Experimental investigation of the glass transition of polystyrene thin films in a broad frequency range

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(Received 1 October 2017; published 10 January 2018)

In this study, we investigate the α process of a polystyrene thin film using inelastic neutron scattering (INS), dielectric relaxation spectroscopy (DRS), and thermal expansion spectroscopy (TES). The DRS and TES measurements exhibited a decrease in glass transition temperature (T_g) with film thickness. On the other hand, an increase in T_g was observed in INS studies. In order to interpret this contradiction, we investigated the temperature dependence of the peak frequency (f_m) of the α process probed by DRS and TES. The experiments revealed an increase in the peak frequency (f_m) with decreasing film thickness in the frequency region. This observation is consistent with the observed decrease in T_g with thickness. Interestingly, the increase in T_g with film thickness was confirmed by fitting the temperature dependence measurements of the peak frequency with the Vogel-Fulcher-Tammann equation, within the frequency region probed by INS. The discrepancy between INS and DRS or TES descriptions of the α process is likely to be attributed to a decrease in the apparent activation energy with film thickness and reduced mobility, due to the impenetrable wall effect.

DOI: 10.1103/PhysRevE.97.012501

I. INTRODUCTION

Polymer thin films are employed in various industrial applications such as lubrication, coating, and lithography. The increased demand in advanced applications requires a reduction in the polymer thin film thickness. The glass transition temperature (T_g) is one of the most significant parameters used to characterize the thermal properties of amorphous materials. Recent studies have revealed that the T_g of low molecular weight and polymeric glass formers is severely affected by spatial confinements [1]. Polymer thin film is a representative example of polymeric glass formers under spatial confinement. In a study carried out by Keddie *et al.*, where the thickness dependence of the physical properties of polystyrene (PS) thin films supported on silicon (Si) substrates was investigated using ellipsometry, it was found that the T_g of the thin films was lower than that of the corresponding bulk systems [2]. After the pioneering work of Keddie *et al.*, several research groups extensively studied the T_g of supported PS thin films using various methods [3–10], supporting that T_g decreases with decreasing film thickness. The decrease was attributed to the presence of a mobile surface layer, which was directly confirmed by Kajiyama *et al.* employing scanning probe microscopy (SPM) [11]. Recently the T_g at the interface between substrate and polymer thin film (interfacial T_g) has been determined through advanced experimental techniques such as fluorescence spectroscopy [12] and neutron reflectivity [13]. It was reported that the interfacial T_g was higher than its corresponding bulk value. The unusual behavior of T_g in the interfacial region suggests that the heterogeneous structure is one of the possible factors controlling T_g in polymer thin films, though other factors [14] like wetting and size effects cannot be discarded.

The glass transition is a dynamic transition and not a thermodynamic one. The study of dynamic is advantageous because it can provide important insights into the glass transition mechanisms in polymer thin films. Several state-of-the-art techniques have been previously used in dynamic studies to probe the glass transition response in thin films. Examples of these techniques are dielectric relaxation spectroscopy (DRS) [7–10], x-ray photon correlation spectroscopy [15], SPM [11], and inelastic neutron scattering (INS) [16–19]. However, it is still unclear which mechanism is responsible to explain the glass transition observations. Various techniques can be used to study the α process, which is linked to the glass transition temperature. Specifically, for the bulk amorphous polymers the α process can be investigated within the frequency range between 10^{-3} Hz and 10^{10} Hz [20] to construct relaxation time maps for amorphous polymers. Therefore, a thorough understanding of the α process in polymer thin films requires the building of the corresponding relaxation time map. The dielectric loss signal from PS has been shown to be quite small due to its low polarity [8]. In turn, the dielectric loss signal is significantly weak, predominantly at high- and low-frequency ranges. The coverage of the broad frequency range of PS thin films using the DRS technique is practically inaccessible.

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However, a combination of spectroscopic techniques can be applied to overcome this obstacle. Such techniques include thermal expansion spectroscopy (TES), which can cover the frequency range from 10^{-1} to 10^{-3} Hz (low-frequency range), DRS spectroscopy, which can cover the frequency range from 10^1 to 10^4 Hz (intermediate-frequency range), and INS (high-frequency range) spectroscopy to study the α process of PS thin film covering a broad frequency range.

