Macromolecules **2003,** *36,* 4937−4943

Anomalous Surface Relaxation Process in Polystyrene Ultrathin Films

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Received January 1, 2003; Revised Manuscript Received April 30, 2003

ABSTRACT: Monodisperse polystyrene (PS) films with various thicknesses were spun-coated on silicon wafers with native oxide layer. Surface relaxation behavior in the PS films was studied as a function of thickness by lateral force microscopy (LFM). In the case of a thick PS film, a clear lateral force peak corresponding to surface α_a-relaxation process of segmental motion was observed at a temperature much lower than the bulk glass transition temperature, T_g. As the film became thinner than 3−4 times the radius of gyration of an unperturbed consistent chain, the peak on lateral force vs temperature curve started to broaden out with decreasing thickness and eventually split into two peaks. The appearance temperature of the surface α_a-relaxation peak was invariant with respect to the film thickness even in such an ultrathin state, meaning that surface T_g was insensitive to the thickness. On the other hand, the ultrathinning-induced relaxation process, called surface β-relaxation, was strongly dependent on the thickness in terms of relaxation temperature and apparent activation energy. Finally, possible origins of the surface β-relaxation process were proposed.

Introduction

In the past decade, molecular motion and dynamics in polymer ultrathin films have been extensively explored by many research groups with the advent of modern experimental techniques related to their technological applications as well as fundamental interests of polymer science.[1] Here, our definition of *ultrathin state* is that the film thickness is comparable to, or less than, the dimension of an unperturbed constituent chain.[2] So far, it has been widely reported that chain dynamics in such polymer ultrathin films quite differs from that in the bulk.[3−29] It seems to us that the anomalous thermal behavior observed in the ultrathin films is closely related to the presence of surface and interface. For example, in the case of polymer ultrathin films supported on substrates, the glass transition temperature, T_g, is strongly dependent on the interaction with the substrate.[23−29] An attractive interaction induces a higher T_g value of the ultrathin films, suggesting that segmental motion at the polymer/substrate interface would be restricted.[23−29] On the other hand, thermal properties at surfaces are generally regarded to be vigorous in comparison with the interior bulk region.[30−45] Hence, the presence of surface renders chain mobility in thin and ultrathin states active. At a given thickness, thin and ultrathin films with lower surface T_g layer concurrently exhibit lower T_g.[13] Such a surface effect on chain mobility in the thin and ultrathin films can be more clearly seen in the pioneer work by Forrest, Dutcher, and co-workers using free-standing polystyrene (PS) films, which possess two free surfaces at both sides.[6,7] When the interfacial effect can be ignored, T_g decreases with decreasing film thickness, once the film becomes thinner than a critical thickness.[3−19] This behavior can be mainly explained in terms of increasing surface-to-volume ratio of the system. Then, our interest is whether surface mobility in thin and ultrathin films is the same as that in the thick ones. To the best of our knowledge, little information is available for this question at present.

We have systematically studied on surface molecular motion of PS thick films supported on substrates using a family of scanning force microscopy[33] and elucidated that T_g at the surface, T_g^s, is discernibly lower than the corresponding bulk T_g, T_g^b.[32,33] Activation of surface molecular motion might be accounted for by an excess free volume induced by chain end localization at the surface,[31−33] a reduced cooperativity for the surface segmental motion owing to the existence of the free space,[33,46] and a loosen entanglement of surface chains.[44,45,47] However, we have thought that other responsible factors on enhanced surface mobility might exist in addition to the aforementioned reasons. Chain conformation at the surface is now recognized to be flattened rather than random coil conformation.[48,49] Can this be reason why T_g at the surface must be lowered? When the film thickness falls short of the dimension of an unperturbed chain, namely an ultrathin state, the extent of chain distortion along normal to the surface becomes more remarkable. Then, what will happen with T_g^s? If the value alters, we are able to reach a conclusion that the distorted conformation of surface chains is one of the responsible factors on enhanced mobility at the surface.

In this study, the film thickness dependence of T_g^s for spun-coated PS thin and ultrathin films on silicon wafers with native oxide layer is studied by lateral force microscopy (LFM). Results obtained would be direct answers to the questions mentioned above.

