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Glass Transition Temperature of Poly(*tert*-butyl methacrylate) Langmuir–Blodgett Film and Spin-Coated Film by X-ray Reflectivity and Ellipsometry

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The glass transition temperature (T_g) of poly(*tert*-butyl methacrylate) (PtBMA) Langmuir–Blodgett (LB) films relative to that of spin-coated films on a silicon substrate is investigated by ellipsometry and X-ray reflectivity. The T_g of spin-coated films on an oxide-free silicon wafer decreases as the film thickness decreases, which is consistent with the majority of the previous reports in the literature. However, the transition temperature of the LB films is nearly independent of the total thickness, that is, the number of accumulated layers, which is much different from the case for spin-coated films. After sufficient thermal annealing of the LB film, it recovers the thermal transition behavior of the spin-coated film with an equivalent thickness. The layer structure of the LB film is deemed to be responsible for the departure from the behavior of the spin-coated film.

Introduction

In recent years, physical properties of thin polymer films have been investigated intensively due to the great technological importance of a wide variety of applications of thin polymer films such as dielectric layers, lubrication layers, and biocompatible surfaces.^{1,2} In these applications, the thermal properties of thin polymer films are of crucial importance since they are frequently used in a wide temperature range. The thermal properties of the polymer thin film are expected to be different from those of the bulk due to its large surface area/volume ratio. Polymer chains near the surface exhibit different properties compared to those in the bulk. For example, the air–polymer interface is thought of as a region of enhanced mobility. It has been argued that the chain ends of the polymers located near the interface tend to move toward the surface, which results in the increase of the local free volume and the chain mobility near the surface.^{3–5} On the other hand, studies of polymer diffusion in the region near the solid substrate indicated the opposite behavior—reduction in the chain mobility.^{6,7} These variations in chain mobility consequently affect the thermal properties of the thin polymer films.

There are a number of reports on the film thickness dependency of the glass transition temperature T_g of thin polymer films by X-ray reflectivity,^{8–10} ellipsometry,^{11–14} positron lifetime spectroscopy,¹⁵ and optical waveguide

spectroscopy.¹⁶ There is a consensus that the T_g of a thin polymer film ($d \leq 100$ nm) decreases with decreasing thickness when no specific interaction exists between the polymer film and the substrate,^{8,9,11–13,15,16} and T_g increases when a strong interaction such as hydrogen bonding exists between them.^{10,12,14} There also exist a few reports on the thermal properties of polymer LB films. Prucker et al. reported that LB films and grafted films of poly(methyl methacrylate) on a silicon wafer showed T_g values similar to those of spin-coated films and concluded that T_g behavior is independent of the intermolecular architecture and organization of the macromolecular chains in the various films—spin-coated, LB, and grafted films.¹⁶ However, we feel that a more systematic study is called for to reach a conclusion, since the experiments of Prucker et al. were carried out rather coarsely to span a wide range of film thickness and there exist other seemingly conflicting results on the transition temperature of LB films. For example, Hsiung et al. and Mabuchi et al. reported that T_g values of polymer LB films were similar to those of bulk polymer by second-harmonic generation measurement and energy-transfer measurement, respectively.^{17–19}

In the present study, we carried out a systematic study on the thermal transition behavior of PtBMA LB films relative to spin-coated films by ellipsometry and X-ray reflectivity measurements, which are well-established methods to observe the thermal transition behavior of thin polymer films. PtBMA was chosen, since LB films

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can be deposited with a good transfer ratio and the structure of the LB films was well characterized recently.^{20,21}

Experimental Section

Film Preparation. Single-crystal silicon wafers with a (1,0,0) crystal plane were used as the solid substrate, and the native oxide layer on the silicon wafer was removed by treatment with 10% hydrofluoric acid for 10 min. Removal of the oxide layer was necessary to obtain a high-quality PtBMA LB film. The transfer ratio of the PtBMA monolayer at the air–water interface to the silicon wafer with the native oxide layer was not good. In addition, we would like to remove the specific interaction between the solid substrate and PtBMA in order to compare with the polystyrene thin films, the most extensively studied materials.^{11,15,22,23} After the native oxide layer was removed, the silicon wafer was rinsed several times with acetone and dried under vacuum for 1 h. The silicon wafers were kept under nitrogen before use. The contact angle of water on the oxide-free silicon wafer was 68° when measured before the deposition of LB films. The root-mean-square (rms) roughness of the oxide-free silicon wafer was determined as about 5 Å by atomic force microscopy (AFM) (DME, Dualscope), which is similar to the rms roughness of the silicon wafer before the hydrofluoric acid treatment, 4 Å.