II. EXPERIMENTAL

PS samples with molecular weight $M_w = 2.9 \times 10^5$ g/mol and molecular weight distribution $M_w/M_n = 1.06$ were considered. Here M_w and M_n are the weight average and number average of the molecular weight, respectively, for the INS and ellipsometric measurements. Initially, the PS thin films for the INS measurements were prepared by spin-coating toluene solutions on flat glass plates. Thereafter, the prepared thin films were removed from glass plates to water surface. Subsequently, the thin films were collected onto a 15 μm-thick Al foil and annealed at 413 K for 12 h under vacuum, after being annealed at room temperature for two days. The PS thin films for the ellipsometric measurements were prepared by spin-coating toluene solutions on Al-deposited Si substrates. Post-annealing was followed at 413 K for 12 h under vacuum, again after being annealed at room temperature for two days. PS samples with $M_w = 2.8 \times 10^5$ g/mol and 1.8×10^6 g/mol, as well as samples satisfying the conditions $M_w/M_n = 1.03$, were used for both DRS and TES measurements.

The PS thin films employed in these measurements were directly prepared by spin coating on an Al-deposited glass substrate. After annealing at 343 K in vacuum for several days to remove any residual solvent, an Al layer was directly deposited onto the polystyrene-coated surface to serve as an upper electrode for the DRS and TES measurements. Prior to the measurements, the PS thin films were annealed at 383 K for at least 30 min because any residual solvent would affect the thermal properties of the polymer thin film. Zhang *et al.* [21] studied the effect of residual solvent in polymer thin films using neutron reflectivity and IR spectroscopy. They reported that PS thin films annealed at temperature below bulk T_g exhibited no trace of residual toluene inside the thin film. Since the annealing temperature was kept well above the bulk T_g, the contribution of residual solvent was considered negligible in present PS thin films.

INS measurements with energy resolutions of 3 μeV and ~13 μeV were performed using the DNA high-energy resolution near-backscattering spectrometer [22] in the Material and Life Science Experimental Facility (MLF) at J-PARC, Tokai, Japan. In order to broaden the frequency range probed by INS, we also included the results of previous INS measurements with energy resolutions of 0.8 μeV and 25 μeV [18]. DRS and TES measurements were performed with an LCR (inductance-capacitance-resistance) HP4284A meter. Details on the experimental set-up and experimental conditions can be found in our previous publications [7,8].

III. RESULTS AND DISCUSSION

The thickness dependence of T_g was examined using ellipsometric measurements and measurements recording the real part of the complex capacitance with the DRS technique [7], as shown in Fig. 1. The glass transition temperature measured is the so-called thermal T_g, corresponding to T_g at zero frequency. It can be seen from the graph that T_g decreases with film thickness, consistent with previous studies [2–4]. In addition, the thickness dependence of T_g taken from ellipsometric measurements coincides with the DRS data in which samples were sandwiched with Al layers. It is considered that free surface feature was not detracted by the Al layer coating in present PS thin films.

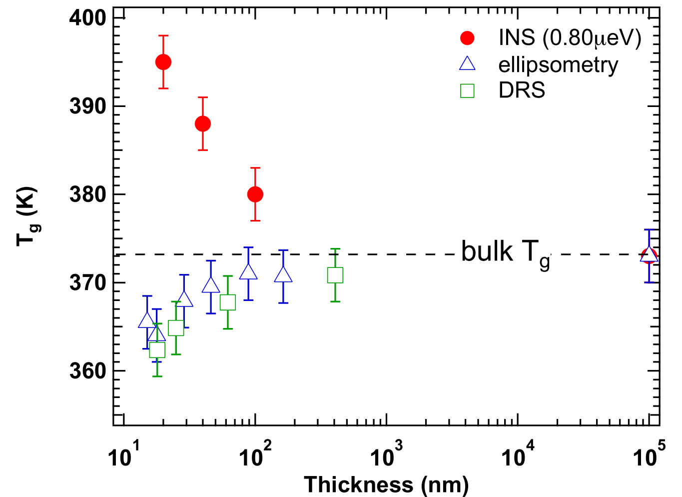

FIG. 1. Thickness dependence of thermal T_g values obtained from DRS, ellipsometry and INS with energy resolution of 0.8 μeV.