Experimental Section

Monodisperse PSs with number-average molecular weight, M_n, of 1.46M, 3.63M, and 6.24M were used. These samples

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10.1021/ma034001y CCC: $25.00

Table 1. Characterizations of Monodisperse PS Used in This Study

M_n	M_w/M_n	R_g/nm	T_g^b/K
1.46M	1.04	33	378
3.63M	1.05	52	378
6.24M	1.09	68	379

were purchased from Polymer Laboratories Ltd. and used without any purification. Table 1 shows M_n, molecular weight dispersity, M_w/M_n, where M_w is weight-average molecular weight, the radius of gyration of an unperturbed chain, R_g, and T_g^b of these samples. R_g was calculated by $(Nb^2/6)^{1/2}$, where N and b are the segment number and the statistical segment length, respectively. T_g^b was measured by differential scanning calorimetry (DSC) under dry nitrogen purge at the heating rate of 10 K min^{-1}. PS films with various thicknesses were spun-coated from toluene solutions onto substrates. In this study, three different substrates were used: cleaned silicon wafers with native oxide layer, hydrophilic silicon wafers treated with piranha solution, and hydrophobic silicon wafers treated with *n*-octadecyltrimethoxysilane (OTMS). Film thickness was controlled by changing the solution concentration within the range of 0.3−3 wt % and/or the spinning rate of 2000−5000 rpm. To remove any residual solvent molecules and eliminate the residual stress imposed by the spin-coating procedure, the films were dried at 296 K for more than 24 h and then annealed above T_g^b for 24 h in a vacuum dryer. After annealing, the film was cooled to room temperature at a rate of 0.5 K min^{-1}. Film thickness was evaluated by ellipsometric measurement. The monochromatic Xe light with a wavelength of 632.8 nm was used as a source, and the incident angle was 60°.

The surface relaxation behavior of the PS films was examined by using an LFM (SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. A cantilever used was fabricated from Si_3N_4, of which both sides were uncoated, and possessed a bending spring constant of 0.1 N m^{-1}. The normal force onto the cantilever was set to be 10 nN in a repulsive force region. It was preconfirmed that the sample surface was not damaged by scanning a tip under the current conditions. Lateral force as a function of temperature was examined at a heating rate of 0.4 K min^{-1} under vacuum.

Results and Discussion

Frictional behavior of polymeric materials is closely related to their viscoelastic properties.[50] Hence, it is possible to examine surface relaxation in PS thin and ultrathin films by using LFM.[33,36,51] That is, when mechanical energy at the surface imposed by a sliding tip starts to dissipate due to the release of molecular motion, lateral force increases. Thus, it can be postulated that lateral force alteration with measuring temperature is essentially similar to temperature dependence of dynamic loss modulus or loss tangent.[33,36]

Surface Relaxation Behavior. To study how a PS ultrathin film differs from a thick one in terms of surface dynamics, if any, LFM measurement for PS films with various thicknesses was made at first. Figure 1 shows the temperature dependence of lateral force for three different PS films with M_n of 1.46M. The films are 170, 81, and 30 nm in thickness and are displayed as typical examples for being thicker than, or comparable to, and thinner than the chain dimension of 67 nm, respectively. LFM measurement was carried out at a fixed scanning rate, ν, of 1 μm s^{-1}. In the case of the 170 nm thick film, a lateral force peak was clearly observed at around 350 K. On the basis of our previous study,[33] this peak is assignable to surface α_a-relaxation process corresponding to segmental motion, namely, glass−rubber transition. The temperature region at which the surface α_a-relaxation appeared was much lower than the T_g^b of 378 K. This result makes it clear that surface molecular motion is more active than the corresponding bulk one and consistently agrees with our previous results.[33] Since a chain end effect on the surface mobility should be negligible for such a high-M_n sample, the enhanced segmental mobility at the surface would be explained in terms of a reduced cooperativity and/or a loosen chain entanglement. When the film thickness became closer to the chain dimension, surface relaxation behavior started to deviate from what was observed for the thick film. The surface relaxation peak for the 81 nm thick PS film apparently broadened due probably to overlapping two peaks. This inclination began to be remarkable with decreasing film thickness, and eventually, two peaks were completely separated for the PS ultrathin film such as 30 nm, as shown by curve 3 in Figure 1. We here denote these relaxation peaks observed at the higher and lower temperature sides as surface α_a- and β-relaxation processes, respectively. Deferring the assignment of the anomalous surface relaxation, β-process, it is next discussed how these relaxation processes are related to the thickness.

