

Glass Transition Behavior of Spin-coated Thin Films of a Hydrophilic Polymer on Supported Substrates^{*}

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Abstract Using ellipsometry, it is found the glass transition temperature of the spin-coated polyacrylamide (PAL) thin films on the supported silicon (Si) substrates with an oxide layer decreases with decreasing the film thickness. But T_g s of the as-prepared thin films are much higher than that of the bulk sample. Such observations can be attributed to the combined result of the “surface effect” and increased hydrogen bonding interaction between PAL chains due to spin coating/thin film confinement.

Keywords: T_g ; Thin film; Hydrophilic polymer; Ellipsometry.

INTRODUCTION

The importance of the polymer thin film comes from its application in micro-electronics, adhesion and coating industry^[1, 2]. It has been a focusing point because of the fact that the glass transition temperature (T_g) of the polymer thin film differs from that of its bulk state as the thickness lowers to a certain extent, namely, nano-size. Due to its nano-confinement on the substrate or in a freely-standing state, this polymer thin film is highly metastable^[3]. The physical origin about the T_g deviation from the bulk has attracted much attention and many studies have been done on focusing the glass transition behaviors of polymer thin films. Although a global model or description for T_g s of polymer thin films has not been acquired, experimental results have indicated that the free surface^[4–8] has substantial effect on the T_g deviation as well as the interfacial interaction^[9–12]. Across the T_g transition, many physical properties of polymers go through a detectable change which makes the measurement feasible, such as differential scanning calorimetry (DSC)^[13, 14], ellipsometry^[4, 9, 11], Brillouin light scattering (BLS)^[5, 15], dielectric relaxation spectroscopy (DRS)^[16, 17], X-ray reflectivity^[6, 10, 18–23], neutron scattering^[20–24], positron annihilation lifetime spectroscopy (PALS)^[21, 25], fluorescence spectroscopy^[26, 27] and sum frequency generation (SFG) vibrational spectroscopy^[28–31]. Most of the previous studies were focused on the hydrophobic polymers like polystyrene (PS) and polymethyl methacrylate (PMMA) and the measured T_g decreased with reducing the thin film thickness. A few studies indicated an increased T_g with reducing the film thickness when

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the polar interaction exists between the polymer and substrate^[9–11]. To the best of our knowledge, none of the previous reports dealt with thin films of polymers with chain units which can form strong polar interactions like hydrogen bonding. In this paper, we report the T_g measurement of the spin-coated polyacrylamide (PAL) thin films on the supported silicon substrates using ellipsometry. Different T_g behaviors from the previous studies are presented and the reasons behind are discussed with relation to the hydrophilic nature of PAL.

EXPRIMENTAL

Preparation of PAL Thin Films

PAL ($M_w = 5\text{--}6 \times 10^6$, Polysciences, Warrington, PA.) was dissolved in deionized water. The bulk film was obtained by casting the solution on a flat Teflon surface. The PAL thin films were prepared on the treated Si substrates by a spin coater (Spin coater, P6700, Speciality Coating Systems Inc.) The Si substrates (Silicon polished wafer, N-type, Grimm, Inc.) were soaked in the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ (3:7 volume ratio, 35 wt% H_2O_2 solution, 98 wt% H_2SO_4) for 2 h. Then the Si substrates were taken out and washed by the deionized water and dried by purged nitrogen gas. Ellipsometric measurements indicated a layer of ~ 4 nm SiO_x on top of the substrate. Thicknesses of the PAL thin films on the Si substrates were adjusted by the solution concentration. All the PAL film samples were put in the vacuum oven (Shel lab 1410, Shalton Mfg Inc.) and annealed at 185 °C for 4 h. Then the samples were placed in a desiccator before further characterization.

Characterization of the PAL Thin Films by Ellipsometer

The ellipsometer (Vase Angle Spectroscopic Ellipsometer, Software M-44 systems, J. A. Woollam Co., Inc.) was used to measure the ellipsometric parameters of the thin films on the Si substrates from the dynamic scan. We built up a customized heating accessory with a programmable temperature controller (Model UP150 Program Temperature Controller, Yokogawa M&C Co.) fitting for the ellipsometer. The temperature of the sample film was calibrated by Mettler Toledo calibration substances (Benzoic acid and Caffeine, Sigma-Aldrich Inc.). The ellipsometer and the heating accessory were combined together to capture the ellipsometric parameters in the dynamic scan for our thin film samples. During the dynamic scan, the noise of the temperature was estimated to be (± 0.5) K. The ellipsometric parameters were collected in terms of the temperature. A temperature scan range from 100 °C to 250 °C was chosen at the heating rate of 2 K/min; and the same two continuous scans were run and the measured apparent T_g s were averaged values.

