Glass Transition Temperature and Dynamics of $\alpha$-Process in Thin Polymer Films

K. Fukao and Y. Miyamoto
Faculty of Integrated Human Studies, Kyoto University, Kyoto 606-8501, Japan
(Received July 29, 1998)

The glass transition temperature $T_g$ and the temperature $T_\alpha$ corresponding to the peak in the dielectric loss due to the $\alpha$-process have been simultaneously determined as functions of film thickness $d$ through dielectric measurements for thin films of polystyrene. A decrease of $T_g$ was observed with decreasing film thickness, while $T_\alpha$ was found to remain almost constant for $d > d_c$ and decrease drastically for $d < d_c$. Here, $d_c$ is a critical thickness dependent on molecular weight. The thickness dependence of $T_g$ is related to the distribution of relaxation times of the $\alpha$-process, not to the relaxation time itself.

PACS numbers: 64.70.Pf, 68.60.-p, 77.22.Gm

Although many properties of glass transitions in glass-forming materials have been clarified by recent experimental and theoretical works, the nature of glass transitions is not yet fully understood [1]. Understanding the characteristic length scale of the dynamics of supercooled liquids near the glass transition is the most important issue in such studies. Molecular dynamics simulations reveal the existence of significant large scale heterogeneity in particle displacements, so-called dynamical heterogeneity in supercooled liquids [2]. As the temperature decreases to $T_g$, the dynamical heterogeneity grows. This phenomenon can be interpreted as the growth of the cooperatively rearranging range (CRR) with decreasing temperature in the supercooled liquid state [3]. Multi-dimensional NMR [4] and dielectric hole burning [5] reveal evidence of dynamical heterogeneity. These topics concerning heterogeneity are closely related to the length scale of dynamics near glass transitions.

One of the most useful approaches to studying the length scale involved in dynamic glass transitions is to investigate the finite size effect on these transitions, i.e., to investigate the systems confined to nanopores [6] or thin films [7] [8]. In such systems, deviation from bulk properties is expected to appear if the system size is comparable to the characteristic length scale. In particular, $T_g$ of thin films has to this time been measured by several experimental techniques, including ellipsometry [9], positron annihilation [10], Brillouin light scattering [11], and X-ray reflectivity [12]. Keddie et al. measured $T_g$ of thin polymer films for the first time. For polystyrene films on hydrogen-passivated Si, $T_g$ was found to decrease with decreasing film thickness $d$ for $d<40\text{nm}$ [13]. In the case of freely standing polystyrene films, $T_g$ decreases much more rapidly with decreasing film thickness [13]. These results suggest that the interaction between polymers and the substrate competes with surface effects. This competition leads to the more gradual decrease of $T_g$ in the former case. For a strong attractive interaction between polymers and the substrate, an increase in $T_g$ was observed [13].

The dynamics related to the glass transition in thin films have been investigated by many methods. Second harmonic generation reveals that the distribution of relaxation times broadens with decreasing film thickness, while the averaged relaxation time of the $\alpha$-process remains constant for the supported films of a random copolymer [14]. Atomic force microscopy [15] and photon correlation spectroscopy [16] studies show the existence of a mobile layer near the free surface of thin films of polystyrene. However, it is not yet clear whether properties of the $\alpha$-process change together with the change in $T_g$ displayed as film thickness decreases.

In this Letter, we report on dielectric measurements made to determine the $d$-dependence of $T_g$ in atactic polystyrene (a-PS) by the temperature dependence of the electric capacitance, that is, to check whether $T_g$ of thin films goes up or down compared with that of the bulk samples by another independent technique, and also we report on an investigation of the relation between the $d$-dependence of $T_g$ and that of the dynamics of the $\alpha$-process. We have successfully determined the $d$-dependence of $T_g$. These results agree well with those obtained by ellipsometry on supported PS films. The $d$-dependence of the width of dielectric loss peak of the $\alpha$-process is closely related to that of $T_g$, while $T_\alpha$ corresponding to the peak in the dielectric loss due to the $\alpha$-process remains almost constant. We also found the existence of a critical thickness at which the dynamics of the $\alpha$-process change drastically. We hope that these findings lead to a breakthrough in the investigation of the characteristic length scale of the glass transition.