To investigate the thickness dependence of T_g at high frequencies, INS measurements were performed on the bulk polymer and on thin films having thicknesses of 20 nm, 40 nm, and 100 nm. Figure 2 shows the temperature dependence of the mean square displacement ($\langle u^2 \rangle$) evaluated from the Q^2 dependence of elastic scattering for the bulk polymer and for the 20-, 40-, and 100-nm thin films, with an energy resolution of 0.8 μeV. $\langle u^2 \rangle$ was found to decrease with decreasing film thickness, suggesting a lower mobility with thickness. For all samples investigated, a change in the slope of the $\langle u^2 \rangle$ versus T graph was observed in the temperature range 370 K to 400 K. The change in slope denotes the onset of the relaxation process at fixed energy resolution. To estimate the inflection temperature without inconsistency, linear fits were performed to the temperature dependence of $\langle u^2 \rangle$ by selecting the data points for glassy and molten state (Fig. 5). The χ^2 value is evaluated from the glassy state (χ_g^2), the molten state (χ_m^2), and the defined total χ^2 values, by summing up the values of χ_g^2 and χ_m^2. It was shown that the smallest total χ^2 values (dashed arrows in Fig. 6), resulted in determining the change of slope of $\langle u^2 \rangle$ for all films investigated (see the Appendix). In the case of the bulk sample, the change in the slope of $\langle u^2 \rangle$ was observed at 373 K, consistent with the T_g determined by differential scanning calorimetry (DSC). At present, the exact physical reason for the detection of the α process through INS is unknown. The hierarchy of the α process in both a temporal and spatial scale is considered. The same criterion was employed to estimate the T_g of the thin films from the INS data. The solid arrows in Fig. 2 indicate

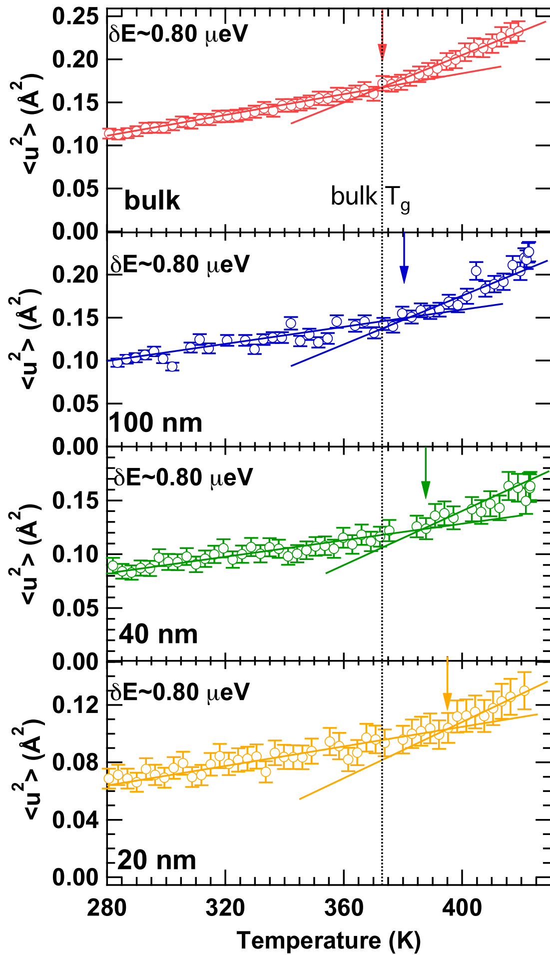

FIG. 2. Temperature dependence of $\langle u^2\rangle$ measured with 0.8-μeV energy resolution for the bulk (red circles), and for film thicknesses of 100 nm (blue circles), 40 nm (green circles), and 20 nm (yellow circles). Solid arrows pointing downwards indicate the T_g value determined from INS measurements.