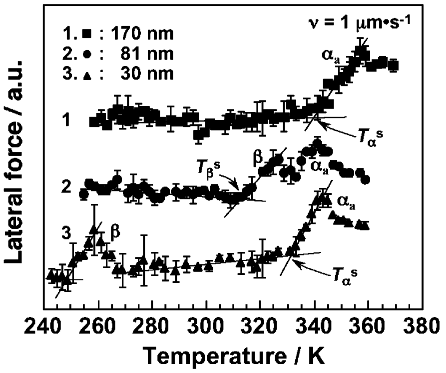

Figure 1. Lateral force−temperature curves for the spun-coated PS 1.46M films with the thickness of 170, 81, and 30 nm at a scanning rate of 1 μm s^{-1}. These films are typical examples of thicker than, or comparable to, and thinner than the unperturbed chain dimension.

Relaxation Temperature. Figure 2 shows the film thickness dependences of surface α_a- and β-relaxation temperatures, T_α^s and T_β^s, for the PS films. The relaxation temperature was defined as a temperature at which lateral force started to increase. Hence, T_α^s could be hardly determined when the two relaxation peaks were overlapped as shown by the curve 2 in Figure 1. In that case, only T_β^s was determined. The data for PS films with M_n of 1.46M, 3.63M, and 6.24M are collected in Figure 2 so that an effect of chain confinement on surface dynamics can be universally seen. Under the current scanning rate of 1 μm s^{-1}, it has been already established that T_α^s corresponds to T_g^s.[33] The T_g^s value was invariant with respect to both film thickness and M_n, meaning that surface segmental motion is neither affected by film thickness nor M_n. This was the case even for ultrathin films thinner than the chain dimension. In a sense of the chain end effect, it is quite reasonable that T_g^s was insensitive to M_n in such a high-M_n region. However, the thickness independence of T_g^s is somewhat surprising and directly indicates that the chain distortion at the surface is not responsible for the manifestation of enhanced mobility at the surface.

So far, the film thickness dependence of glass transition behavior for PS films has been widely explored by many research groups, as mentioned in the Introduction. A conclusion obtained seems to be arrived that T_g

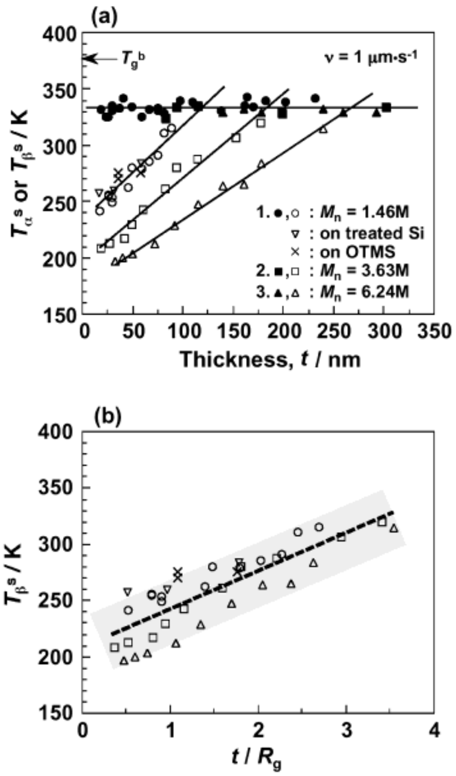

Figure 2. Film thickness dependences of $T_\alpha{}^s$ and $T_\beta{}^s$ for the PS films with M_n of 1.46M, 3.63M, and 6.24 M, supported on silicon wafers with native oxide layer. For the PS 1.46M, the films were also prepared on hydrophilic silicon wafers treated using piranha solution and on hydrophobic OTMS monolayers. The $T_g{}^b$ value marked by the arrow was from DSC measurement. Panel b shows the dependence of $T_\beta{}^s$ on the normalized thickness by radius of gyration of an unperturbed constituent chain. Symbols in panel b are the same as shown in panel a.

