

# Distribution of glass transition temperature in multilayered poly(methyl methacrylate) thin film supported on a Si substrate as studied by neutron reflectivity

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We studied the distribution of glass transition temperature ( $T_g$ ) through neutron reflectivity in a poly(methyl methacrylate) (PMMA) thin film supported on a silicon substrate with a five-layered PMMA thin film consisting of deuterated-PMMA and hydrogenated-PMMA. The depth distribution of  $T_g$  was successfully observed in the PMMA thin film. Compared to the previously reported distribution of  $T_g$  in a polystyrene thin film, the presence of a long-range interfacial effect, supposedly caused by an interaction between PMMA and the substrate, is considered to be responsible for the differences in both the distribution of  $T_g$  and the thickness dependence of  $T_g$  in both polymers. Therefore, it is expected that the thickness dependence of  $T_g$  reported for single-layered polymer thin films can, in principle, be understood from the viewpoint of the difference in the depth distribution of  $T_g$ .

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## I. INTRODUCTION

Extensive studies have found that the physical properties of polymer thin films are quite different from those of bulk. The thickness dependence of glass transition temperature ( $T_g$ ) [1–12], thermal expansivity [5], ultraslow relaxation process [13,14], and dewetting even at temperatures below bulk  $T_g$  [15,16] are typical examples for the anomalous physical properties of polymer thin films. Among these, the glass transition in polymer thin films was studied extensively through various methods, including ellipsometry [2–4], x-ray, neutron reflectivity [5–7], positron annihilation lifetime spectroscopy (PALS) [8], dielectric relaxation [9,10], and inelastic neutron scattering (INS) [11,12], because  $T_g$  is directly related to the thermal stability of amorphous polymer thin films. A decrease in  $T_g$  with film thickness was observed for a polystyrene (PS) thin film supported on a silicon (Si) substrate [2–4]. To determine the origin of the decrease in  $T_g$  with film thickness, some researchers have studied the surface  $T_g$  of PS thin films with a scanning probe microscope (SPM) [17,18]. These studies revealed that the surface  $T_g$  of PS thin film was lower than the bulk  $T_g$ , and hence the surface mobile layer was supposedly responsible for the reduction in  $T_g$  with thickness. Compared to evaluation of the surface  $T_g$ , the evaluations of  $T_g$  near the thin film–substrate interface (interfacial  $T_g$ ) have not been as extensive because of experimental difficulties with selective analysis. Despite these experimental difficulties, some researchers have tried to evaluate the interfacial  $T_g$  with time- and space-resolved fluorescence spectroscopy [19,20] or neutron reflectivity (NR) [21]. They reported that the interfacial  $T_g$  was higher than the corresponding bulk  $T_g$ .

Through the evaluation of the surface or interfacial  $T_g$ , meaningful results for  $T_g$  in polymer thin films were obtained; however, direct information on  $T_g$  as a function of distance

from the substrate or free surface was still missing. Therefore, we attempted to evaluate  $T_g$  as a function of distance from the substrate in thin film using multilayered thin films consisting of deuterated PS (d-PS) and hydrogenated PS (h-PS) studied through NR [22]. We observed a continuous change of  $T_g$  from the free surface to the substrate side. Thus, we experimentally clarified the depth distribution of  $T_g$  and heterogeneous dynamics for PS thin film. To correctly interpret the distribution of  $T_g$  in supported PS thin films, the  $T_g$  behavior in both low molecular and polymeric glass formers confined in nanoporous glass, thin film, and so on must be taken into account. Zheng and Simon studied the glass transition behavior of glycerol and propylene glycol confined in nanoporous glass [23] and observed two  $T_g$  values for these glass formers. To explain this anomalous phenomenon, they discussed their results in terms of interfacial effect, wetting, size effect, and so on. A similar complicated situation also exists in polymer thin film systems. Drastic depressions of  $T_g$  with decreasing film thickness were reported for free-standing PS thin films having two free surfaces [24,25]; hence it was previously considered that the free surface was responsible for the enhancement of free-standing polymer thin film dynamics. On the other hand, some experimental results that deviated from the above interpretation have been reported [26–29]. O’Connell and McKenna reported that poly(vinyl acetate) (PVAc) thin films exhibited only weak or no dependence of  $T_g$  on film thickness [26,27] and Sharp and Forrest also reported only a small change in  $T_g$  with a change in film thickness for free-standing PMMA thin films [28]. Another recent interesting topic is the observed absence of an enhanced mobile layer in free-standing poly( $\alpha$ -methylstyrene) (PAMS) thin films [29] despite a reduction of  $T_g$  with film thickness [30]. Hence, it is expected that the free-surface layer is not the only leading factor for describing the observed  $T_g$  or dynamics in free-standing thin films. In the case of a “supported polymer thin film,” the  $T_g$  is apparently determined by competition between the surface and interfacial  $T_g$ ; however, Wang and McKenna reported that the thickness dependence of  $T_g$  for a PS thin film supported on the surface of liquid glycerol was different from that of a PS thin film supported on SiO<sub>2</sub> substrates