RESULTS AND DISCUSSION

The Ellipsometric Parameters Analysis

In general, the discontinuity of the ellipsometric parameters as functions of the temperature can be directly correlated to the thermal transition of a polymer thin film. This method was first employed by Keddie *et al.*^[4, 9] and the curves of ellipsometric parameters in terms of the temperature (T) were used to obtain T_g . In principle, the ellipsometric parameters Δ and Ψ contain the optical information of the “phase” and “amplitude” relationship between the reflected p- and s- polarized lights, which can be expressed as functions of the film thickness and the refractive index. If a polymer thin film goes through the glass transition, the abrupt change of the film thickness and refractive index will render the synchronized change of Δ and Ψ . This is the inherent reason why the ellipsometry can be used to characterize T_g of a polymer thin film. In this paper, T_g s of the PAL thin films were acquired from the Δ - T and Ψ - T curves as demonstrated by Keddie *et al.*^[4, 9].

The PAL bulk T_g was obtained from the PAL bulk film using DSC with a heating rate of 2 K/min, as shown in Fig. 1. Since the sample went through the thermal annealing, a distinct enthalpy relaxation peak appeared and mediated the step transition. The normal methods used to extract T_g , such as fictive, inflexion, half C_p extrapolated points, are not suitable in this case. We used the peak maximum (~ 193 °C) as the indication of T_g . T_g s of the PAL thin films with different thicknesses were obtained from the dynamic ellipsometric measurement. The example Δ - T and Ψ - T curves from the ellipsometric dynamic measurement are shown in Fig. 2. T_g of the PAL thin film was acquired from the point at which the abrupt change takes place in the Δ - T and Ψ - T curves.

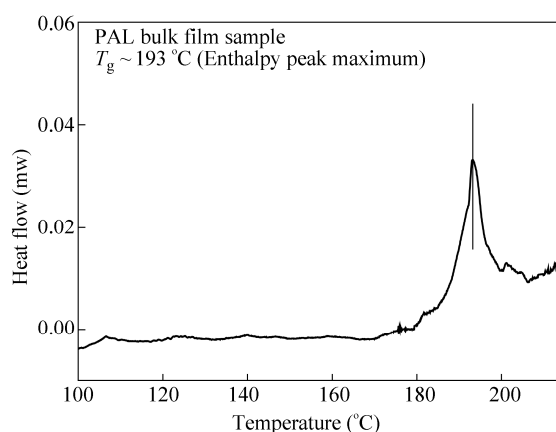


Fig. 1 The DSC curve of the PAL bulk sample (Heating rate is 2 K/min.)

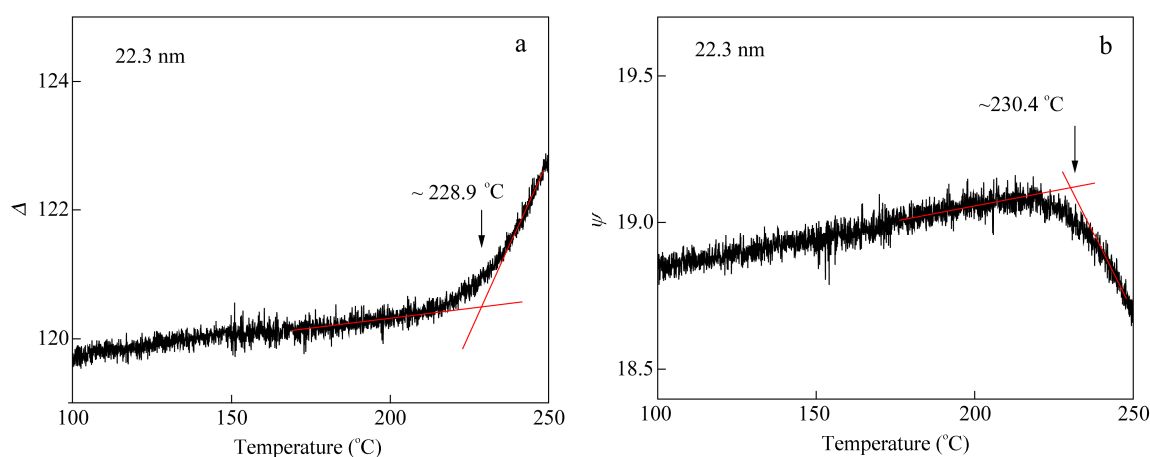


Fig. 2 The Δ - T (A) and Ψ - T (B) curves for a 22.3 nm thick PAL thin film obtained from the dynamic ellipsometric measurement