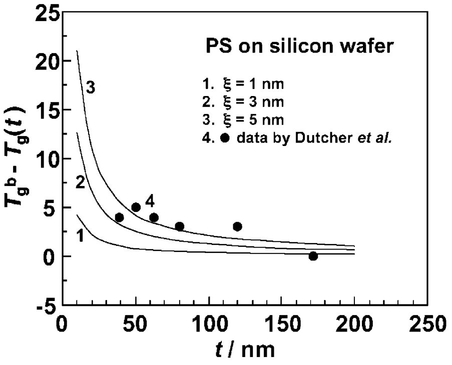

Figure 3. Prediction of T_g depression for the PS films with decreasing thickness. The $T_g{}^b - T_g(t)$ value was simply calculated by $-(\xi/t)(T_g{}^s - T_g{}^b)$, where ξ is a parameter and may possess the physical meaning of surface layer thickness. T_g of PS thin and ultrathin films with M_n of 2.07M, coated on silicon wafers, was obtained by Dutcher et al. using ellipsometry.

of ultrathin PS films themselves differs markedly from $T_g{}^b$.[3−14,19] This knowledge for T_g of the ultrathin PS films was not directly analogous to what was observed here, namely $T_g{}^s$ in the PS ultrathin films. Thus, we tried to confirm whether our $T_g{}^s$ results were consistent with the reported relation between thickness and T_g for the ultrathin PS films. Figure 3 shows the T_g depression for supported PS films with M_n of 2.07M as a function of thickness by Dutcher et al.[6] Although their M_n is a little higher than ours of 1.46M, T_g of the ultrathin PS films would be not dependent on M_n in this M_n region,[4] as shown in Figure 2. The T_g depression is expressed in terms of $T_g{}^b - T_g(t)$. Given that the surface layer does not alter, structurally and dynamically, with decreasing film thickness, T_g of an ultrathin film with a thickness, t, can be given by[7]

$$T_g(t) = T_g{}^b + (\xi/t)(T_g{}^s - T_g{}^b) \qquad (1)$$

where ξ is a parameter with the dimension of length. In the case of the free-standing film, the second term in the right side is multiplied by two because the film has two surfaces. The current form of equation 1 assumes that the chain mobility on the substrate is the same as that in the bulk. Taking our results, $T_g{}^s$ of 336 K and $T_g{}^b$ of 378 K, three solid curves in Figure 3 are drawn for $\xi = 1$, 3, and 5 nm, respectively. As the ξ is 5 nm, our $T_g{}^s$ data seem to well reproduce the thickness dependence of T_g for the PS thin and ultrathin films. This indicates that $T_g{}^s$ is not necessarily dependent on the thickness even in such an ultrathin state. In other words, the argument made here proves the plausibility of our data for the film thickness dependence of $T_g{}^s$. The meaning of ξ might correspond to the thickness of the surface layer, in which chain mobility is enhanced, rather than the characteristic length scale for segmental cooperativity.[4,7,12] Once this notion is accepted, the surface layer thickness of 5 nm is in good agreement with our previous results[38] as well as the results by other groups.[4,12] Also, an interfacial effect on T_g for the ultrathin films might be incorporated into eq 1, as follows:

$$T_g(t) = T_g{}^b + (\xi/t)(T_g{}^s - T_g{}^b) + (\zeta/t)(T_g{}^i - T_g{}^b) \qquad (2)$$

where ζ and $T_g{}^i$ are the interfacial layer thickness and T_g at the interface with the substrate, respectively. Assuming that the ζ is the same as the ξ of 5 nm, $T_g{}^i$ is calculated to be 462 K. This means that the chain mobility on the substrate is highly depressed.[5,6,9,22−26]

On the other hand, $T_\beta{}^s$ was strongly dependent on both film thickness and M_n, once the surface β-relaxation process appeared. The $T_\beta{}^s$ value monotonically decreased with decreasing film thickness, as shown in Figure 2. And also, the threshold thickness, at which the surface β-relaxation started to appear, decreased with decreasing M_n. To compare the data set among different molecular weights, the film thickness, t, was normalized by R_g. Figure 2b shows the relation of $T_\beta{}^s$ to t/R_g. When the film thickness felt short of $3{\sim}4R_g$, the surface β-relaxation appeared. And then, the $T_\beta{}^s$ value linearly decreased with decreasing t/R_g. This trend is universal among three PSs with different M_n employed. Thus, it is conceivable that the anomalous β-relaxation process is closely related to the chain confinement.