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[31]. However, the detailed mechanism for the difference between them is not yet clear. Their result implies that only considering competition between surface  $T_g$  and interfacial  $T_g$  is not necessarily adequate for describing the  $T_g$  in supported polymer thin films. Summarizing the  $T_g$  behavior reported so far for glass formers under nanoconfinement,  $T_g$  is severely influenced by factors such as surface, interfacial effect, size effect, and wetting. In other words, we have not been able to easily specify a dominating factor for  $T_g$  behavior in glass formers under nanoconfinement. Therefore, determining a correct physical interpretation concerning the distribution of  $T_g$  in supported PS thin films is not a trivial task at present. Many more experimental and theoretical approaches are required to consistently reconcile all the reported results for  $T_g$  of glass formers under nanoconfinement. Therefore, we have extended our work to studying the depth distribution of  $T_g$  in other supported polymer thin films.

A reduction of  $T_g$  with thickness is not necessarily a characteristic of polymer thin films. In fact, an increase in  $T_g$  with decreasing film thickness was reported for PMMA thin films supported on Si substrates, in which a strong interaction between PMMA and the substrate existed [2]. So far, no experimental approaches concerning the evaluation of  $T_g$  distribution have been adopted for PMMA thin films supported on Si substrates. If the distribution of  $T_g$  was also observable in PMMA thin films, a clue to understanding the controversial thickness dependence of  $T_g$  in polymer thin films might be obtained by comparing that of multilayered PS thin films.

In this paper, we study the  $T_g$  distribution in a PMMA thin film with a multilayered PMMA thin film consisting of deuterated PMMA (d-PMMA) and hydrogenated PMMA (h-PMMA) through NR and discuss the origin of the difference in thickness dependence of  $T_g$  between them.

## II. EXPERIMENT

The d-PMMA used in the study was atactic PMMA (aPMMA) with a molecular weight ( $M_w$ ) of  $6.07 \times 10^5$  and a molecular weight distribution ( $M_w/M_n$ ) of 1.10, and atactic h-PMMA with a molecular weight ( $M_w$ ) of  $6.31 \times 10^5$  and a molecular weight distribution ( $M_w/M_n$ ) of 1.17. The bulk  $T_g$  values determined through differential scanning calorimetry (DSC) were  $393 \pm 2$  K for both h-PMMA and d-PMMA. We prepared a d-PMMA/h-PMMA/d-PMMA/h-PMMA/d-PMMA five-layered thin film with a  $\sim 200$ -Å-thick component layer. The details of preparation of such a multilayered thin film are given in our previous publication [22]. Here, we summarize the procedure briefly. First, a single d-PMMA layer was directly spin coated onto a 3-in.-diameter Si substrate by spin coating a toluene solution at 2000 rpm and then drying it in a vacuum oven at room temperature for 2 days and then at 343 K for 24 h to remove any residual solvent. For the preparation of the subsequent layers, we used the water-floating method [32,33]. We prepared an h-PMMA layer on a  $100 \times 100$  mm<sup>2</sup> square quartz substrate and the prepared h-PMMA layer was transferred from the quartz substrate onto a water surface and collected on the first d-PMMA layer. The prepared h-PMMA–d-PMMA bilayer thin film was then dried in the vacuum oven through the same drying process described above. By repeating these procedures

four times, we obtained a d-PMMA/h-PMMA/d-PMMA/h-PMMA/d-PMMA five-layered PMMA thin film.