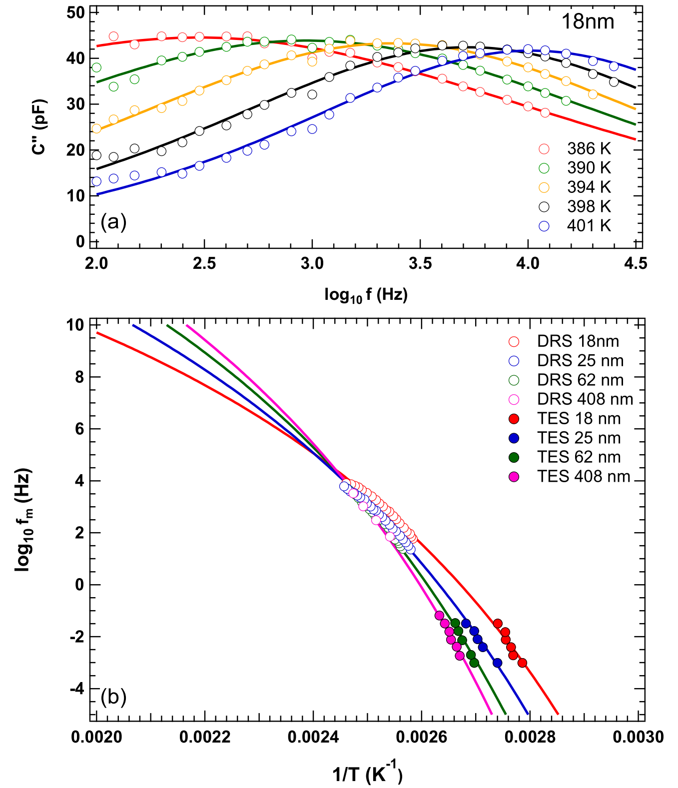

FIG. 3. (a) Frequency dependence of the imaginary part of the complex capacitance (dielectric loss) for 18-nm thin PS at 386 K (red circles), 390 K (green circles), 394 K (yellow circles), 398 K (black circles), and 401 K (blue circles). Solid curves correspond to fits with the Havriliak-Negami equation. (b) Peak frequency of dielectric loss due to the α process as an inverse function of temperature for PS thin films with thicknesses of 18 nm (pink circles), 25 nm (blue circles), 62 nm (green circles), and 408 nm (pink circles), obtained through a combination of TES (filled symbol) and DRS (open symbol) methods. The solid curves with the same color as the corresponding symbols represent fits with VFT equation.

the T_g values, denoting an increase in T_g with decreasing film thickness. This result is also highlighted in Fig. 1, showing that the INS data confirm the contradictory dependence of thermal T_g on film thickness.

In order to find the physical origin for the contradictory dependence of thermal T_g as a function of thickness in DRS and INS measurements, the imaginary part of the complex capacitance (dielectric loss) of the DRS is considered. Figure 3(a) shows the frequency dependence of the dielectric loss for an 18-nm-thick film of PS, recorded at five different temperatures. Broad peaks, corresponding to the peak frequencies of the α process, were observed within the frequency range explored. The solid curves in Fig. 3(a) show that the peak frequency of dielectric loss is well described by the Havriliak-Negami equation [23]. To assess the temperature dependence of the peak frequency of the α process for various film thicknesses, the temperature dependence of the relaxation rate (f_m) from DRS (intermediate-frequency) and TES (low-frequency) is plotted in Fig. 3(b). An interesting feature of the α process also emerges from the relaxation time map. With increasing frequency, the difference in peak frequency f_m among the samples decreases, and surprisingly, the curves illustrating the temperature dependence of f_m seem to merge at a frequency of $\sim 10^4$ Hz. Since f_m could not be accessed at frequencies above 10^4 Hz due to limitations of the present experimental setup, we fitted the temperature dependence of f_m with the Vogel-Fulcher-Tammann (VFT) equation [24] to predict the T dependence of f_m in a broader frequency range. The fit curves obtained using VFT, shown as solid lines in Fig. 3(b), highlight a decrease in temperature dependence of the relaxation time. Forrest *et al.* studied the α process of PS thin films using variable cooling rate ellipsometry [25] and observed a similar decrease in activation energy with thickness. Simon *et al.* [26] also reported a similar tendency from calorimetry studies. In addition, the fitted curves corresponding to different film thicknesses were observed to merge at frequencies around 10^4 Hz; this merging frequency has henceforth been referred to as crossing frequency (f_c). The predicted behavior of f_m as a function of film thickness at frequencies above f_c is different from the behavior observed by DRS and TES. In other words, the fitting results predict a slowing down of the α process or