In general, it has been widely accepted that the glass transition in ultrathin films is strongly affected by the physicochemical nature of substrate.[23−29] For example, if there is a strong interaction between polymer and substrate, T_g in the ultrathin film is higher than the bulk value.[23−29] If not, such as PS ultrathin films on inert substrates, T_g in the ultrathin film decreased.[3−19] Here, we examined whether $T_\beta{}^s$ depends on surface hydrophilicity or hydrophobicity of substrates, using a silicon wafer treated with piranha solution and

Table 2. Fitting Parameters for Eq 3

M_n	$T^{s}_{\alpha,ave}$/K	t_o/nm	m/K nm^{-1}
1.46M	333 ± 5	114 ± 5	0.92 ± 0.07
3.63M	333 ± 5	183 ± 6	0.75 ± 0.05
6.24M	333 ± 5	269 ± 8	0.59 ± 0.02

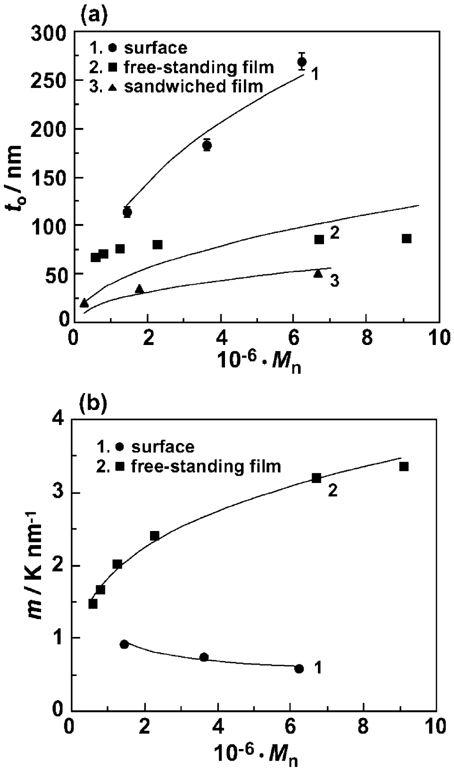

Figure 4. M_n dependences of t_o and m in eq 4 for the surface relaxation in the PS ultarthin films. The surface data are compared with those of free-standing PS films by Dutcher et al. and of sandwiched PS films by Fukao et al.

an OTMS monolayer. Open opposite triangles and crosses in Figure 2 denote T_β^{s} for the PS ultrathin films coated on the treated silicon wafers and the OTMS monolayers, respectively. Since a substrate effect on T_β^{s} was not discernible, it seems most likely that T_β^{s} was independent of polymer/substrate interaction in the thickness range employed. In a sense, this result suggests that a long-range interaction from the interface is not effective for such a long distance of 30 nm.

The film thickness dependence of T_β^{s} observed in this study is quite similar that of T_g in PS ultrathin films,[6,12] and thus, both are compared. Dutcher and co-workers expressed the relation of T_g to film thickness as follows:[6]

$$T_g = T_g^{\,b} + m(t - t_o) \qquad (3)$$

where t_o was the onset thickness, at which T_g started to decrease, and m was the linear slope for the relation between T_g and t. Here, T_g and T_g^{b} are simply replaced by T_β^{s} and T_α^{s}, respectively. That is

$$T_\beta^{\,s} = T_\alpha^{\,s} + m(t - t_o) \qquad (4)$$

The solid lines shown in Figure 2 are best-fit ones, and the fitting parameters, t_o and m, are tabulated in Table 2. Parts a and b of Figure 4 show the M_n dependences of t_o and m. In part a, the M_n-t_o relations for freely standing PS ultrathin film by Dutcher et al.[6] and for sandwiched PS ultrathin film by Fukao et al.[12] are also