The  $T_g$  values of the component layers are usually determined by using the difference in thermal expansivity between the glassy and molten states; therefore, a negative thermal expansivity [6,7,13] originating from a lack of annealing would be problematic for our study. A negative thermal expansivity has not been reported for PMMA thin films experimentally; however, it is expected that annealing five-layered PMMA thin films at a temperature above the bulk  $T_g$  is indispensable for the evaluation of  $T_g$ , taking into account the experimental analogy reported for PS thin film studies [22]. On the other hand, annealing for too long at a temperature above  $T_g$  causes interdiffusion between the h-PMMA and d-PMMA layers due to the relatively small  $\chi$  parameter of the d-PMMA/h-PMMA blend [34]. We need to determine an optimum annealing condition, considering the balance between negative thermal expansivity and mutual interdiffusion. Referring to a reported root mean square displacement of the center of mass of bulk PMMA [35], the contribution from interdiffusion between the d-PMMA and h-PMMA layers because of annealing at 433 K for 5 min was less than 10 Å after correction for  $M_w$ . Therefore, we adopted this annealing condition for the prepared five-layered PMMA thin film. NR measurements were performed with a MINE-II reflectometer [36] installed at the JRR-3 reactor, Tokai, and the measurements were performed at temperatures ranging from 298 to 433 K in a vacuum cell. To avoid the interdiffusion between the d-PMMA and h-PMMA layers as much as possible, especially at temperatures above the bulk  $T_g$ , we limited the  $Q$  range from 0.009 to  $0.07 \text{ \AA}^{-1}$ .

In addition to an evaluation of the distribution of  $T_g$  in the five-layered PMMA thin film, we evaluated the  $T_g$  of single-layered PMMA thin films as a function of film thickness through both NR and ellipsometry. For NR measurements, we used the MINE-II reflectometer with the same experimental setup and performed the ellipsometry measurements using a spectroscopic ellipsometer (M-2000U, J. A. Woolam, USA) equipped with a homemade temperature-controlled vacuum cell.

## III. RESULTS AND DISCUSSION

Figure 1(a) shows the NR profiles of a single-layered PMMA thin film at temperatures below and above the bulk  $T_g$ . We used a program based on a recursion formula derived by Parratt [37] to analyze the reflectivity profiles. Wallace *et al.* reported that the density of polymer thin films was the same as that of the bulk within a 0.50% experimental error [38]; therefore, we decided to use the value of scattering length density (SLD) of bulk PMMA for fitting the observed reflectivity profiles. A single-layer model seems to describe the observed NR curves well as shown by the solid lines in Fig. 1(a), indicating that a single-layer model is appropriate for describing the experimental results. Figure 1(b) shows a plot of thickness as a function of temperature, and a clear inflection point was observed at approximately 400 K. Using the difference in thermal expansivity between the glassy and molten states, we observed that the  $T_g$  of the single-layered PMMA thin film ( $\sim 187.5$  Å thick) was higher by

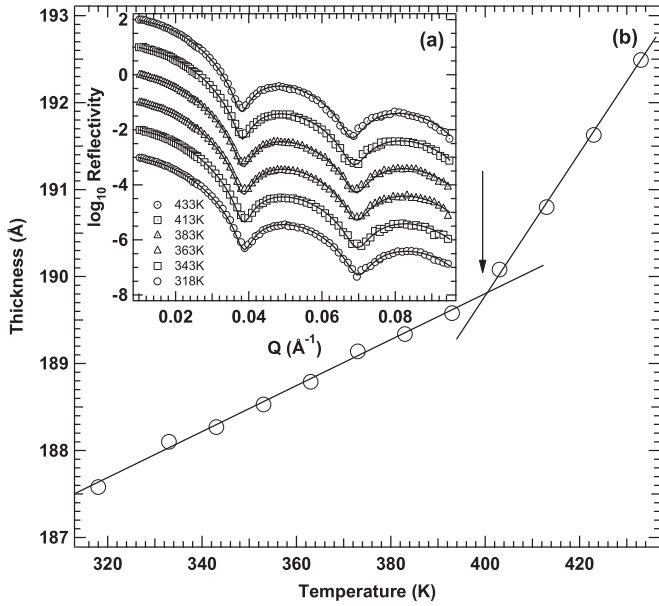


FIG. 1. (a) Neutron reflectivity profiles from a single-layered PMMA thin film observed at several temperatures. Solid lines are the results of a fit using a single-layer model. For clarity, each reflectivity profile is shifted vertically. (b) Temperature dependence of film thickness evaluated from neutron reflectivity for a single-layered PMMA thin film ( $\sim 188$  Å thick). The solid arrow corresponds to the evaluated  $T_g$ .