PtBMA ($M_w = 175\text{K}$, $M_w/M_n = 2.33$, $T_g = 107^\circ\text{C}$) was purchased from Aldrich and used without further purification. The triad distribution of PtBMA was determined by ^1H NMR (Bruker, DPX 300) as iso/hetero/syndio = 11:37:52, employing the method in the literature.²⁴ A toluene (Aldrich, HPLC grade) solution of PtBMA was spun on oxide-layer-free silicon wafers at 2000 rpm for 30 s. Film thickness was controlled by changing the concentration of the polymer solution. The films were annealed at 135 °C in a vacuum oven for 20 h and then cooled to room temperature in a vacuum at a cooling rate of 0.5 °C/min.

PtBMA LB films were prepared using a LB film deposition apparatus (KSV5000). A 0.50 mg/mL chloroform (Aldrich, HPLC grade) solution of PtBMA was spread on a deionized water subphase at 20 °C, which was distilled and passed through a water purification system (Barnstead, E-pure). PtBMA LB films were deposited as Y-type at $\pi = 10\text{ mN/m}$ at a dipping speed of 5 mm/min. The deposited LB films were dried in air. Complete drying was checked by the absence of an OH stretching peak in the FT-IR spectrum, and the LB films were kept in a moisture-free environment before use.

Ellipsometry. Ellipsometry measurements were performed by using a spectroscopic ellipsometer (J. A. Woolam, Model VASE) equipped with a homemade hot-stage and a programmable temperature controller (Eurotherm 808). We recorded the ellipsometric angles (Δ and Ψ , $\tan \Psi \equiv |r_p|/|r_s|$ and $\Delta \equiv \delta_p - \delta_s$) every 15 s while the sample temperature was raised from room temperature at a constant rate of 2 °C/min. The incident angle was 75°, and nine different wavelengths were selected between 400 and 800 nm to perform spectroscopic and kinetic ellipsometric scans. The refractive index of bulk PtBMA and the thickness measured by X-ray reflectivity were used as the initial guess to deduce the refractive index and thickness of the films.

X-ray Reflectivity. X-ray reflectivity measurements were carried out at the 3C2 X-ray diffraction beamline of the Pohang Light Source (PLS), Pohang Accelerator Laboratory, Pohang, Korea. The X-ray beam the radiated from bending magnet of the PLS storage ring is focused by platinum-coated toroidal silicon mirrors. A fixed exit double-crystal monochromator provides a monochromatic X-ray beam at $\lambda = 1.540\text{ Å}$ and $\Delta\lambda/\lambda = 1.5 \times 10^{-4}$.²⁵ The photon flux is typically on the order of 10^{10} photons/

Table 1. Thickness and Refractive Index of Spin-Coated Films before Thermal Treatment and Their Glass Transition Temperatures Determined from a Kinetic Ellipsometric Scan

ellipsometry		X-ray reflectivity	
thickness (Å)	refractive index	thickness (Å)	glass transition temp (°C)
105	1.4715	85	55 ± 3
186	1.4598	191	57 ± 3
224	1.4664	223	62 ± 3
378	1.4677	365	70 ± 3
417	1.4666	401	78 ± 3
498	1.4508	514	97 ± 3
565	1.4655	566	106 ± 3
714	1.4501	729	112 ± 3

Table 2. Thickness of PtBMA LB Films as Prepared and Their Transition Temperatures Determined by Kinetic Ellipsometric Scan

number of layers	ellipsometry		X-ray reflectivity	
	thickness (Å)	refractive index	thickness (Å)	transition temp (°C)
10	98	1.4945	95	82 ± 3
20	191	1.4596	185	80 ± 2
30	284	1.4610	277	76 ± 2
40	380	1.4615	367	83 ± 4
60	536	1.4514	544	81 ± 5

(mm² s). A homemade hot-stage was used to change the temperature of the thin films, and the temperature was controlled with a programmable temperature controller (Eurotherm 808). We also used a conventional X-ray diffractometer using nickel-filtered Cu K α ($\lambda = 1.54\text{ Å}$) radiation of a rotating anode source (Rigaku, RINT 2500, 60 mA/40 kV).

