig. 1. Optics of RA-FTIR with a high incidence angle φ.

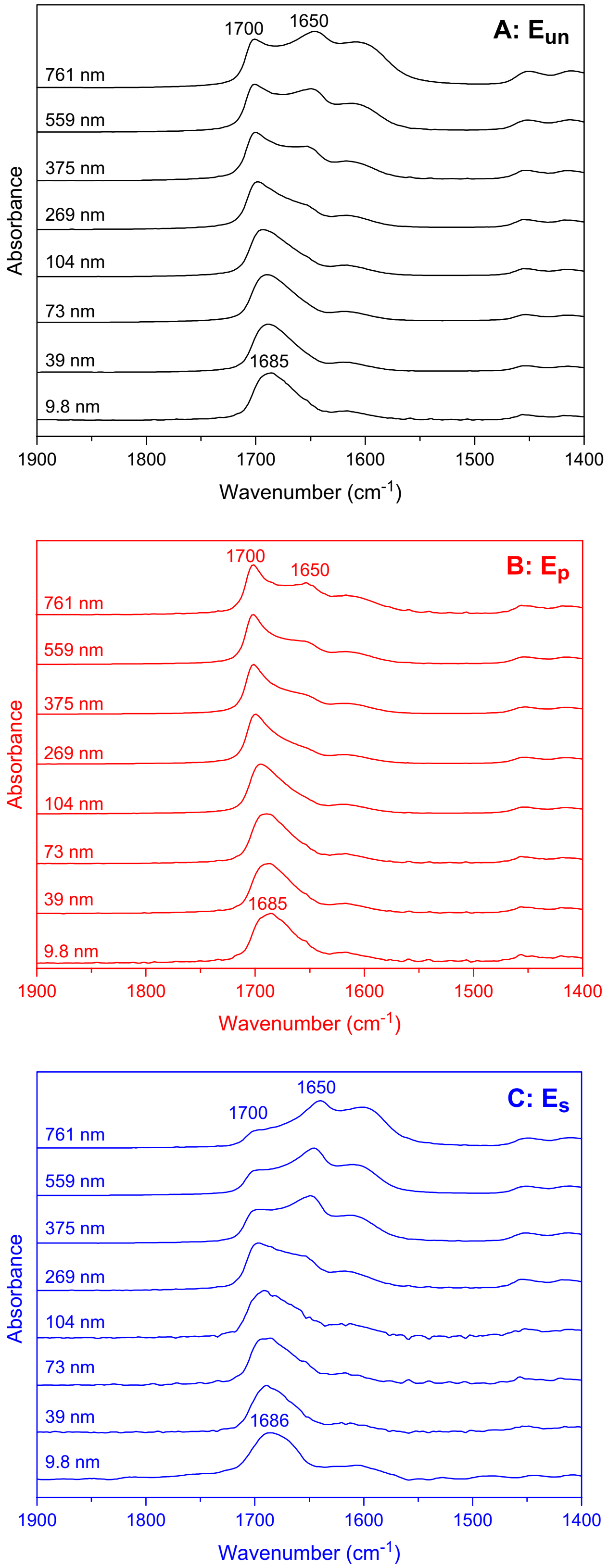

Fig. 2. Splitting of the amide I band with un-polarized light (A), p-polarized light (B) and s-polarized light (C) for spin-coated films with different thicknesses. The incidence angle is 85°. The band doublet is at 1700 cm^{-1} and 1650 cm^{-1}.

groups in the thicker PAL films (Fig. 2C, 1650 cm^{-1}) is more parallel to the Au surface. Based on the split of the amide I band and the relative band intensities, we concluded that the band at 1650 cm^{-1} shows parallel characteristic stretching to the Au surface and the band at 1700 cm^{-1} shows perpendicular characteristic stretching to the Au surface. We can conclude that the chain orientation is random for the films less than 73 nm thick, but for the thicker spin-coated films the orientation occurs. It should be noted that the band split does not justify the orientation. It is the peak ratio at 1650 cm^{-1} over 1700 cm^{-1} for p- and s-polarized lights that gives the proof of the chain orientation. A previous study of the orientation of peptide nanotubes in lipid membranes reveals the existence of the two amide I bands due to the infrared dichroism of the carbonyl group [23]. Fig. 3 shows the spectra of the amide I band vibration from 1900 cm^{-1} to 1400 cm^{-1} for the solution-casting films with different thickness. It shows that the split of the amide I band does occur for thicker solution-casting films both for p- and s-polarized lights due to the dichroism. However, the major difference between Figs. 2 and 3 should be noted. In Fig. 2C, as the thickness of the spin-coated films increases, the 1650 cm^{-1} band starts to appear and then surpasses the 1700 cm^{-1} band for the s-polarized light, which demonstrates the formation of chain orientation parallel to s-polarized light (parallel to the Au surface). In Fig. 3, as the thickness of the solution-casting films increases, the band splitting occurs at 1650 cm^{-1} and 1700 cm^{-1}, but the relative intensity remains the same for p- and s-polarized lights. Fig. 3 suggests that the solution-casting film has a uniform structure without orientation and the band split is from the dichroism alone. In this study, we not only report the spin-coating induced orientation, but also found that the spin-coating induced main chain orientation for the PAL films on the Au surface can only occur beyond a certain thickness-threshold. Due to the hydrophilic nature of the PAL molecules and the hydrophobic nature of the Au surface, the PAL molecules, which are in close contact with the Au surface by spin coating, firstly arrange themselves as a dewetting layer