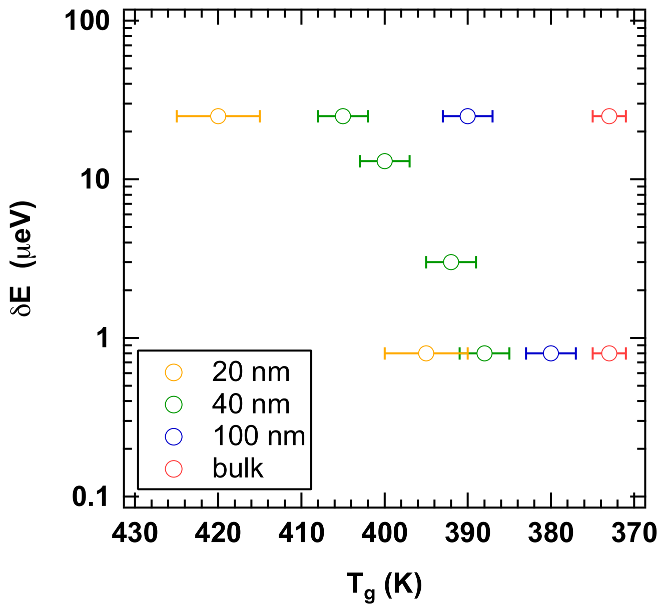

FIG. 4. Energy resolution as a function of T_g for bulk polymer (red circles) and for films with thicknesses of 100 nm (blue circles), 40 nm (green circles), and 20 nm (yellow circles).

an increase in T_g with decreasing film thickness at frequencies above f_c.

This prediction of increase in T_g with decreasing film thickness by VFT is qualitatively consistent with an increase in T_g with decreasing film thickness observed by INS.

Next, we assessed the possible decrease in the temperature dependence of relaxation time with increasing film thickness at frequencies above f_c. Since the energy resolution is inversely related to the detectable time range, lower energy resolution corresponds to an increase in accessible f_m. Assuming that $f_{m1} > f_{m2}$, T_g would be higher at f_{m1} than at f_{m2}. In addition, the rate of increase in T_g as a function of f_m would be enhanced with decreasing film thickness: T_g should exhibit a stronger dependence on energy resolution or frequency with decreasing film thickness. When T_g is plotted as a function of the INS energy resolution (Fig. 4), it shifts to higher temperatures with decreasing energy resolution (or increasing frequency). Furthermore, the frequency dependence of T_g is enhanced with decreasing film thickness. These results support the hypothesis that temperature dependence of relaxation time weaknes with decreasing film thickness at frequencies above f_c.

A reduction in mobility at infinitely high frequencies may represent a crucial factor to explain the contradictory dynamic behavior in addition to the decrease in apparent activation energy with film thickness. The segmental motion of glass formers under spatial confinement is more hindered than their motion in a less spatially confined system due to the stronger interaction between the glass formers and the substrate or pore surface ("wall effect"). In fact, Scheidler *et al.* [27] reported a reduction in segmental motion due to the wall effect using MD simulations. The different thickness dependences of the α process of PS thin films observed by INS and TES/DRS can thus be understood based on these effects.

Such a controversial dynamic dependence on frequency or temperature has been observed before for glass formers under nanoconfinement. Schönhals *et al.* [28] studied the dynamics of the polymeric glass former poly(methyl phenyl siloxane) confined in a porous glass with nanosized pores using INS, DRS, and temperature-modulated DSC. They observed a similar decrease in both apparent activation energy and crossing frequency with decreasing pore size in the relaxation time map, and discussed such contradictory results based on the concept of "cooperatively rearranging region" (CRR). If the pore size approaches the length scale of the CRR, the glass formers cannot adequately extend to the CRR, resulting in loss of motional cooperativity or in transition to Arrhenius behavior. However, the film thicknesses studied herein are still larger than the CRR size of PS [29]; hence, it is difficult to conclude that the film thickness directly affects the CRR. Ediger and Forrest [30] also discussed such an experimental observation in their review. They reported that the surface mobility in thin films exhibited weaker temperature dependence than bulk mobility. The contribution of the surface layer of the film increases with decreasing film thickness. Thus, the averaged thin film dynamics would be affected by the surface dynamics with small temperature dependence in the relaxation time of the α process, resulting in the small temperature dependence in the

