Distribution of glass transition temperatures T_g in polystyrene thin films as revealed by low-energy muon spin relaxation: A comparison with neutron reflectivity results

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In a previous paper [Phys. Rev. E **83**, 021801 (2011)] we performed neutron reflectivity (NR) measurements on a five-layer polystyrene (PS) thin film consisting of alternatively stacked deuterated polystyrene (dPS) and hydrogenated polystyrene (hPS) layers (dPS/hPS/dPS/hPS/dPS, ~ 100 nm thick) on a Si substrate to reveal the distribution of T_g along the depth direction. Information on the T_g distribution is very useful to understand the interesting but unusual properties of polymer thin films. However, one problem that we have to clarify is if there are effects of deuterium labeling on T_g or not. To tackle the problem we performed low-energy muon spin relaxation (μ SR) measurements on the above-mentioned deuterium-labeled five-layer PS thin film as well as dPS and hPS single-layer thin films ~ 100 nm thick as a function of muon implantation energy. It was found that the deuterium labeling had no significant effects on the T_g distribution, guaranteeing that we can safely discuss the unusual thin film properties based on the T_g distribution revealed by NR on the deuterium-labeled thin films. In addition, the μ SR result suggested that the higher T_g near the Si substrate is due to the strong orientation of phenyl rings.

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I. INTRODUCTION

Properties of polymer thin films are very different from those of bulk and are essential for industrial applications, such as adhesives, lubricants, coating, and so on. Hence, extensive studies on polymer thin films have been performed for the past two decades [1–29] to reveal interesting but unusual properties of polymer thin films. One of the most interesting findings is the thickness dependence of the glass transition temperature T_g revealed by various experimental techniques, such as ellipsometry [5–7], x-ray or neutron reflectivity [8–10], positron annihilation lifetime spectroscopy [11], dielectric relaxation [12,13], and inelastic neutron scattering [14,15]. Nowadays, it is well established that T_g of polystyrene (PS) thin films on a Si substrate decreases with film thickness. The decrease in T_g has been often assigned to the high mobility of the surface layer. On the other hand, T_g increases with decreasing the film thickness in the case of poly(methylmethacrylate) (PMMA) on a Si substrate [5]. This must be due to the interfacial hard layer near the substrate because of strong interactions between the PMMA and the Si surface. These results as well as recent intensive studies [22–29] suggest that polymer thin films have very heterogeneous dynamics or structure along the depth direction, consisting of a surface mobile layer, a middle bulklike layer, and an interfacial hard layer.

We have performed neutron reflectivity measurements on five-layer PS and PMMA thin films consisting of alternatively stacked deuterated PS (dPS) and hydrogenated PS (hPS) (or PMMA) layers (dPS/hPS/dPS/hPS/dPS) [27] (or dPMMA/hPMMA/dPMMA/hPMMA/dPMMA) [28] to evaluate the heterogeneous dynamics of thin films directly. In these experiments, we have evaluated the thickness of each layer

as a function of temperature and estimated T_g of each layer. Very clear distributions of T_g were observed along the depth direction, showing the heterogeneous dynamics of polymer thin films. A similar distribution of T_g was reported by Ellison and Torkelson [29] using a fluorescence labeling method. We believe that these data surely show the heterogeneous dynamics or wide distribution of T_g in polymer thin films. However, there are some problems in these experiments. (i) We have to prepare multilayered thin films. For neutron reflectivity (NR) measurements, for example, we have to prepare alternatively stacked thin films of deuterated and hydrogenated polymers. In the case of the fluorescence labeling method, they have to prepare stacked films of fluorescence molecule-labeled and nonlabeled layers. It is very hard to prepare a multilayered film thinner than 5 nm, suggesting a thickness limit for experiments. (ii) The second is a mixing problem. Once they (dPS and hPS layers or labeled and nonlabeled layers) are mixed up, we cannot estimate the T_g of each layer, but the interface of neighboring layers should be completely mixed up to avoid interfacial effects. The control of mixing is not so easy and is hard to confirm. (iii) Strictly speaking, nobody knows if there are any effects of labeling by D/H or by fluorescence molecules on T_g . We have to assume that the effects are negligible in the discussion on the T_g distribution. In order to overcome the problems, we have to see the distribution of T_g in polymer thin films without any labeling (labeling by D/H or fluorescence molecules). At the moment, low-energy muon (LEM) experiments on polymer thin films are the only method to realize this experiment. In a pioneering work Pratt *et al.* [30] showed that the LE muon spin-relaxation (μ SR) technique could detect the depth dependence of T_g in a PS film. The μ SR depolarization rate λ was found to be highly sensitive to the dynamics of the polymer, and λ provided a local probe of changes in the dynamical correlation time around the glass transition. The stopping distances of the LEM into a polymer thin film were controlled by tuning the