Thin films of a-PS with various thicknesses from 4 nm to 489 nm were prepared using a spin-coat method from a toluene solution of a-PS on Al-deposited slide glass. The thickness was controlled by changing the concentration of the solution. Two different a-PS’s were used, one was purchased from Scientific Polymer Products, Inc. ($M_W=2.8\times10^5$), and the other from Aldrich Co., Ltd. ($M_W=1.8\times10^6$, $M_W/M_M=1.03$). After annealing at 70°C in the vacuum system for several days to remove solvents, Al was vacuum-deposited again to serve as an upper electrode. Heating cycles between room temperature
and 110°C (\(>T_g\)) were carried out more than once before the dielectric measurements to relax the as-spun films and obtain reproducible results. Dielectric measurements were done using an LCR meter (HP4284A) for the frequency range from 20 Hz to 1MHz during heating (cooling) processes in which the temperature was changed at a rate of 2K/min.

FIG. 1. Temperature dependence of the capacitance normalized with respect to the values at 303K during the heating process for various frequencies (∙ corresponds to 100Hz, △ to 1kHz, ⊗ to 10kHz, and ◊ to 100kHz) and three different thicknesses ((a), \(d=91\text{nm}\) and \(M_w=1.8\times 10^6\); (b), \(d=20\text{nm}\) and \(M_w=2.8\times 10^5\); (c), \(d=11\text{nm}\) and \(M_w=1.8\times 10^6\)). The solid lines were obtained by fitting the data at 10kHz to a linear function below and above \(T_g\). The arrows indicate the values of \(T_g\).

Film thickness was evaluated from the capacitance at room temperature of as-prepared films by using the formula for the capacitance \(C'\) of a flat-plate condenser, \(C'=\varepsilon\varepsilon_0 S/d\), where \(\varepsilon'\) is the permittivity of a-PS, \(\varepsilon_0\) is the permittivity of the vacuum, \(S\) is the area of the electrode (\(S=8.0\text{mm}^2\)), and \(d\) is the thickness of the films. The value of \(\varepsilon'\) at room temperature is \(≈2.8\) for the bulk PS and is assumed to be independent of \(d\). In the temperature range below that where the dielectric dispersions are observed, the effect of dielectric dispersion can be neglected; i.e., here \(\varepsilon'(T)\approx\varepsilon_\infty(T)\). In this case, the temperature dependence of \(C'(T)\) comes only from that of \(\varepsilon_\infty\varepsilon_0 S/d\), where \(\varepsilon_\infty\) is the permittivity in the high frequency limit. If we assume that the films are constrained along the substrate surface, the thermal expansion along this surface can be neglected. Then the linear thermal expansion coefficient normal to the substrate \(\alpha_n\) is given by \(\alpha_n = (1 + \nu)/(1 − \nu)\alpha_\infty\), where \(\alpha_\infty\) is the bulk linear coefficient of thermal expansion and \(\nu\) is Poisson’s ratio [10]. After taking account of the contributions from \(\varepsilon_\infty\) we obtain the temperature coefficient of capacitance \(\tilde{\alpha}\) as follows: \(\tilde{\alpha} = -\frac{1}{C'(T_0)} \frac{dC'(T)}{dT} \approx 2\alpha_n\).

We thus see that the temperature coefficient of \(C'\) is proportional to \(\alpha_n\) [13]. Here, \(T_0\) is a standard temperature. It is therefore expected that the temperature coefficient should change at \(T_g\).

![Graph](image)

FIG. 2. Thickness dependence of \(T_g\) of a-PS films obtained during the heating process (∙ corresponds to \(M_w=2.8\times 10^5\), and △ to \(M_w=1.8\times 10^6\)). The values of \(T_g\) are determined as the crossover temperature between the straight lines characterizing \(C'(T)\) at 10kHz below and above \(T_g\). The solid line was obtained from the equation \(T_g(d) = T_\infty (1 − a/d)\). The symbols • and △ represent the data obtained for uncapped supported films of a-PS by Forrest et al. using ellipsometry for a-PS (\(M_w=7.67\times 10^5\)) [14].