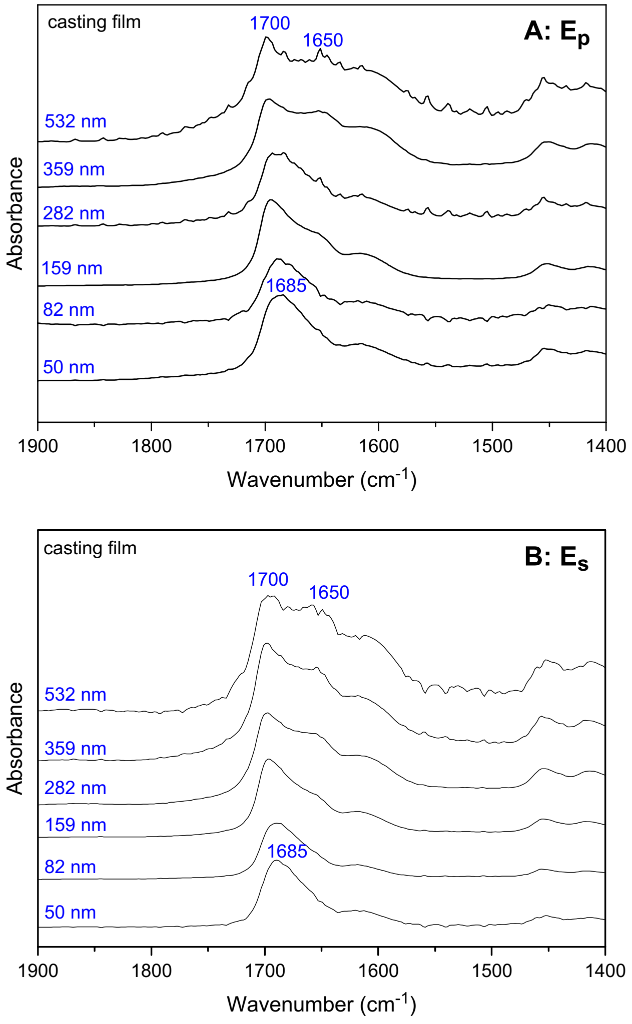

Fig. 3. Splitting of the amide I band with p-polarized light (A) and s-polarized light (B) for solution-casting PAL films with different thicknesses. The incidence angle is 85°. The band doublet is at 1700 cm^{-1} and 1650 cm^{-1}.