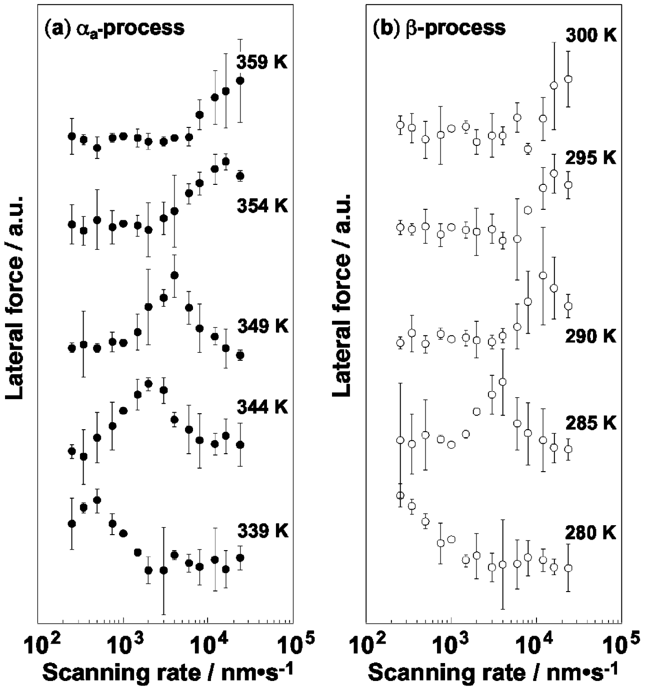

Figure 5. Scanning rate dependence of lateral force with various temperatures for the PS 1.46M film with the thickness of 57 nm: (a) surface α_a-relaxation process; (b) surface β-relaxation process.

shown, provided that their t_o's are for T_g in ultrathin films shown in eq 3. Given that the manifestation of the surface β-relaxation process is closely related to the chain confinement, it seems reasonable to surmise that t_o is correlated to the chain dimension, namely $M_n^{1/2}$. The curves shown in part a are bets-fit ones under the assumption of $t_o \sim M_n^{1/2}$. At the surface, t_o seems to be well proportional to $M_n^{1/2}$, whereas this was not the case for the freely standing ultrathin films. Besides, the t_o value at the surface was much larger than those for the freely standing films and the sandwiched films. Such a difference might imply that molecular chains at the outermost surface are easily distorted in comparison with bulk chains, owing probably to the asymmetric environment at the free surface. On the other hand, the m value decreased with increasing M_n at the surface, as shown in panel b of Figure 4. This trend was completely opposite to the M_n dependence of m for the freely standing films. Interestingly, the m value at the surface and for the freely standing ultrathin films could be expressed by $M_n^{-0.3}$ and $M_n^{0.3}$, respectively. Although it is difficult to understand the meaning of an index number of M_n at present, the M_n dependence of m at the surface seems to be reasonable. This is because the relative order of chain distortion with decreasing thickness of 1 nm is more prominent for a shorter chain due to the less internal freedom. Thus, Figure 4 advocates that the anomalous β-process observed at the surface was induced by the chain confinement into the narrow space.

Activation Energy. We now turn to apparent activation energy for the surface α_a- and β-relaxation processes. Figure 5 shows the scanning rate vs lateral force curves for the α_a- and β-relaxations of the 57 nm thick PS ultrathin film as a typical example. The T_α^{s} and T_β^{s} for the film were approximately 340 and 280 K, respectively. As the measuring temperature reached

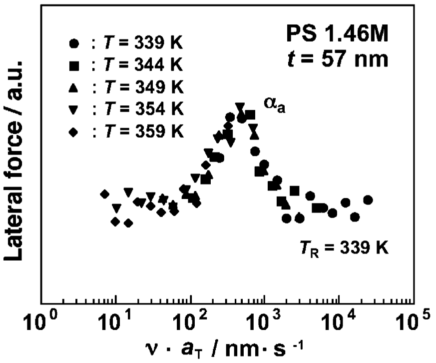

Figure 6. Master curve of the scanning rate–lateral force relation for the PS 1.46M film with the thickness of 57 nm. The curve was for the surface α_a-relaxation process and drawn from the each curve in Figure 5a. A reference temperature of 339 K was used.