Figure 1 displays the temperature dependence of the capacitance, normalized with respect to the value at 303K during heating processes. In Fig.1(a) we can see that the values with thickness 91 nm for different frequencies can be reduced to a single straight line and decrease with increasing temperature for the temperature range from room temperature to approximately 370K. At higher temperature the normalized capacitance decreases with increasing temperature more steeply than at lower temperature. Here, the values for different frequencies can no longer be fitted by a single line, but are dispersed due to the appearance of the \(\alpha\)-process. For the tem-
temperature range shown in the figure, however, there is almost no effect of the dispersion above 10KHz. Therefore, the temperature at which the slope of the straight line of $C'(T)$ changes discontinuously can be determined unambiguously as the crossover temperature between the straight line characterizing the lower temperature side and that characterizing the higher temperature side for frequencies above 10KHz. This crossover temperature can be regarded as $T_g$, because the thermal expansion coefficient changes through the crossover temperature. The temperature coefficients of $C'$ obtained by fitting the data to the two lines are $2.6 \times 10^{-4}$K$^{-1}$ for $T < T_g$ and $8.7 \times 10^{-4}$K$^{-1}$ for $T > T_g$ in the case $d=91$nm. These values agree well with those estimated from the values of $\alpha_\infty$ and $\nu$ in the literature [10]. As $d$ decreases, $T_g$ also decreases, as shown in Figs.1(b) and (c).

Figure 2 displays the $d$-dependence of $T_g$ for a-PS films determined as a crossover temperature at which the temperature coefficient of the capacitance at 10 kHz changes during heating process. When the films are thinner than about 100 nm, a decrease of $T_g$ is observed. The value of $T_g$ for films of 6 nm thickness is lower by about 30K than that of films of 489 nm thickness. The dependence of $T_g$ on $d$ can be expressed by a relation of the form $T_g(d) = T_g(\infty)(1-a/d) \approx T_g(\infty)(1+a/d)^{-1}$, where $T_g(d)$ is the measured glass transition temperature for a film of thickness $d$. The best fit parameters are $T_g(\infty)=370.2 \pm 0.4$ K and $a=0.43 \pm 0.03$ nm. Because these results agree well with those reported by Forrest et al. [10], it can be concluded that $T_g$ of thin films has successfully been determined by measurements of electric capacitance for the first time. Here, we should note that $a$ is much smaller than the values of $d$ in our measurements. The value $a$ may be related to heterogeneous distribution of mobility within films, as discussed later.

![FIG. 3. Reduced dielectric loss as a function of temperature for various film thicknesses ($M_w=2.8 \times 10^5$). The symbols correspond to $d=105$ nm, $\triangle$ to $d=26$ nm, and $\square$ to $d=9$ nm. The curves were obtained by fitting the data to the equation $\tan \delta = \tan \delta_{\text{max}}/(1+((T-T_\alpha)/\Delta T_\alpha)^2)$.](image)

We now discuss how the dynamics of the $\alpha$-process change with decreasing $T_g$ resulting from decreasing $d$. Figure 3 shows the reduced dielectric loss as a function of temperature at 100Hz in a-PS of thickness 9nm, 26 nm and 105 nm. Above $T_g$ the dielectric loss $\tan \delta$ at constant frequency displays an anomalous increase with temperature due to the $\alpha$-process, and it possesses a maximum at the temperature $T_\alpha$. The value of $T_\alpha$ and the width of the $\alpha$-peak, $\Delta T_\alpha$, also depend on $d$, as shown in Fig.3. Here, $\Delta T_\alpha$ is defined as the temperature difference between the temperature $T_\alpha$ and the lower temperature at which $\tan \delta$ is half its peak value. As shown in Fig.4(b), the width $\Delta T_\alpha$ begins to increase at about 100 nm, and continues to increase monotonically.