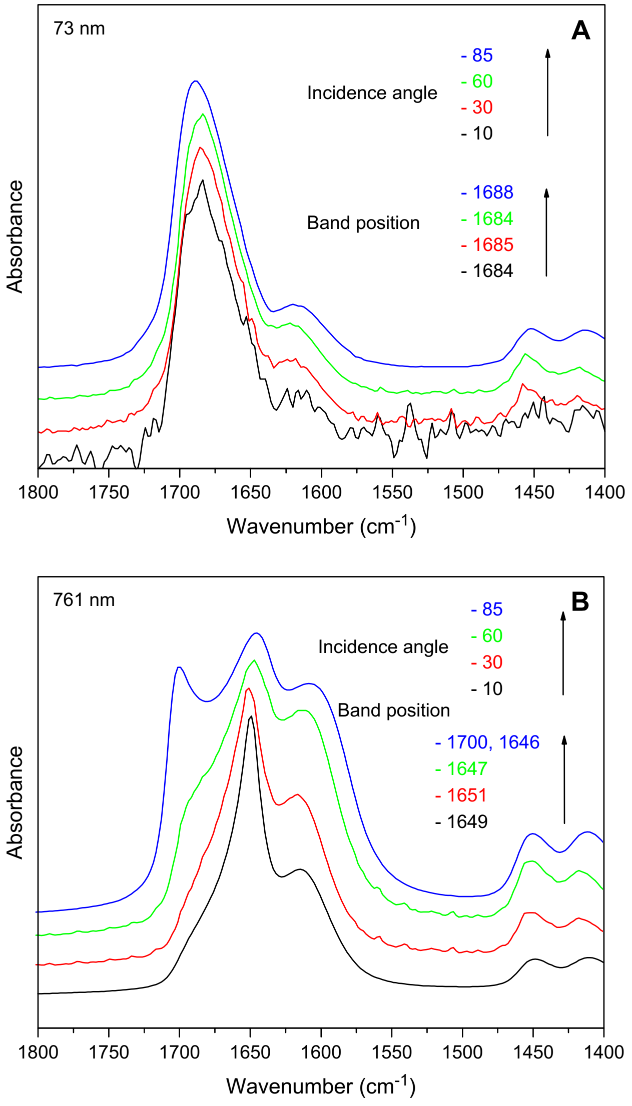

Fig. 4. The shape variations of the amide I band with changing incidence angles of un-polarized light; optically isotropic for the film thickness of 73 nm (A) and optically anisotropic for the film of 761 nm (B). The incidence angles are 10°, 30°, 60°, and 85°.

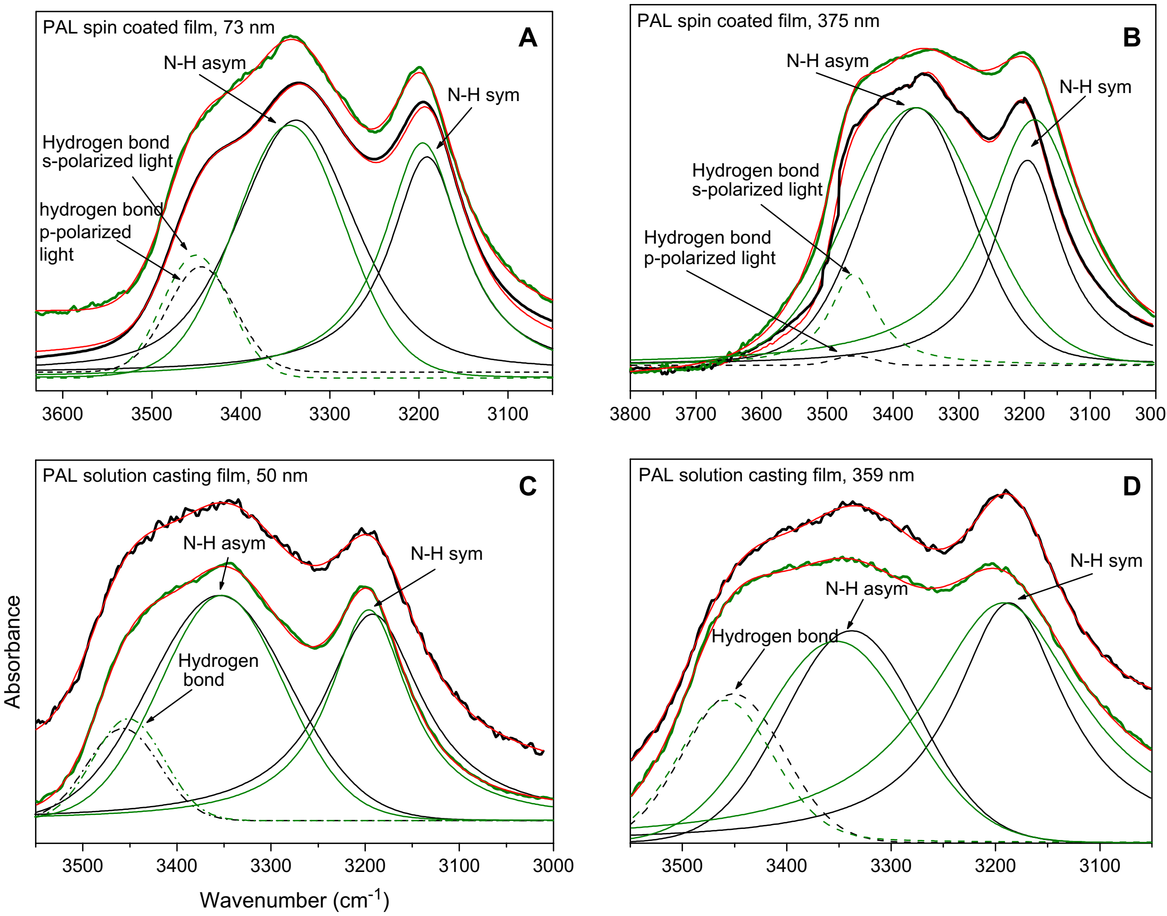

Fig. 5. The hydrogen bonding effect on N–H asymmetric and N–H symmetric stretchings with p- and s-polarized lights for spin-coated films (A and B) and solution-casting films (C and D) at different thickness. The green curves are for s-polarized light and the black curves are for p-polarized lights. The thinner black curves are the deconvolutions of the real spectra. The red curves are deconvolution curve fitting results. The hydrogen bond stretching for p-polarized light is dashed black curve and for s-polarized light is dashed green curve.