approximately 6 K as compared to the bulk  $T_g$ . Figure 2 summarizes  $T_g$  as a function of film thickness for single-layered PMMA thin films on Si substrates, showing an increase in  $T_g$  with decreasing film thickness.

Figure 3 shows NR profiles of a five-layered PMMA thin film at temperatures both below and above the bulk  $T_g$ . Clear fringes originating from the multilayered structure were clearly visible even at temperatures above bulk  $T_g$ , indicating that severe interdiffusion did not occur during the annealing process or measurements. We then tried to fit the NR profiles assuming a five-layered model for a five-layered PMMA thin film and found that a five-layered model could describe the NR profiles of the five-layered PMMA thin film. Initially, we paid attention to the temperature dependence of the total film thick-

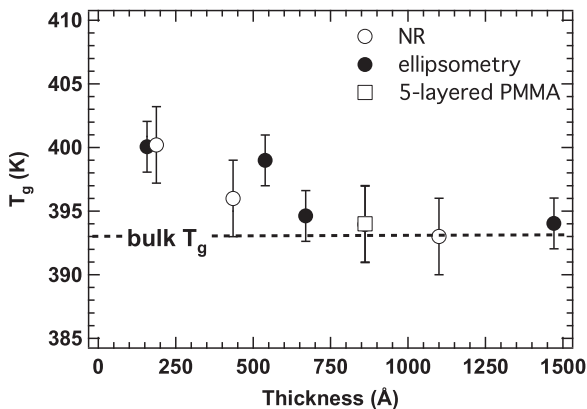


FIG. 2. Thickness dependence of  $T_g$  evaluated from both ellipsometry and neutron reflectivity for a single-layered PMMA thin film.

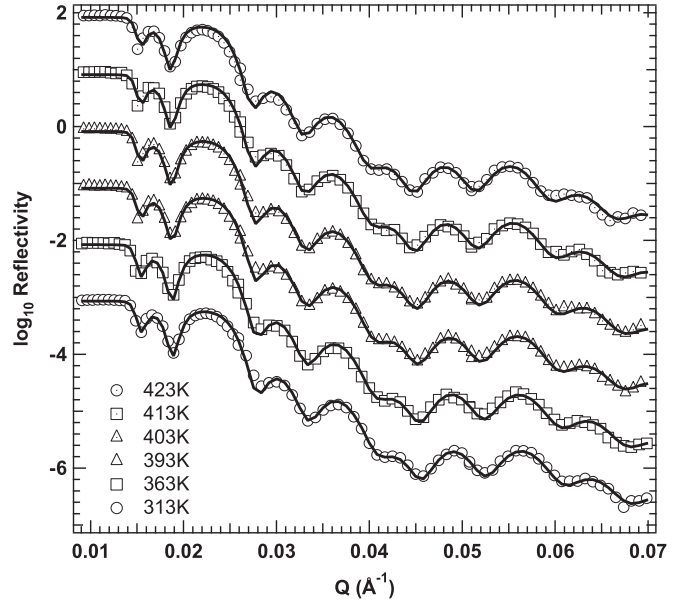


FIG. 3. Neutron reflectivity profiles from a five-layered PMMA thin film at 313, 363, 393, 403, 413, and 423 K. Solid lines are the results of fit using a five-layer model. For clarity, each reflectivity profile is shifted vertically.

ness, as shown in the top panel of Fig. 4. The  $T_g$  evaluated for the total film thickness was  $394 \pm 3$  K and this value coincided with bulk  $T_g$  within experimental error, implying that the total film thickness exhibited bulklike behavior with respect to  $T_g$ .