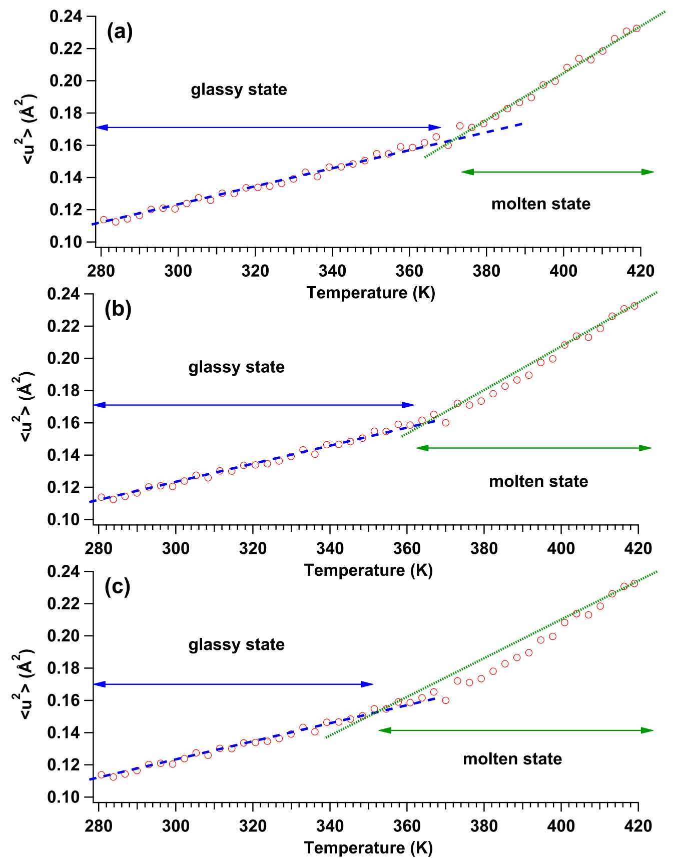

FIG. 5. (a) Temperature dependence of $\langle u^2 \rangle$ of bulk. First 30 data points were selected for glassy state, and the rest were selected for molten state. (b) Temperature dependence of $\langle u^2 \rangle$ of bulk. First 27 data points were selected for glassy state, and the rest were selected for molten state. (c) Temperature dependence of $\langle u^2 \rangle$ of bulk. First 24 data points were selected for glassy state, and the rest were selected for molten state.

relaxation time of the α process with decreasing thickness. The detailed mechanism of the weakening in temperature dependence of relaxation time with decreasing film thickness is still unclear, and further experimentation would be necessary for solving this problem. Using dynamic measurements covering a broad frequency range (achieved by combination of several methods), Schönhlas *et al.*, in agreement with the present work, revealed a dynamic behavior in contrast with other results. For glass formers under nanoconfinement, the dynamical behavior strongly depends on the temperature or frequency range. Hence, the specific frequency range represents another essential parameter that must be considered to describe the thickness dependence of T_g or of the α process in future dynamic studies.

Finally, we would like to briefly discuss the T_g estimated from $\langle u^2 \rangle$ by INS in the high-frequency region. The T_g evaluated from $\langle u^2 \rangle$ for bulk PS is almost the same as the thermal T_g measured by DSC (Fig. 1) despite the INS in the high-frequency region. In the current INS study, the relaxation time of the α process has not been measured directly. If we measure the relaxation time, the T_g (so-called dynamics T_g) would be higher than the observed one, according to the relaxation time map [Fig. 3(b)] in the INS frequency region. The T_g obtained from $\langle u^2 \rangle$ showed the high-frequency nature, as discussed in the paper, but seems to reflect the thermal T_g from DSC. Presently we have no explanation for that.

IV. SUMMARY

In this work, we have studied the α process in PS thin films using DRS, TES, and INS in a broad frequency range. The combination of TES and DRS measurements revealed a decrease in T_g with decreasing film thickness, in agreement with previous results. On the other hand, INS showed an increase in T_g with decreasing film thickness. To reveal the origin of such a controversial thickness dependence of T_g from INS, we focused on the temperature dependence of the peak frequency (f_m) of the α process probed by DRS and TES. In line with the decrease in T_g with thickness, increase in f_m at a given temperature was obtained by DRS and TES in the studied frequency range. In order to predict the temperature dependence of f_m above 10^4 Hz, we fitted the T dependence of f_m at lower frequencies using the VFT equation. The fitted curves predict a decrease in f_m with decreasing film thickness at frequencies above the crossing frequency (or the frequency range covered by INS). Slowing of the α process was also qualitatively detected by INS, based on the energy resolution dependency of $\langle u^2 \rangle$ in the thin films. The contrast between the TES or DRS and INS descriptions of the thickness dependence of the α process in PS thin films can be attributed to the reduction in apparent activation energy with film thickness and the reduction in mobility at infinitely high frequencies due to the wall effect.