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energy of the LEM from 0.5 to 4.5 keV. Finally, they have preliminarily evaluated the depth dependence of T_g in a PS thin film from the spin-relaxation rate as a function of muon implantation energy although their experiment was zero-field μ SR. Recently, McKenzie *et al.* [31] performed β -detected nuclear spin-relaxation (β -NMR) measurements to probe the depth dependence of molecular dynamics in deuterated polystyrene thin films without any labeling. Their results clearly showed direct evidence for a region near the free surface with enhanced molecular dynamics compared with the bulk.

In this experiment, we have performed longitudinal-field μ SR (LF- μ SR) experiments on a five-layer dPS/hPS/dPS/hPS/dPS thin film, a single-layer dPS thin film, and a single-layer hPS thin film to measure the distribution of T_g . All the films were prepared on a Si substrate and were ~ 100 nm thick. The results are compared with neutron reflectivity results [26,27] to see the effects of D/H labeling and the characteristic features of the μ SR measurements.

II. EXPERIMENT

We used hPS with a molecular weight M_w of 769 000 and molecular weight distributions M_w/M_n of 1.18 and dPS with a molecular weight M_w of 730 800 and molecular weight distributions M_w/M_n of 1.08. The bulk T_g 's determined by differential scanning calorimetry were 103°C for both hPS and dPS. We prepared a five-layer dPS/hPS/dPS/hPS/dPS thin film with each component layer ~ 20 nm thick. Although the preparation of five-layer thin films has been reported elsewhere [27], we describe the preparation method briefly. First we prepared a dPS layer onto a 4-in.-diameter Si substrate with a hydrophilic surface by spin coating toluene solutions at 2000 rpm and dried in a vacuum oven at 343 K for 24 h after drying in a vacuum oven at room temperature for 2 days to remove the residual solvent. Second, we prepared a hPS layer using a water-floating method. A subsequent layer in multilayered thin films (hPS layer) was transferred from the 4-in.-diam Si substrate onto a water surface and collected onto the first dPS layer, which was already prepared on a 2-cm² Si substrate. The collected hPS/dPS bilayer thin film was then dried in the vacuum oven with the same drying process as described above. Repeating the same procedures, we could finally obtain a five-layer dPS/hPS/dPS/hPS/dPS thin film. It is well known that annealing thin films at above bulk T_g was indispensable for a reliable evaluation of the distribution of T_g by neutron reflectivity. On the other hand, annealing for too long above T_g causes the hPS layers and dPS layers to mix up due to interdiffusion, and evaluation of T_g at different layers would be impossible as a result. Considering the balance between the structural relaxation and the mutual interdiffusion, we annealed the thin films at 130°C for 5 min [27]. In this experiment we also used the same annealing condition for the muon measurements to compare the results with the NR ones.

The μ SR measurements were performed at the Swiss Muon Source S μ S at the Paul Scherrer Institut, Switzerland using the low-energy μ SR facility LEM at the μ E4 muon beam line [32,33]. Polarized low-energy μ^+ 's with keV energy are generated by a moderation technique where a high intensity 4-MeV μ^+ beam ($>10^8 \mu^+/\text{s}$) is slowed down in a solid ~ 200 nm thin Ar film with an ~ 10 nm N₂ capping layer,

FIG. 1. (Color online) Calculated normalized stopping distance distribution $S(l)$ [39] for muons with energies of 1–4 keV in PS. l is the stopping distance from the surface.