Subsequently, we focused on the temperature dependence of component layers in the five-layered PMMA thin film. We termed each component layer as the first second, third, fourth, and fifth layers from the substrate to the free surface. The  $T_g$  of the fifth layer (top layer) was 393 K and this value coincided with bulk  $T_g$  within experimental error. As we approached the inside layers (fourth, third, and second layers) of the five-layered PMMA thin film, the evaluated  $T_g$  values shifted to a higher temperature. Only a small thermal expansivity was observed for the first layer (bottom layer), indicating that the  $T_g$  shifted out of the experimental temperature range. Lu *et al.* [39] studied the orientation of polymer chains in a PMMA thin film near the interface between the PMMA thin film and a silver (Ag) substrate through sum-frequency generation (SFG) vibrational spectroscopy. They reported the dominant presence of ester methyl groups in addition to methylene and alpha methyl groups near the interface between the PMMA thin film and the Ag substrate, indicating the orientation of polymer chains at the interface between PMMA thin film and Ag substrate. Hydrogen bonding, in particular, is supposed to exist between the PMMA and native oxide of the Si substrate because of a pair of unshared electrons in the methacrylate side group for the PMMA thin film supported on a Si substrate [2]. Hence, a more oriented structure seems to exist near the interface between the PMMA and Si substrate than for the interface between the PMMA and Ag substrate. This is related to a fairly high  $T_g$  or small thermal expansivity of the first layer (bottom layer) in the five-layered PMMA thin film.

Figure 5(a) shows that a distribution of  $T_g$  similar to that of the PS thin film [22] was present in the five-layered

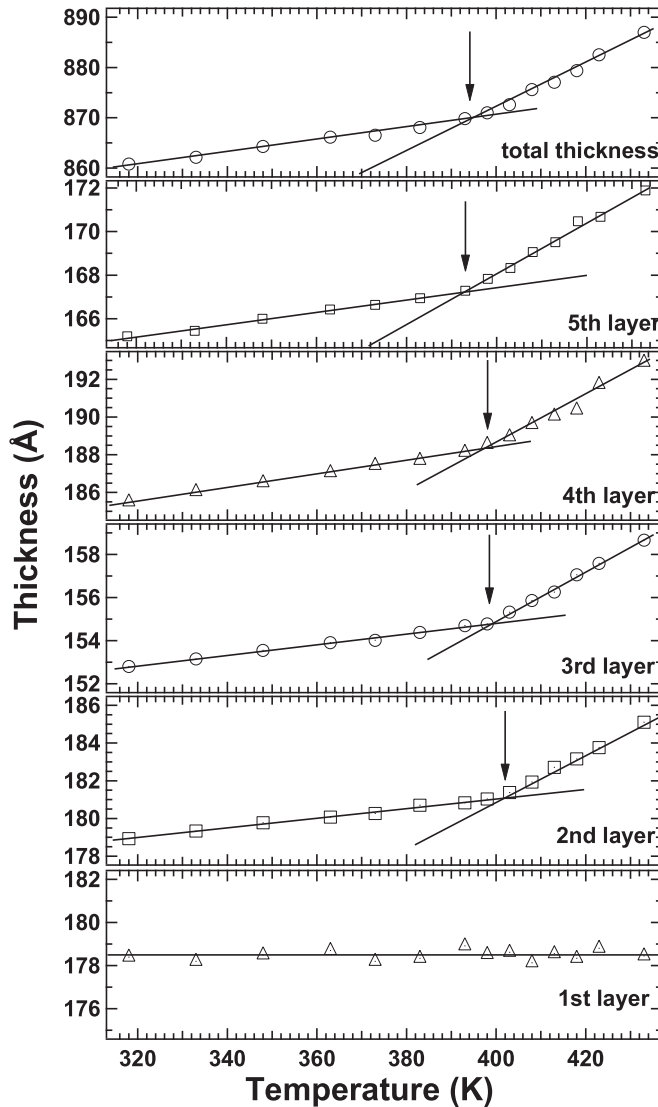


FIG. 4. Temperature dependence of total film thickness, fifth through first layers of a five-layered PMMA thin film. Solid arrows correspond to the evaluated  $T_g$  values.