T_g Deviation of the PAL Thin Films from the Bulk Value

T_g s of the PAL thin films acquired from the ellipsometric measurement were shown in Fig. 3. The measured T_g s of the PAL thin films in the thickness range from several nanometers to a hundred nanometers located neither near nor lower than but higher than the T_g of the bulk PAL. Our previous experiment has proved that the strong polar interaction through hydrogen bonding exists between the SiO_x layer and PAL^[32]. So this is not strange at all. The similar phenomena were also found by Keddie *et al.*^[9] and van Zantán *et al.*^[10] when the polymers can form strong interactions with the substrates. However, T_g of the PAL thin films decreases as the film thickness decreases which is against the same reports. Considering the reported polymers of PMMA^[9] and poly-(2)-vinylpyridine (P2VP)^[10], although they can form certain interactions with the bottom substrates, comparable interactions do not exist between the chain units. The chain units of PAL used in this study can form strong interaction both to the substrate and by themselves through hydrogen bonding. This structural characteristic combined with the surface effect could be the reason leading to the decreasing T_g with decreasing the PAL film thickness. But this still can not explain the higher thin film T_g s than the bulk since the hydrogen bonding between the PAL chain units also exists in the bulk film. A previous study has already shown T_g of PAL single chain globules with less entanglement/interpenetration is higher than that of the bulk film^[33], indicating the confinement can easily change the PAL T_g behavior associated with the chain conformational state. A polymer thin film can geometrically be considered to be in a one-dimensional (1-D) confined state. When the film

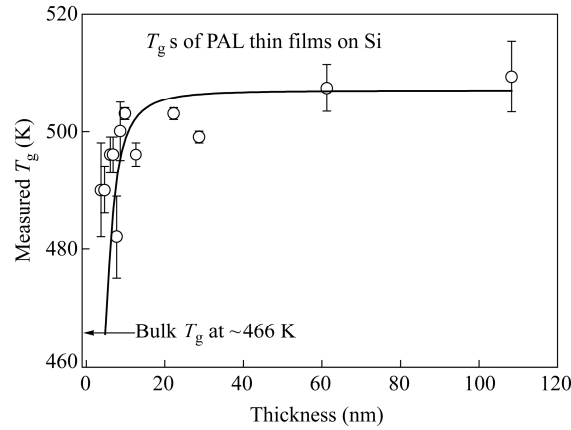


Fig. 3 The measured T_g s of the PAL thin films in terms of the film thickness. The solid line is the fitted curve using the empirical equation.

thickness decreases to certain characteristic length threshold, the polymer chains may adopt a two-dimensional (2-D) expanded conformation. Upon vitrification during the thin film preparation *via* spin coating, the expanded conformation could be solidified and quasi-stabilized by the macromolecular cohesive interaction. The recent experiments on the residue stress of the polymer thin films confirmed the non-equilibrium conformational state of the spin-coated thin film and this non-equilibrium chain conformation is difficult to relax back^[34–36]. Our spectroscopic experiment also indicates the existence of the expanded chain conformation for PAL prepared *via* spin coating^[37]. The expanded chain conformation may render a high chain packing density in the direction of the surface normal. We could expect the hydrogen bonding interactions associated with the aforementioned 2D expanded chain conformation should account for the observed T_g behavior. Here we provide a simple scaling argument hopefully to help understand the thermal behavior of the PAL thin films in terms of the film thickness. For all the PAL thin films prepared *via* spin coating, a similar two-dimensional expanded conformation of the PAL chains can be assumed. If T_g is correlated to the chain segment motion, the thermal energy should be comparable to the net energy barrier in order to activate the segmental motion.