deposited on a patterned Ag substrate held at 10 K [34]. Epithermal muons with a mean energy of ~ 15 eV are emitted into vacuum on the downstream side of the moderator with a conversion efficiency of 10^{-5} – 10^{-4} [35]. The μ^+ 's are then accelerated electrostatically up to 20 keV and transported to the low-energy μ SR spectrometer by use of electrostatic elements. The final muon implantation energy is adjusted by applying a positive bias to the sample. In our case, we used implantation energies between 1 and 4 keV, corresponding to mean implantation depths of 15 and 55 nm, respectively (Fig. 1). Calculated normalized stopping distance distribution $S(l)$ [36] is shown in Fig. 1 for muons with energies of 1–4 keV in PS. Plastic scintillators outside the LEM vacuum vessel are surrounding the sample to detect the positrons from the muon decay. This allows for measuring of the time evolution of the muon spin polarization in the sample due to the anisotropic muon decay. Using a static spin rotator in the LEM beam line [37] the muon spin was rotated by 90° to be aligned parallel to an applied magnetic field (parallel to the sample normal) to be able to carry out so-called LF- μ SR measurements, which are well suited to study dynamical properties. The measured decay asymmetry $A_{\text{LF}}(t)$ as a function of time t in positron detectors located upstream and downstream of the sample is proportional to the polarization of the muon ensemble. The presence of dynamics may cause relaxation of the muon spin polarization in the radical state, resulting in an exponentially decaying asymmetry $A_{\text{LF}}(t)$ with a depolarization rate of $\lambda_{\text{LF}} \sim \Delta^2 \{ \nu / [\nu^2 + \Delta^2 + (\omega_e + \omega_\mu)^2] \}$, where $\Delta \sim 20$ MHz is the electron-muon dipolar coupling in the muoniated radical in PS, ν is the inverse of the dynamic correlation time, and ω_e and ω_μ are the respective Larmor frequencies of the electron and the muon [38,39].

In PS more than 50% of the implanted muons form muonium (hydrogenlike bound state of a μ^+ with an e^-), which reacts with the phenyl ring in the polymer to form a muoniated radical state, which serves as a sensitive probe of polymer dynamics [30,38]. The glass transition temperature T_g

FIG. 2. (Color online) Observed decay asymmetry $A_{LF}(t)$ for a five-layer dPS/hPS/dPS/hPS/dPS thin film ~ 100 nm thick at 40, 70, 110, and 130 °C for muon implantation energy E_i of 4 keV in a longitudinal field of 85 G. Each asymmetry is vertically shifted by 0.08. Solid lines are the results of fits with a single exponential function.

where the dynamical correlation time of the polymer rapidly changes is detected by a kink in the temperature dependence of λ_{LF} .

The magnetic LF was fixed at 85 G, and the measurements on the thin films were performed in a temperature range of 40°–130 °C, covering the bulk glass transition temperature of $T_g = 103$ °C.

III. RESULTS AND DISCUSSION

The observed asymmetry $A_{LF}(t)$ is shown for the five-layer thin film at 40, 70, 110, and 130 °C below and above the bulk T_g for muon implantation energy of 4 keV in Fig. 2. The data points are rather scattered, and it is not so easy to extract the systematic change in the relaxation rate with temperature. We assumed a single exponential function in Eq. (1) rather than a stretched exponential function. This will be described later,

$$A_{LF}(t) = A_R \exp(-\lambda_{LF}t) + A_D, \quad (1)$$

where A_R , λ_{LF} , and A_D are the asymmetry of the single exponential decay, its relaxation rate, and the so-called “diamagnetic” fraction, respectively. We first tried the so-called global fits where we assume that A_R and A_D are the same for all temperatures at a given implantation energy and let only the relaxation rate λ_{LF} be a free parameter for each individual run. This seems to work well for the 4 keV data but not for the 1 keV data. Then, we fitted the single upstream

or downstream histograms directly where the background of each decay histogram is fitted. This procedure seems to work better for both the 4 keV and the 1 keV data to estimate the A_R and A_D for each implantation energy. Then, we fitted all the data of the five-layer thin film and single-layer dPS and hPS thin films with the estimated A_R and A_D .