PMMA thin film. To obtain a clue for the physical origin of the difference in the  $T_g$  thickness dependence, we plotted in Fig. 5(b) the difference between  $T_g$  and the bulk  $T_g$  as a function of distance from the substrate for both the five-layered PMMA and PS thin film. Compared to the bulk  $T_g$ , the observed  $T_g$  was lower for all layers of the five-layered PS except for the first layer. On the other hand, compared to the bulk  $T_g$ , no change in the  $T_g$  was observed even for the fifth layer (free surface) of the five-layered PMMA. Does this mean that no intrinsic surface effect is observable even for the surface  $T_g$  of PMMA thin films? Referring to the reported surface  $T_g$  of a PMMA thin film [2,40] is helpful for answering the above question. For example, a decrease of  $T_g$  with thickness was reported for PMMA thin films supported on an Au-coated Si substrate [2], and this result indirectly supports the enhancement of mobility at the surface region in PMMA thin films. More direct experimental evidences concerning the surface  $T_g$  of PMMA thin films have been reported by Fujii *et al.* [40]. Through lateral force microscopy (LFM), they studied the surface  $T_g$  of syndiotactic

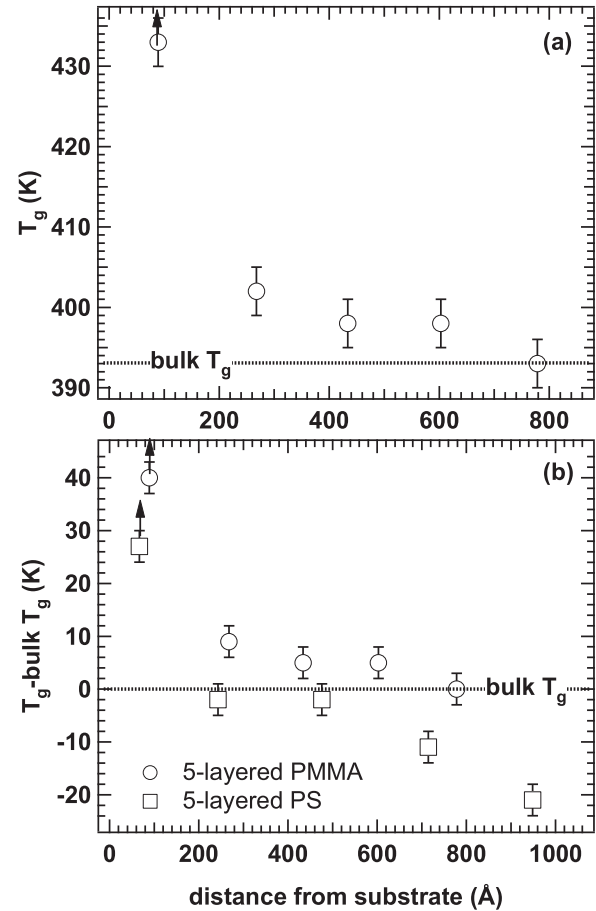


FIG. 5. (a) Distribution of  $T_g$  as a function of distance from the substrate for a five-layered PMMA thin film. (b) Difference between  $T_g$  and bulk  $T_g$  as a function of distance from the substrate for a five-layered PMMA and PS thin film.

and isotactic PMMA thin films ( $\sim 4600$  Å thick) supported on a Si substrate and found that the surface  $T_g$ 's of both PMMAs were lower than the corresponding bulk  $T_g$ . It was inferred that compared to the bulk  $T_g$ , the absence of a change in  $T_g$  at the fifth layer of the five-layered PMMA thin film is the result of competition between surface  $T_g$  and interfacial  $T_g$  in the thin film. Though we cannot deny other possibilities or factors explicitly, as explained in the Introduction, the idea of competition between the surface and interfacial effects seems to be one of the interpretations of the observed distribution of  $T_g$  in the five-layered PMMA thin film [2]. Therefore, in this paper, we attempt to interpret the physical origin of the depth distribution of  $T_g$  in a PMMA thin film in terms of the competition between the surface and interfacial effects.