ACKNOWLEDGMENTS

This work was partially supported by the Photon and Quantum Basic Research Coordinated Development Program from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The INS measurements were performed with DNA at J-PARC facility under proposal No. 2013A0093. Grants-in-Aid for Scientific Research (B) (No. 16H04036) from the Japan Society for the Promotion of Science.

APPENDIX: PROCEDURE FOR THE EVALUATION OF INFLECTION TEMPERATURE FROM THE TEMPERATURE DEPENDENCE OF $\langle u^2 \rangle$

Since thermal expansion is different between glassy and molten states, the difference in the slope of temperature dependence of $\langle u^2 \rangle$ between glassy and molten state was used for the determination of T_g. The arbitrary choice of data points belonging to glassy or molten state delivers an unreliable thickness dependence of T_g from the present INS studies. To exclude such arbitrariness, we changed the number of data points belonging to glassy state (or molten state) within the focused temperature range. For example, Figs. 5(a), 5(b), and 5(c) correspond to the selection of data points for glassy state as 30, 27, and 24, respectively. We independently performed

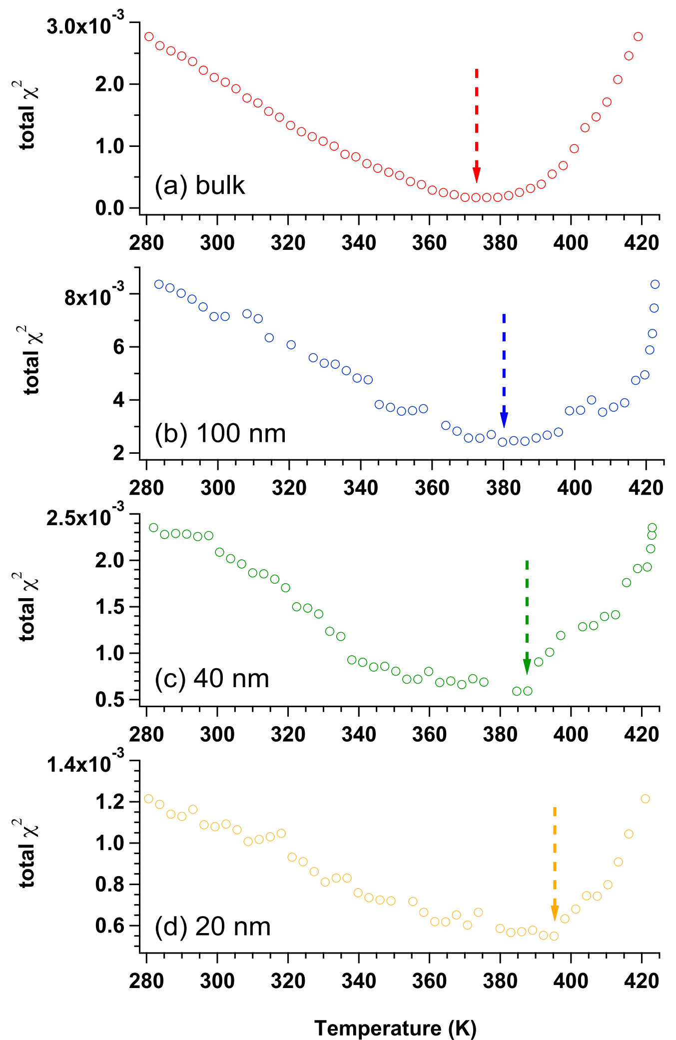

FIG. 6. Temperature dependence of total χ^2 for bulk (a), for 100 nm thick (b), for 40 nm thick (c), and for 20 nm thick films. The dashed arrows correspond to the smallest total χ^2 value among the temperature range examined.

linear fits to the temperature dependence of $\langle u^2 \rangle$ for glassy and molten state. From the results of the linear fits to both states, we evaluated χ^2 from glassy state (χ_g^2) and molten state (χ_m^2). We then evaluated the total χ^2 by summing up χ_g^2 and χ_m^2 and constructed the temperature dependence of total χ^2 for the bulk and PS films of thicknesses 100 nm, 40 nm, and 20 nm (Fig. 6). We searched the smallest total χ^2 value in the temperature range for all film thicknesses. The dashed arrows in Fig. 6 correspond to the data point (temperature) that exhibited the smallest total χ^2 value for all the film thickness examined. Based on the results shown in Fig. 6 (dashed arrows), we evaluated T_g for the film thickness investigated.

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