in a random-coiled state. Consequently, for the spin-coated films with thicknesses less than 73 nm in Fig. 2, the single band at 1685 cm^{-1} in the spectra stands for a non-orientation state. Beyond this thickness-threshold, the second layer of the oriented PAL molecules starts to form, which is observed as the band doublet at 1700 cm^{-1} and 1650 cm^{-1}. Therefore, the dewetting layer is estimated at around 70–100 nm, which is in the same order of the end-to-end distance (R_{ee}, 67 nm) of the PAL molecules used in this study with a molecular weight of $\sim 10^6$.

Since the bottom layer is composed of PAL molecules without orientation and the top layer is composed of PAL molecules with orientation, the optical isotropy and anisotropy are expected. Fig. 4 shows the two sets of the normalized spectra of the un-polarized light collected with four incidence angles of 10°, 30°, 60°, and 85°. When the film thickness is 73 nm, shown in Fig. 4A, a single band with the same band shape appears at the band maximum around 1685 cm^{-1} at the incidence angle of 10°, 30°, 60°, and 85°. When the film thickness is 761 nm, shown in Fig. 4B, at the incidence angle of 85°, a band doublet at 1700 cm^{-1} and 1646 cm^{-1} appears corresponding to the bottom layer and the top layer, respectively. At the incidence angle of 60°, the band at 1700 cm^{-1} becomes a shoulder. At the incidence angles of 30° and 10°, the band at about 1650 cm^{-1} is dominant and the band at around 1700 cm^{-1} cannot be detected. Referring to Fig. 1, one can see that the *E* vectors (both for p- and s-polarized components) are nearly parallel to the Au surface at small incidence angles, which accounts for the dominant effect at 1650 cm^{-1} for the incidence angles of 30° and 10° in Fig. 4B. Therefore, Fig. 4B provides another proof of the chain orientation for the thicker PAL films spin-coated on the Au surface.

Another noteworthy evidence is illustrated in Fig. 5 in which the orientation of hydrogen bond is verified by the p- and s-polarized lights. Fig. 5A and B shows the spectra of p- and s-polarized lights for the spin-coated films and Fig. 5C and D are the spectra of the p- and s-polarized lights for the solution-casting films. The thicker solid curves are the real spectra and the thinner curves are the deconvolution peaks. The black color is for the p-polarized light and the green color is for s-polarized light. The red solid curves are the fitting to the real spectra. The main contribution in Fig. 5 is from the N–H symmetric stretching and N–H unsymmetric stretching. The shoulder is from the hydrogen bonding effect. The hydrogen bonding, the N–H symmetric stretching, and the N−H unsymmetric stretching are deconvoluted as shown in Fig. 5. The hydrogen bond stretchings for p- and s-polarized lights are plotted in dashed curves in Fig. 5. The green curve is for the s-polarized light and the black curve for the p-polarized light. For PAL molecules, the hydrogen bonds form between the amino groups and the carbonyl groups. When the film thickness is 73 nm, shown in Fig. 5A, there is almost no spectral difference between the p- and the s-polarized lights, indicating that the hydrogen bond does not have preferred orientation between p- and s-directions. When the film thickness is 375 nm, shown in Fig. 5B, the hydrogen bonding effect for the s-polarized light is much stronger than that for the p-polarized light. It means that the bond direction of nitrogen and hydrogen atoms in the amino group prefers to be parallel to the Au surface for the thicker spin-coated films. Referring to Fig. 5C and D, one finds that there is no difference in the intensity of the hydrogen bond stretching for both p- and s-polarized lights for the films of 50 nm and 359 nm thickness, which indicates that the solution-casting film has uniform (random) orientation. However, for thicker PAL films spin-coated on the Au surface, there is a bi-layered structure in the film. The PAL molecules in the bottom layer arrange randomly due to the dewetting effect of the Au surface. The PAL molecules in the top layer show a parallel orientation to the Au surface due to the spin-coating effect.

4. Conclusion

In this study, we report that for thin spin-coated films (less than 100 nm), there is no spin-coating induced chain orientation; for thicker spin-coated films, we discovered that the bi-layered structure of PAL molecules is formed on the Au surface by spin coating. The bottom layer is composed of randomly packed PAL molecules with a thickness of around 70−100 nm. This suggests that the length scale of the dewetting is of the order of the molecular size (R_{ee}). The dewetting effect of the Au surface creates a layer of the randomly packed PAL molecules. The upper layer of PAL molecules shows the orientation, induced by spin coating, with the main chain and side chain parallel to the Au surface.

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