Results and Discussion

The thicknesses and refractive indexes of the polymer films used in this study were measured by X-ray reflectivity and ellipsometry at room temperature before the temperature scan, and the results of spin-coated films and LB films are listed in Tables 1 and 2, respectively. The thicknesses measured by two independent methods are identical within experimental uncertainty except for the thin films under the thickness 100 Å. As shown in Tables 1 and 2, the refractive indexes of the thin samples also show a discrepancy not seen with all other, thicker polymer films. We do not have a good explanation for the discrepancy but suspect that the precision of ellipsometry for such a thin film would not be as good as that for thicker ones. Otherwise, the refractive indices of the spin-coated films and LB films obtained by ellipsometry are 1.462 ± 0.006 and 1.457 ± 0.004 in the 95% confidence limit at the wavelength 599.3 nm, respectively, which are favorably compared with the literature value 1.4638 at the wavelength 589.3 nm.²⁶ We think that the slightly lower value found in LB films is due to the lower density of the LB films compared with spin-coated films. The density of the LB film calculated from the transfer ratio and the film thickness was around 1.00 while the density of bulk PtBMA is 1.02. We will come to this point later.

Figure 1 shows the X-ray reflectograms of the 60-layer PtBMA LB film at various temperatures. They show a clear Kiessig fringe pattern, and the film thickness can be determined from the peak maxima. If we neglect the deviation of the refractive index at the X-ray wavelength from unity, the angle of the fringe maxima θ_n is related to the total thickness of the film d , the number of layers

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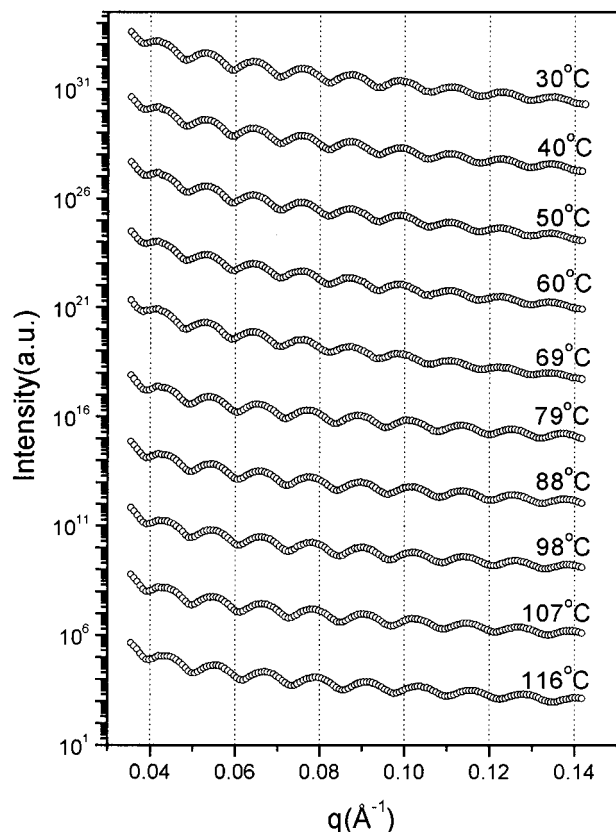


Figure 1. X-ray reflectivity curves of a 60-layer PtBMA LB film at various temperatures. The reflectivity curves were shifted vertically for visual aid. A clear shift of the Kiessig fringe toward higher angles with heating is observed. $q = 4\pi \sin \theta / \lambda$.