Note that we also tried to fit a stretched exponential function $A_{LF}(t) = A_R \exp[-(\lambda_{LF}t)^\beta] + A_D$, ($0 < \beta < 1$) to the decay curves because a wide distribution of the relaxation rates is expected: Our system is a glass-forming material which usually has a wide distribution of dynamic correlation times, and contributions of both muonium-forming and non-muonium-forming muons and muons in the ortho-, meta-, or parapositions are expected, resulting in a wide distribution of the relaxation rate. However, the fitting parameters (λ_{LF} and β) did not show any systematic change with temperature. It is expected that the emperature dependence of the relaxation rate λ_{LF} must be smooth (except at T_g) from many experimental data on polymer thin films [40]. It was found that the single exponential function fit gave more systematic changes in the parameter (λ) with temperature than the stretched exponential fit. This is because the stretched exponential function is more flexible (more freedom in the function) than the single exponential function. In this paper, we are mainly focusing on the glass transition temperature T_g as a function of the muon energy (or the stopping depth). For this purpose we need a smooth temperature dependence of the relaxation rate (except at T_g) rather than the shape of the decay function (or the decay mechanism). Therefore, we employed the results of the single exponential function in this paper. We also tried the fits in three time ranges: 0–6, 0–8, and 0–10 μ s. The most systematic change in λ_{LF} with temperature was obtained for the time range of 0–6 μ s. This is due to the very low counting statistics in the time range of 6–10 μ s. We then employed the results of a single exponential function fit with the fixed A_R and A_D in the time range of 0–6 μ s. Examples of the fits are shown as solid curves in Fig. 2.

The relaxation rates λ_{LF} evaluated from the fits are plotted in Fig. 3 for the five-layer thin film as functions of temperature at the muon implantation energies of 1–4 keV. The temperature dependence of the relaxation rate λ_{LF} shows a kink at a certain temperature for each implantation energy, demonstrating that λ_{LF} can detect the glass transition T_g . The evaluated T_g 's are 83 ± 4 , 87 ± 3 , 97 ± 3 , and 103 ± 3 °C for the muon implantation energies of 1–4 keV, respectively, for the five-layer thin film. As the muon implantation energy increases the stopping distance increases, and hence the higher energy muons see the dynamics at a deeper position in the thin film. The results clearly show that T_g near the surface is the lowest and increases with approaching the Si substrate.

It is also clear that the temperature dependence of the relaxation rate becomes steeper with increasing muon implantation energy below and above the glass transition temperature T_g . The reason is not clear at the moment. One possibility is that the fluctuation rate of the PS motion (the inverse of the dynamic correlation time) has different temperature dependences at different depths. If this assumption is correct closest to the surface at the lowest implantation energy, the fluctuation rate would increase less fast as a function of temperature. However, it is impossible to conclude this with the present data.

FIG. 3. (Color online) The relaxation rates λ_{LF} evaluated from the fits for the five-layer thin film as a function of temperature at muon energies of 1–4 keV.

We also plotted the relaxation rate λ_{LF} in an Arrhenius form to discuss the polymer motions affecting the muon relaxation around the glass transition although the plots are not shown here. It seems that the Arrhenius plot also works to describe the temperature dependence of the relaxation rate within experimental error. At the moment, unfortunately, it is hard to judge which is better, the linear plot in Fig. 3 or the Arrhenius plot because of the large experimental errors. In such a situation, it is hard to discuss what type of motion is related to the muon relaxation. However we would like to point out a possible motion. Generally speaking, the glass transition is dominated by the so-called α process as shown in many publications [41]. Therefore, we believe that muon relaxation is dominated by the α process near T_g . However, the motional correlation time of the α process at T_g (~ 100 s) is much slower than the muon lifetime. It seems hard for muons to detect the α process. As is well known, however, the α process has a very wide distribution in the motional correlation time [41]. Hence, the muons are sensitive to the high frequency tail of the α process, which must be related to conformation transitions in polymers as revealed in quasielastic neutron scattering [41].