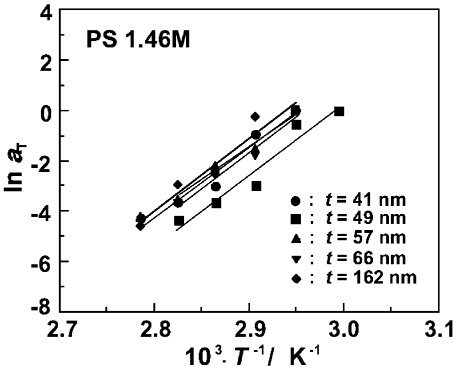

Figure 7. Semilogarithmic plots of shift factor, a_T, vs reciprocal absolute temperature for the PS 1.46M films with various thicknesses.

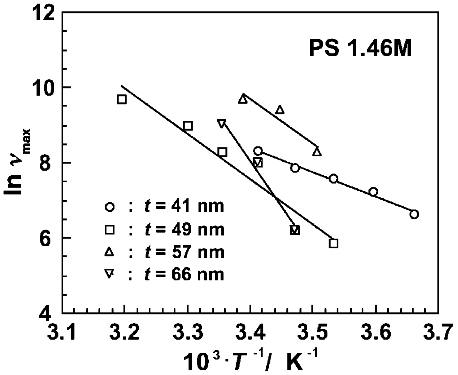

Figure 8. Semilogarithmic plots of scanning rate, at which lateral force reached maximum, vs reciprocal absolute temperature for the PS 1.46M films with various thicknesses.

Table 3. Apparent Activation Energies for the PS Films with M_n of 1.46M

t/nm	ΔH_α*/kJ mol^{-1}	ΔH_β*/kJ mol^{-1}
162	240 ± 30	
66	240 ± 30	200 ± 30
57	210 ± 20	100 ± 30
49	230 ± 30	100 ± 10
41	230 ± 30	54 ± 5

a surface relaxation temperature, an absorption peak appeared on the scanning rate–lateral force relation. And then, the peak position shifted toward the higher scanning rate side with increasing temperature. The overall profile in part a of Figure 5 clearly reflects a successive transition of the surface molecular motion from the glassy state to the rubbery one via the transition with increasing temperature. The shape of each curve in part a suggests that the master curve related to the lateral force–scanning rate relation would be obtained by the horizontal and vertical shifts.[33,36] Since an error bar was not necessarily small, only the horizontal shift, a_T, was quantitatively evaluated.

Figure 6 shows a master curve of the scanning rate–lateral force relation for the surface α_a-relaxation process drawn by horizontal and vertical shifts of each curve shown in part a of Figure 5. In this procedure, the reference temperature, T_R, of 339 K was taken. Figure 6 makes it clear that the time–temperature superposition principle can be also applied to the surface relaxation process even in the PS ultrathin film. Assuming that the shift factor, a_T, which is the amount of horizontal shift to obtain the master curve, has a functional form of Arrhenius type, the apparent activation energy for the surface α_a-relaxation process, ΔH_α*, is given by

$$\ln a_T = \frac{\Delta H_\alpha{}^*}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right) \tag{5}$$

where R and T are the gas constant and the measuring temperature, respectively. Figure 7 shows the relations between ln a_T and the reciprocal absolute temperature for the PS 1.46M films with various thicknesses ranging from 41 to 162 nm. The ΔH_α* calculated from each slope of Figure 7 are collected in Table 3. The ΔH_α* was almost 230 kJ mol^{-1} for all films employed, meaning that the ΔH_α* was independent of the film thickness within the experimental accuracy. This value was also in excellent accordance with our previous ΔH_α* of the PS thick films[33] and much smaller than the reported values for bulk PS samples.[52] From the point of view for the apparent activation energy, it seems reasonable to consider that the segmental motion at the surface is not discernibly altered by film thickness in the thickness range examined.