![FIG. 4. (a) Thickness dependence of $T_\alpha$ and (b) $\Delta T_\alpha$ during the heating process at constant frequency. The symbol $\bullet$ corresponds to $f=100$Hz and $M_w=2.8 \times 10^5$, $\blacktriangle$ to $f=1$KHz and $M_w=2.8 \times 10^5$, $\square$ to $f=100$Hz and $M_w=1.8 \times 10^5$, and $\bigtriangledown$ to $f=1$KHz and $M_w=1.8 \times 10^5$. The solid lines in (a) were drawn for $M_w=2.8 \times 10^5$ and the dotted lines, for $M_w=1.8 \times 10^5$. These lines were drawn by the equation $T_\alpha(d) = T_\alpha(\infty)(1 - (d-d_c)/\zeta)$ for $d < d_c$, where $T_\alpha(\infty)$ and $\zeta$ are constants. The curve in (b) was obtained from the equation $\Delta T_\alpha(d) = \Delta T_\alpha(\infty)(1+a'/d)$.](image)
cally with decreasing $d$. The $d$-dependence of $\Delta T_\alpha$ can be expressed by the equation $\Delta T_\alpha(d) = \Delta T_\alpha^\infty (1 + \frac{d}{d_c^\alpha})$, where $d^\alpha=6.9\pm0.6$ nm and $\Delta T_\alpha^\infty=10.2\pm0.4$ K. Comparing the $d$-dependence of $\Delta T_\alpha$ with that of $T_g$ (Fig.2), we find that the lowering of $T_g$ is directly correlated with the broadening of the $\alpha$-peak as follows: $\delta(T_g(d))/T_g^\infty = -6.0 \times 10^{-3}(\Delta T_\alpha(d))/\Delta T_\alpha^\infty$, where $\delta T_g(d)=T_g(d)-T_g^\infty$ and $\delta(\Delta T_\alpha(d))=\Delta T_\alpha(d)-\Delta T_\alpha^\infty$. In other words, the broadening of the distribution of relaxation times for the $\alpha$-process is closely correlated to the reduction of $T_g$.

Contrastingly, Fig.4(a) shows that $T_g$ remains almost constant as $d$ is decreased, down to a critical thickness $d_c$, at which point it begins to decrease linearly with $d$. The values of $d_c$ clearly depend on the molecular weight ($M_w$) of a-PS: $d_c=11$ nm for $M_w=2.8\times10^5$ and $d_c=20\sim23$ nm for $M_w=1.8\times10^6$. These values seem to be related to the radius of gyration of the bulk polymer coil ($R_g=0.028\times\sqrt{M}$(nm)): $R_g=15$ nm for $M_w=2.8\times10^5$ and 38 nm for $M_w=1.8\times10^6$. The $M_w$- and $d$-dependences of $T_g$ are quite different from those of $T_g$ and $\Delta T_\alpha$ in the present and previous measurements on supported PS films $\text{[4,5]}$, or rather, they are similar to that of $T_g$ for freely standing films of a-PS $\text{[6]}$.

In case of thin polymer films supported on substrate, not only the surface effects but also the interaction between the substrate and films strongly affects the dynamics and the glass transition of the thin films. A three-layer model was introduced in order to explain such surface and interfacial effects $\text{[1]}$. In this model it is assumed that within a thin film there are a mobile layer and an immobile layer in addition to a bulk-like layer. The $d$-dependence of $\alpha_t$ observed in our measurements also supports the model $\text{[1]}.\text{[1]}$. On the basis of this model, the existence of mobile and immobile layers with constant layer thicknesses broadens the distribution of relaxation times of the $\alpha$-process with decreasing $d$, i.e., $\Delta T_\alpha$ is increased. Because $T_g$ can be regarded as the temperature at which the anomalous increase in $\varepsilon''$ begins, $T_g$ decreases with increasing $\Delta T_\alpha$. On the other hand, the temperature $T_\alpha$ remains constant, because $T_\alpha$ is the temperature at which $\varepsilon''$ has a maximum. If $d$ reaches a critical thickness $d_c$, the thickness of the bulk-like layer becomes comparable to the characteristic length scale of the $\alpha$-process and, as a result, the dynamics change drastically. For $d<d_c$, $T_\alpha$ decreases or increases depending on whether contributions from the mobile layer are stronger than those from the immobile layer. In the present case, $T_\alpha$ happens to decrease drastically.