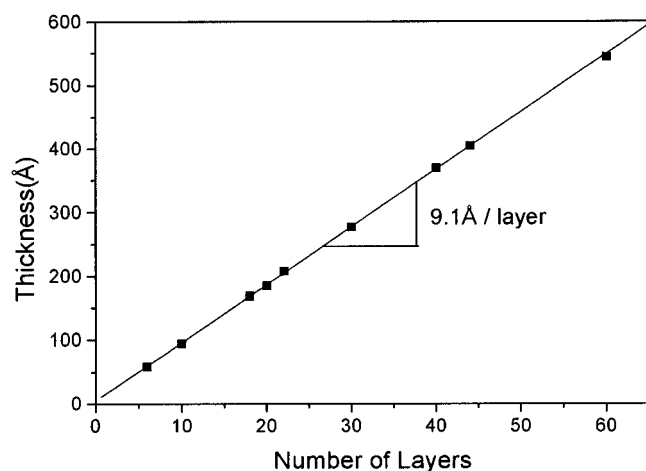


Figure 2. Thickness of PtBMA LB films as a function of the number of deposited layers. From the slope of the straight line, the average thickness of the PtBMA monolayer is determined as 9.1 Å.

n , and the X-ray wavelength λ by the following formula.²⁷

$$\sin \theta_n = n \frac{\lambda}{2d}$$

The thus-determined film thickness of the as-deposited LB film shows an excellent linear relationship with the number of layers deposited, as displayed in Figure 2. The monolayer thickness of PtBMA determined from the slope

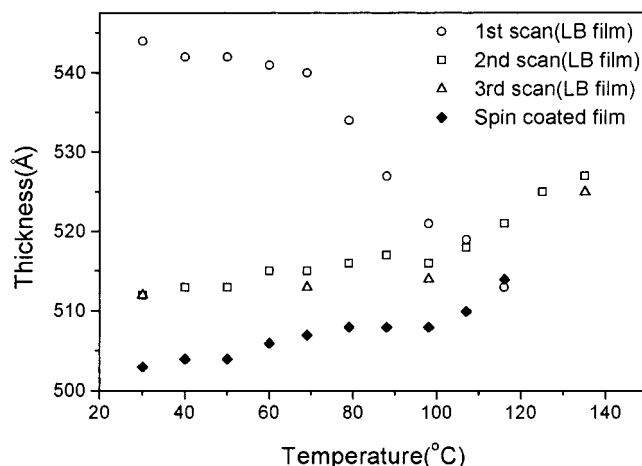


Figure 3. Thickness change of a 60-layer PtBMA LB film (open symbols) and a spin-coated film (filled diamonds) upon thermal treatment by X-ray reflectivity measurement: first scan (○); second scan (□); third scan (△); spin-coated film (◆).

of the straight line is 9.1 Å, which is in good agreement with other reports.^{20,21} This indicates that the LB films would possess a well-defined layer structure before the thermal treatment.

When the LB film is subjected to thermal treatment, as shown in Figure 1, the Kiessig fringe pattern shows a clear trend for the reflectivity profiles to shift to higher angles, indicating the decrease of the film thickness upon heating. This is opposite to usual thermal expansion behavior of thin polymer films. To test the reversibility, we performed successive heating and cooling cycles of the LB films. To avoid film damage due to the excess radiation dosage, the position of the X-ray illumination was changed after a heating/cooling cycle. Possible film thickness variation at different positions was checked when we translated the sample. The thickness of the LB film was confirmed to be uniform within experimental uncertainty, while the spin-coated film showed a little variation. The results of film thickness changes during the heating and cooling cycles are displayed in Figure 3. During the first heating process up to 120 °C the film thickness decreases significantly and the slope of the heating curve shows a transition around 70 °C. In the second and third heating scans, the thickness change with temperature becomes practically identical to that of spin-coated films. For comparison, the thickness change of a spin-coated film of similar thickness with heating is also plotted in the same figure with filled diamonds. The annealed LB films and spin-coated films showed a similar increase of thickness, and the slope of the heating curves showed a similar transition temperature around 100 °C. Sometimes the second heating scan shows an intermediate behavior of an LB film and a spin-coated film, but sufficient annealing always makes the film behave like a spin-coated film. A similar behavior was observed in the separate experiment with a 20-layer PtBMA LB film.