We have calculated the normalized stopping distance distribution $S(l)$ for muon implantation energies of 1–4 keV in PS, which is shown in Fig. 1. Here, l is the stopping distance from the surface. The average stopping distance $\langle l \rangle$ is 17.5, 30.2, 42.5 and 54.0 nm for 1–4 keV, respectively. The distance resolution evaluated by the full half-width of the

FIG. 4. T_g distribution of the five-layer dPS/hPS/dPS/hPS/dP thin film ~ 100 nm thick, evaluated from the neutron reflectivity measurement [27].

distribution Δl is ~ 22 nm for every muon implantation energy. In a previous paper [27] we have evaluated the T_g distribution of the five-layer dPS/hPS/dPS/hPS/dP thin film at ~ 100 nm thick using the NR technique, which is reproduced in Fig. 4. As seen in the figure, T_g at ~ 10 nm from the surface is 82°C , which is lower than the bulk T_g by $\sim 20^\circ\text{C}$ and increases with approaching the interface, and finally T_g at ~ 100 nm near the Si substrate is 130°C . The result is qualitatively very similar with the muon result. In the experiment, each component layer is ~ 20 nm thick, giving a distance resolution of ~ 20 nm. The distance resolution (~ 20 nm) is almost identical with that in the μSR measurement. Using the stopping distance distribution in Fig. 1 and the T_g distribution by NR in Fig. 4, we have calculated the average neutron glass transition temperature $\langle T_g \rangle_{\text{ME}}$ at the corresponding muon implantation energy through Eq. (2),

$$\langle T_g \rangle_{\text{ME}} = \int T_g(l) S(l) dl. \quad (2)$$

The average neutron $\langle T_g \rangle_{\text{ME}}$ is plotted in Fig. 5 as a function of muon implantation energy where the muon T_g evaluated in this experiment is also plotted. The muon T_g is almost identical with the average neutron $\langle T_g \rangle_{\text{ME}}$ near the surface at 1 and 2 keV. On the other hand, the muon T_g is higher than the neutron $\langle T_g \rangle_{\text{ME}}$ at 3 and 4 keV, and the difference increases with the implantation energy. As seen in the muon implantation energy distribution in Fig. 1, the energy tail in the distribution at 4 keV cannot reach 80 nm, showing the average neutron $\langle T_g \rangle_{\text{ME}}$ is not affected by the high T_g ($\sim 130^\circ\text{C}$) at ~ 100 nm near the Si substrate in the averaging procedure. As mentioned in the experimental part, more than 50% of the implanted muons form muonium in PS, which reacts with the phenyl ring in the polymer to form a muoniated radical state [30,38], suggesting that the μSR measurement is sensitive to the phenyl ring motion. It is reported [26,29] that the T_g of PS thin films near the Si substrate is higher than the bulk

FIG. 5. (Color online) The average neutron $\langle T_g \rangle_{\text{ME}}$ ($\circ$), the muon T_g evaluated ($\blacksquare$) for the five-layer dPS/hPS/dPS/hPS/dPS thin film, and the muon T_g for the single-layer hPS ($\times$) and dPS ($\triangle$) thin films, a function of the muon implantation energy.

T_g and the effects of the substrate on T_g last up to ~ 60 nm from the substrate although the interaction between PS and Si is negligibly small. The reason for the higher T_g near the substrate is not clarified at the moment. However, one of the possible reasons is strong orientation of phenyl rings on and near the Si substrate [42,43]. In the μ SR measurement of PS thin films we see mainly the motion of phenyl rings rather than the motion of main chains. If the strong orientation of phenyl rings near the substrate is the origin of the high T_g and lasts up to ~ 60 nm [26,29] the muon T_g would be higher than the neutron T_g near the substrate, corresponding to the present observation.