In this Letter, three different length scales $a$, $a'$ and $d_c$ were extracted from the dielectric measurements. From the above discussions, $d_c$ is expected to be related to the characteristic length scale $\xi$ for the $\alpha$-process of bulk samples. In this case it is difficult to evaluate the exact value of $\xi$ because surface and interfacial effects and the molecular weight dependence of $d_c$ should be taken into account $\text{[4,5,6]}$. However, $d_c$ can at least be regarded as the upper limit of $\xi$.

Recently, Forrest et al. $\text{[3]}$ have obtained the $\alpha$-relaxation data with a characteristic time scale $\langle \tau \rangle \sim 2 \times 10^{-4}$s by a quartz crystal microbalance technique for supported PS films with SiC particles. It was reported that $T_{\text{max}}$, which can be compared with $T_\alpha$, has a $d$-dependence similar to that of $T_g$. The $d$-dependence of $T_{\text{max}}$ observed in their measurements seems to be different from that in our measurements. This may come from the difference between dielectric relaxation dynamics and mechanical relaxation dynamics.

In summary, we have confirmed the reduction of $T_g$ with decreasing $d$ for capped thin films of a-PS by dielectric measurements. The $d$-dependence of $T_g$ is directly correlated to that of the width of the peak due to the $\alpha$-process in the temperature domain, i.e., the distribution of relaxation times of the $\alpha$-process. The dynamics of the $\alpha$-process change drastically for the films with thickness less than a critical thickness.

The work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan.

$\dagger$Electronic address: fukao@phys.h.kyoto-u.ac.jp

[1] “Proceedings of the 3rd International Discussion Meeting on Relaxations in Complex Systems”, J. Non-Cryst. Solids. (1998) (to be published).

[2] T. Muranaka and Y. Hiwatari, Phys. Rev. E51, R2735, (1995); R. Yamanoto and A. Onuki, J. Phys. Soc. Jpn., 66, 2545 (1997); W. Kob et al., Phys. Rev. Lett. 79, 2827 (1997).

[3] G. Adam and J.H. Gibbs, J. Chem. Phys. 43, 139 (1965).

[4] K. Schmidt-Rohr and H.W. Spiess, Phys. Rev. Lett. 66, 3020 (1991).

[5] B. Schiener et al., 274, 752, (1996).

[6] J. Schüller et al., Phys. Rev. Lett. 73, 2224 (1994); M. Arndt et al., Phys. Rev. Lett. 79, 2077 (1997); G. Barut et al., Phys. Rev. Lett. 80, 3543 (1998).

[7] J.L. Keddie, R.A.L. Jones, and R.A. Cory, Europhys. Lett., 27, 59 (1994); J.L. Keddie and R.A.L. Jones, Faraday Discuss. 98, 219 (1994).

[8] G.B. DeMaggio et al., Phys. Rev. Lett. 78, 1524 (1997).

[9] J.A. Forrest et al., Phys. Rev. Lett. 77, 2002 (1996); J.A. Forrest, K. Dalnoki-Veress, and J.R. Dutcher, Phys. Rev. E56, 5705 (1997).

[10] W.E. Wallace, J.H. van Zanten, and W.L. Wu, Phys. Rev. E52, R3329 (1995).

[11] D.B. Hall, J.C. Hooker, and J.M. Tourkelson, Macromolecules, 30, 667 (1997).

[12] T. Kajiyama, K. Tanaka, and A. Takahara, Polymer, 39, 4665 (1998).

[13] J.A. Forrest et al., Phys. Rev. E58, R1226 (1998).

[14] O. Yano and Y. Wada, J. Polym. Sci.: Part A-2, 9, 669 (1971).

[15] K. Fukao and Y. Miyamoto, (in preparation).

[16] Polymer Handbook, 3rd ed., edited by J. Brandrup and E.H. Immergut (John Wiley, New York, 1989).