This rather unexpected behavior of PtBMA LB films—decrease of thickness with temperature increase—is not due to possible artifacts such as the change of surface roughness. In Figure 1, the Kiessig fringe does not deteriorate much with heating, which indicates that the film surface roughness does not change significantly during the thermal treatment. In principle, the film roughness can be estimated by fitting the reflectogram to a model density profile including the surface roughness.^{28,29}

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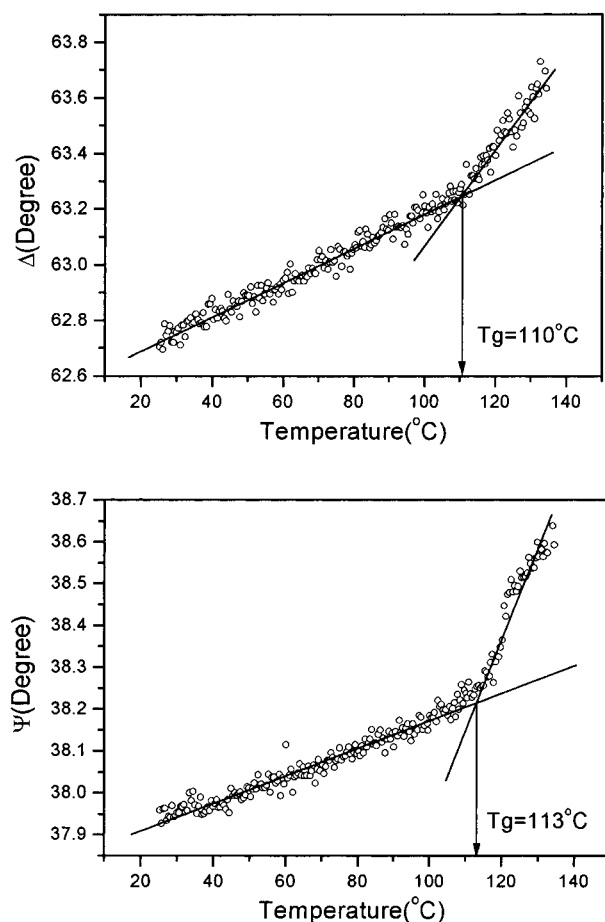


Figure 4. Kinetic ellipsometric scan of a spin-coated PtBMA film ($t_0 = 714$ Å) on an oxide-free silicon wafer. The ellipsometric angles Δ and Ψ are plotted as a function of temperature during the heating scan at a heating rate of 2 °C/min and $\lambda = 497.3$ nm.

To have a more direct experimental confirmation, however, we measured the surface roughness by AFM. In the case of 60 layers of PtBMA LB film, the rms roughness was about 9 Å. And the rms roughness slightly decreased to about 7 Å after the thermal treatment, which is comparable to the rms roughness of spin-coated PtBMA film, determined as about 6 Å. In addition, we have not found any indication of large scale dewetting of the LB film from either AFM or optical microscope observation.

As mentioned above, the change of the slope $[d(\text{thickness})/dT]$, a signature of the "glass transition", takes place at significantly different temperatures for the as-deposited LB film (first scan) and the annealed LB film (second or third scan) or the spin-coated film. To examine the glass transition behavior of the thin polymer films closely, the kinetic ellipsometric scan was performed.^{12,30} Typical data for the 714 Å thick spin-coated film are shown in Figure 4. The abrupt change of the slope for both Δ and Ψ was clearly observed at approximately 112 °C. The thus-determined T_g values of the spin-coated PtBMA films of various thicknesses are summarized in Table 1. These results show the same trend as that reported by Keddie et al. for a polymer thin film on the substrate without specific interaction; T_g increases with the film thickness to the asymptotic limit of the bulk T_g .¹¹