It is expected that the length scale at which the interfacial effect surpasses the surface effect must be larger than the total film thickness of the five-layered PMMA thin film in the present study. Is it possible to realize such a long-range interfacial effect for PMMA thin films supported on a Si substrate? Through a nanohole relaxation method, Qi *et al.* studied the effect of the substrate on the dynamics of the 2–3-nm free-surface region of PMMA thin film supported on a Si substrate [41] and reported that the free-surface dynamics slowed down for PMMA thin films thinner than  $\sim 1800$  Å.

Similarly, Priestley *et al.* observed a retardation of aging dynamics relative to bulk dynamics at a distance of 1000–2500 Å from the substrate using physical aging measurements of PMMA thin film. They also predicted long-range interactions between the surface dynamics and the substrate [42]. Hence, the long-range interfacial effect observed for PMMA thin films does not seem to be unphysical. Why was such an extremely long-range interfacial effect observed for PMMA thin films supported on a Si substrate? We could not unravel an underlying physical origin of the long-range interfacial effect for a PMMA thin film supported on a Si substrate adequately; however, molecular dynamics (MD) simulation approaches seem to be helpful for interpreting our results. Baljon *et al.* [43] performed MD simulations of a polymer thin film supported on an interacting substrate, which is a system similar to a PMMA thin film supported on a Si substrate, using a bead-spring model. Slow, immobile beads were found to exist throughout the film with the probability of their occurrence decreasing with the distance from the substrate; the immobile beads are located near the free surface to cause them to percolate along the depth direction even at the bulk  $T_g$ . Such a percolation of the immobile component in the entire polymer thin film seems to realize the long-range interfacial effect, which suppressed the surface effect of the PMMA thin film. As a result, the contribution of the interfacial effect becomes dominant with decreasing film thickness, resulting in an increase of  $T_g$  for PMMA thin films with decreasing film thickness. On the other hand, in principle, there exists no strong interaction between the PS and Si substrate. In this situation, a percolation of the immobile component through the entire film is assumed to hardly ever occur, resulting in the enhancement of the dynamics with decreasing thickness due to the absence of a long-range interfacial effect in the PS thin film. In other words, the presence or absence of a long-range interfacial effect seems to be related to the difference in the depth distribution of  $T_g$  for PS and PMMA thin films. As a consequence, it is expected that the thickness dependence of  $T_g$  reported for various single-layered polymer thin films is, in principle, understood from the viewpoint of the difference in the depth distribution of  $T_g$  in thin films.

Recently, highly stable glasses have been prepared from low molecular glass-forming materials through the vapor deposition method. Surface dynamics measurements on these prepared glasses were performed through various methods [44, 45]. For example, Swallen *et al.* studied the surface dynamics of glassy 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene through NR [44] and observed an enhancement of dynamics at the surface region. Interestingly, the thickness of the surface layer was almost comparable to that of PS, evaluated through a photobleaching technique [29]. It is thought that both polymeric and low molecular weight glass-forming materials would exhibit a similar tendency with respect to the dynamics near the free surface. It is also expected that the distribution of  $T_g$ , which has been reported for polymer thin film systems only, might be observable for low molecular weight glass formers as well.

#### IV. SUMMARY

In this work, we studied the distribution of  $T_g$  in a PMMA thin film supported on a Si substrate with a five-layered PMMA thin film consisting of d-PMMA and h-PMMA by neutron reflectivity. We succeeded in observing the distribution of  $T_g$  in the PMMA thin film as well as a PS thin film. In order to understand a completely different thickness dependence of  $T_g$  observed for both PMMA and PS thin films, distributions of  $T_g$  in both polymers are reconsidered. Interestingly, no change in  $T_g$  compared to bulk  $T_g$  was observed for the PMMA thin film even at the free surface. Furthermore, a long-range interfacial effect, which was supposed to be caused by an interaction between the PMMA film and the substrate, seems to be related to the fact that there was no enhancement in the dynamics at the free surface of the PMMA thin film. The presence of a long-range interfacial effect in PMMA thin film is responsible for the difference from the distribution of  $T_g$  in the PS thin film, in which the long-range interfacial effect is not observable, resulting in a difference in the thickness dependence of  $T_g$  between the polymers. Therefore, it is expected that the thickness dependence of  $T_g$  reported so far for various polymer thin films was understood from the viewpoint of the difference in distributions of  $T_g$  between the thin films.

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