We also carried out similar LF- μ SR measurements on single dPS and hPS thin films ~ 100 nm thick at muon implantation energies of 1 and 4 keV to see the effects of deuterium labeling. The temperature dependences of λ_{LF} for dPS and hPS thin films at 1 and 4 keV are shown in Figs. 6(a)–6(d), respectively. Similar to the five-layer data, we can clearly observe the glass transition temperature T_g for the single-layer thin films. It is noted that the relaxation rate is much larger in the hPS thin film than in the dPS. It is well known that the magnetic moment of the proton is larger than the one of the deuteron. However, this effect is valid only for zero-field, transverse-field, and low longitudinal-field measurements where the depolarization is caused by nuclear dipolar fields. In the LF geometry at 85 G the nuclear dipoles should be decoupled. Hence, we expect that the observed changes in λ_{LF} as a function of temperature are due to the onset of fluctuations in the electron-muon dipolar coupling, which should not depend on the nuclear moment. Deuterons are two times heavier than protons, and hence the larger relaxation rate of hPS compared to dPS above T_g must be due to faster fluctuations in hPS. On the other hand, the detected T_g 's are identical between hPS and dPS within the experimental error, suggesting that the muon observes local fluctuations.

FIG. 6. (Color online) The relaxation rates λ_{LF} evaluated for the single-layer (a) and (b) hPS and (c) and (d) dPS thin films as a function of temperature at muon energies of 1 and 4 keV.

The muon T_g 's for the single-layer hPS and dPS thin films at 1 and 4 keV are plotted in Fig. 5. The T_g 's are the same as those of the five-layer thin film within the experimental error, suggesting that the deuterium labeling in the five-layer thin film has no significant effects on the T_g distribution in thin films. It is noted that the T_g 's for the single-layer hPS and dPS thin films at 4 keV are higher than the averaged neutron $\langle T_g \rangle_{\text{ME}}$, supporting again the idea that higher T_g near the substrate at 4 keV is probably due to the strong orientation of phenyl rings because implanted muons react with phenyl rings and are sensitive to the dynamics of the phenyl rings [30,38].

Finally we would like to discuss the distribution of T_g in thin films. As many researchers suggested, the lower T_g near the free surface could be attributed to a mobile surface layer. To explain the mobile layer near the surface, several models have been proposed [44–47] which deal with surface mobility or surface glass transition. However, these studies are not able to predict the T_g distribution of thin films on the substrate, which was studied in this paper. In the thin films on the substrate the

dynamics is affected not only by the surface, but also by the substrate. A very hard layer (or dead layer) at the interface to the substrate was also reported in many papers [11,22–27], which may be due to strong interactions between the substrate and the polymers and/or strong orientation of polymers near the substrate. The surface and interface interactions were taken into account to describe the thickness dependence of the T_g of thin films through the simple phenomenological continuous multilayer model [48]. In this model, the T_g distribution in thin polymer films was derived from the dependence of T_g on the total film thickness, which is an indirect method. As shown here, we are now able to evaluate the T_g distribution in polymer thin films without any labeling. Studies along this direction will give very precise information on the T_g distribution and stimulate theoretical works.

IV. CONCLUDING REMARKS

In this paper we have performed LF- μ SR experiments on a ~ 100 nm five-layer dPS/hPS/dPS/hPS/dPS thin film as well as on ~ 100 nm single-layer dPS and hPS thin films as a function of muon implantation energy from 1 to 4 keV to measure the distribution of glass transition temperature T_g without any labeling in the thin films. We have clearly detected T_g from the temperature dependence of the μ SR relaxation rate λ_{LF} at each muon implantation energy. The

results suggest that T_g is the lowest at the surface and increases on approaching the Si substrate, similar to the reported data by neutron reflectivity. The average neutron $\langle T_g \rangle_{ME}$ was calculated based on the T_g distribution evaluated from the neutron reflectivity measurements at each muon implantation energy and compared with the muon T_g . It was found that the muon T_g agreed with the average neutron $\langle T_g \rangle_{ME}$ at low muon energy at 1 and 2 keV, whereas the muon T_g is higher than the average neutron $\langle T_g \rangle_{ME}$ at 3 and 4 keV, suggesting that the muon mainly sees the motion of strongly oriented phenyl rings near the Si substrate. We also found that the deuterium-labeled five-layer thin film has almost the same T_g distribution compared to the single-layer hPS and dPS films, showing that the effects of deuterium labeling have no significant effect on the T_g distribution in polymer thin films.

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