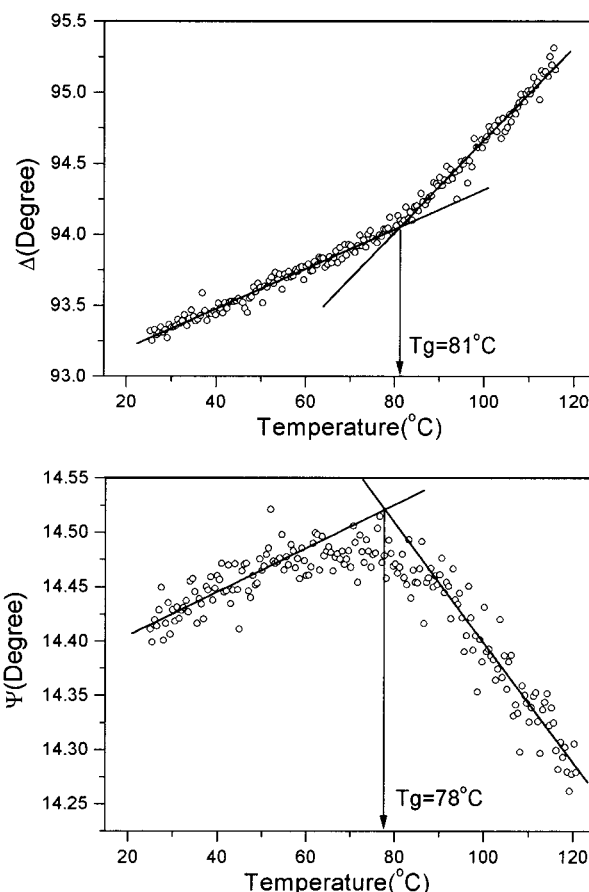


Figure 5. Kinetic ellipsometric scan of a 20-layer PtBMA LB film ($t_0 = 191$ Å) on an oxide-free silicon wafer. Other experimental conditions are the same as those in Figure 4.

In Figure 5 is displayed a result of the kinetic ellipsometric scan of the 20-layer PtBMA LB film. The change of the slopes for Δ and Ψ was again clearly observed at approximately 80 °C. It is interesting to note that the trend of Ψ is opposite to the corresponding data of the spin-coated film shown in Figure 4. This trend is reproducible for all the PtBMA films we have studied. We do not understand the origin of this difference, but it seems to be associated with the anisotropic layer structure of the LB film, which is absent in the spin-coated film. At the moment we concentrate on the transition temperature only. The transition temperatures of the LB films of different numbers of layers are summarized in Table 2 and plotted in Figure 6 (filled circles) together with those for the spin-coated films (open circles). Interestingly enough, the transition temperatures of LB films are nearly independent of film thickness at 80 ± 4 °C. This is entirely different from the thermal transition behavior of spin-coated films, which shows a strong thickness dependence.

We also measured the kinetic ellipsometric scan of 20 and 60 layers of PtBMA LB film annealed for 20 h at 135 °C. As shown in Figure 7 for the annealed 60-layer LB film, the trend of the slopes of Δ and Ψ is identical to that of the spin-coated film shown in Figure 4. In addition, the transition temperatures T_g of the annealed PtBMA LB films are similar to that of the spin-coated film of equivalent thickness, about 110 °C. The data points of the two annealed LB films are added in Figure 6 as filled squares, and the annealed LB films clearly follow the behavior of spin-coated films.

Summarizing the above results, we observed a large difference between the PtBMA LB films and the spin-coated films. The thickness of PtBMA LB films decreases

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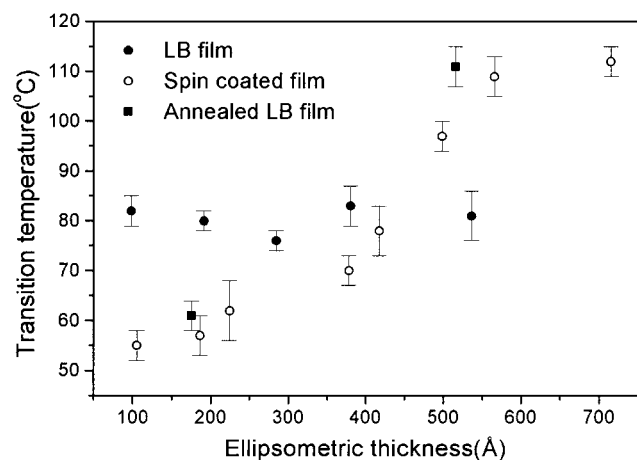


Figure 6. Transition temperatures versus thickness of various PtBMA films: LB films (●); spin-coated films (○); annealed LB films (■). Error bars indicate the uncertainty in the determination of the transition temperature from the kinetic ellipsometric scan as shown in Figures 4 and 5.