$$k_B T \sim E_{\text{coh}} - f(l, d) \cdot TS \quad (1)$$

E_{coh} is the cohesive energy bound to a chain segment (Since we use silicon with a top SiO_x layer as substrate, E_{coh} includes the interfacial interaction between PAL and silicon and this does not affect our analysis.). k_B is the Boltzmann constant. The term “TS” can be viewed as the entropy contribution due to the surface effect causing the T_g reduction as the film thickness decreases. If the surface is somehow considered “free”, then “TS” goes to “ $k_B T$ ” for a motion segmental unit. $f(l, d)$ is a function which describes the restriction of the characteristic length l and the film thickness d to the free surface effect and this function can phenomenologically be obtained by fitting the experimental data. Now we have

$$k_B T \sim E_{\text{coh}} - f(l, d) \cdot k_B T \quad (2)$$

When the film thickness increases, the surface effect diminishes and T_g levels off as shown in Fig. 3. Therefore, we can know for the thick film (~ 100 nm), “ $E_{\text{coh}} \sim k_B T_{g, \text{thick film}} \sim 7.0 \times 10^{-21}$ J”. Compared to the bulk case, $E_{\text{coh, bulk}} \sim k_B T_{g, \text{bulk}} \sim 6.4 \times 10^{-21}$ J, there is a thermal energy difference around $k_B \Delta T \sim 5.6 \times 10^{-22}$ J for a T_g difference of ~ 40 K. Here we use the assumption that the cohesive energy increase is of the same order of the increase of the thermal energy. We notice that the averaged hydrogen bonding energy for a carbonyl group and an amine group in a PAL unit is $E_{\text{HB}} \sim 1.7 \times 10^{-20}$ J. This suggests that the change of the hydrogen bonding has substantial effect on the T_g deviation of the polymer thin film. Formation of an additional hydrogen bond can strongly affect many chain segmental motions with respect to T_g . However, this does not rule out the possibility that the

cohesive energy due to the increased van der Waals force can also contribute to the T_g increase compared to the bulk. However, without the strong polar interaction between chain units, such as PMMA and PS, such phenomena of a decreasing T_g with decreasing film thickness and a higher thin film T_g than the bulk value were never observed before. We recognize the cohesive energy closely related to the hydrogen bonding between the PAL chain units is the fundamental reason causing the observed T_g behavior here.

If we believe the surface has a continuous effect on the thin film T_g across the whole thickness length scale and use $f(l,d) \sim (l/d)^\delta$ as an approximation for restriction of the characteristic length l and the film thickness d to the surface effect, we can reach the following empirical equation similar to Keddie *et al.*'s^[4, 9].

$$T_g \sim \frac{E_{\text{coh}}}{k_B \left[1 + \left(\frac{l}{d} \right)^\delta \right]} \quad (3)$$

The best fitting leads to $l = (0.9 \pm 0.7)$ nm and $\delta = (1.5 \pm 0.5)$. The characteristic length l here is much less than those for PMMA^[4]. This suggests the length scale of the free surface for PAL is much smaller, possibly due to PAL' strong hydrophilicity. Since the characteristic l is small, the restriction of the exponential δ to the T_g reduction with respect to the film thickness is limited within ~ 10 nm. In other words, the thin film T_g approaches to T_g ($d = \infty$) when the film thickness is above 10 nm, as shown in Fig. 3. The smaller characteristic length l appears to be consistent with the hydrophilic nature of PAL.

CONCLUSIONS

We found T_g of the PAL thin film on the supported silicon substrate decreases as the film thickness decreases detected by ellipsometry. However, T_g s of the PAL thin films are generally higher than that of bulk PAL. These phenomena are believed to be correlated to the hydrophilic nature of PAL. The increased hydrogen bonding due to the chain extension on the supported silicon substrate is suggested to be responsible for the higher thin film T_g s than the bulk ones. The "surface effect" is believed to be responsible for the decreasing T_g with decreasing the film thickness. Although the "surface effect" may not be as strong as the hydrogen bonding effect due to the chain extension considering the hydrophilic nature of PAL, we have introduced a surface "TS" term to make the empirical model more meaningful considering the increased freedom of the surface. Computer simulation may help resolve the remaining question on "how the chain conformation affects the hydrogen bonding interaction between PAL chain units" in the future. Overall, the T_g measurement shown in this paper provides a new experimental observation on thin film T_g of polymers with strong molecular interactions and the tentative explanation may promote our understanding on this issue.

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