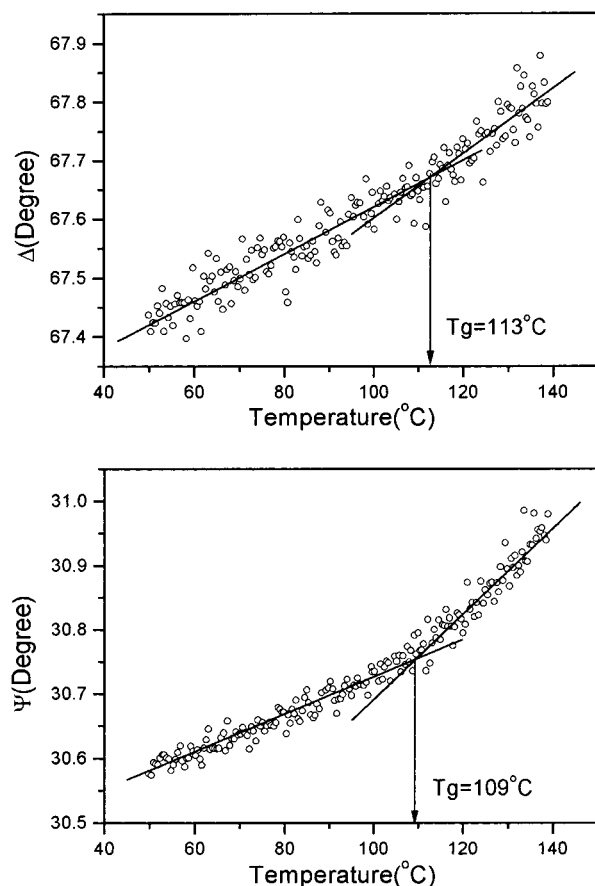


Figure 7. Kinetic ellipsometric scan of an annealed 60-layer PtBMA LB film on an oxide-free silicon wafer. Other experimental conditions are the same as those in Figure 4.

at first with temperature, opposite to the typical thermal expansion behavior of spin-coated films. After sufficient thermal annealing, LB films show similar behavior to that of the spin-coated film. Furthermore, the apparent glass transition behavior of the LB film is quite different from that of spin-coated films. Spin-coated films and annealed LB films show strong thickness dependence, as reported previously, while as-deposited LB films showed the transition temperature to be almost independent of the film thickness. We propose the following explanation for the distinct behavior of the polymer LB films. In preparing

the LB films, the polymer chains spread on the air–water interface are transferred layer by layer to the solid substrate. Therefore, PtBMA molecules in the LB film have a two-dimensionally confined molecular conformation. The polymer molecules are entropically strained and would have extra free volume between the layers. This seems to cause the thickness of the polymer LB film to decrease at first when it is subjected to thermal treatment. During the process, the interlayer free volume is suppressed across the transition temperature around 80 °C. The apparent transition temperature of the LB film is independent of the film thickness if it is mainly governed by the interlayer free volume, which should be independent of the number of layers. Further thermal treatment induces an irreversible interlayer mixing to change the two-dimensional layer structure of the polymer chains to a more entropically favorable three-dimensional conformation. Recently, Mabuchi et al. examined the structural relaxation of a polymer LB film by an energy-transfer method.^{18,19} They reported that the structural relaxation of the polymer LB film with thermal treatment is an irreversible conformational change from the two-dimensional confined structure. We believe that it is the same structural relaxation phenomenon that as what we observed.

Hisung et al. and Mabuchi et al. reported that the transition temperature is close to the bulk T_g .^{17–19} The transition temperature of LB films determined by ellipsometry in this study is still lower than the bulk T_g but much higher than the transition temperature of the spin-coated film of equivalent thickness, and the transition temperature should have some relation with the bulk T_g . We are currently working on other polymers to find out the relation of the transition temperature to the bulk T_g . Although we do not have direct evidence precise enough to confirm the presence of the interlayer free volume proposed here, there exist a few data supporting the idea. For example, Esker et al. observed a Bragg peak from the poly(*tert*-butyl acrylate) (PtBA) LB film but not from the PtBMA LB film, and we also confirmed it experimentally.²⁰ They suggested that the methyl groups of PtBMA along the backbone alter the packing characteristics so that no Bragg peak was detected in PtBMA. In any event, the observation indicates that the interlayer free volume may exist in polymeric LB films. In addition, as mentioned earlier, both the refractive index (measured by ellipsometry) and the density (calculated from the transfer ratio and film thickness) of the PtBMA LB films are lower than those of spin-coated films, which is consistent with the hypothesis. Since the differences in both refractive index and density are not significantly larger than the experimental uncertainty, however, we do not want to make a strong statement on the existence of the interlayer free volume at the moment. Systematic studies on a greater variety of polymers seem to be necessary to reach a conclusion.

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