In the case of the surface β-process, we are not sure whether the time–temperature superposition principle is still effective. This is because the origin of the surface β-process is far from clear for the moment, although it is definitely related to the chain confinement effect as shown above. Hence, the apparent activation energy for the surface β-process, ΔH_β*, was estimated by using the relation between reciprocal measuring temperature and peak scanning rate, ν_{max}, in lieu of shift factor, as follows:

$$\Delta H_\beta{}^* = -R\,\frac{\mathrm{d}\ln \nu_{max}}{\mathrm{d}(1/T)} \tag{6}$$

Figure 8 shows semilogarithmic plots of ν_{max} vs $1/T$ for the PS 1.46M ultrathin films with various thicknesses. ΔH_β* so obtained are tabulated in Table 3 as well. ΔH_β* was smaller than ΔH_α* at a given thickness, and the value monotonically decreased with decreasing thickness in the similar fashion of $T_\beta{}^s$. Again, it is clear that the surface β-process was promoted by the chain confinement effect and possessed a quite different feature from the α_a-process corresponding to the segmental motion.

Possible Origins of Surface β-Relaxation. We finally come to discussion about what is the origin of the surface β-relaxation process observed for the PS ultrathin films. At first, aggregation states of the supported PS ultrathin film are considered. Chain dimensions parallel and normal to the surface would remain Gaussian and be flattened, respectively.[53] Also, the average mass density in the film would be almost the same as the bulk one except surface and interfacial regions.[54] Hence, intermolecular entanglement and intramolecular packing in the ultrathin film are supposed to decrease and increase, respectively. Also, it seems likely that segments in the ultrathin film are statistically oriented parallel to the surface.[46] These inclinations become remarkable with decreasing thickness and, therefore, may be correlated to the manifestation of an anomalous surface relaxation process, namely, the β-relaxation process.

Recently, de Gennes proposed a tentative hypothesis, called sliding motion, to interpret ultrathinning-induced T_g depression.[55] This mode has been thought as collective motion along the chain loop, which requires less free volume than cooperative motion. Hence, the sliding motion is possible to be taken place at a temperature lower than transition temperature for the cooperative motion. However, it does not generally appear in the bulk state due to the hindrance by end groups. In contrast, chains can slide out through the contour of loops directly contacted with the surface, implying that this mode can be easily attained near the surface region. As a result, the sliding motion alters thermal properties in ultrathin films. Thus, it is no wonder the sliding motion is observed in the measurement of surface relaxation, if any. That is, it may be possible that the surface β-relaxation process is assigned to the sliding motion. Dutcher and co-workers have presented that de Gennes' sliding motion was not observed for the PS ultrathin film with M_n smaller than 347K. This was also the case for our surface measurement using supported PS ultrathin films with M_n of 140K and 208K. Although it is too early to conclude the origin of the surface β-relaxation process, it similarly behaves as the sliding mode. An ultrathinning-induced relaxation process has been also observed in ultrathin PMMA films by broadband dielectric spectroscopy.[29]

Conclusions

Surface relaxation behavior in monodisperse PS thin and ultrathin films with M_n of 1.46M, 3.63M, and 6.24M, spun-coated on silicon wafers with a native oxide layer, was studied by LFM and then compared with that in the PS thick film. In the case of the PS thick film, a clear lateral force peak arisen from surface segmental motion was observed at a temperature well below the T_g^b of 378 K. And T_g^s so obtained for the PS thick film was 336 K, being independent of M_n in this higher M_n region. Also, surprisingly, T_g^s was independent of the film thickness. This was the case even for the 20 nm thick PS ultrathin film. This means that enhanced mobility manifested at the film surface would not owe to the distortion of surface chains. Next, it was examined whether the independence of T_g^s on the thickness could be merged to the reported data for the relation of T_g to thickness for supported PS thin and ultrathin films. Invoking that the surface layer, in which mobility is enhanced, of 5 nm, both are quite consistent. Also, once the film thickness felt short of 3−4 R_g, an additional relaxation process appeared at the surface. We called this as the surface β-relaxation. The appearance temperature and apparent activation energy of the surface β-relaxation process decreased with decreasing thickness. Although the origin of the surface β-relaxation process is far from clear for the moment, there is no doubt the surface β-relaxation is induced by ultrathinning. The surface β-relaxation similarly behaved as the sliding motion proposed by de Gennes.

Acknowledgment. This was in part supported by a Grant-in-Aid for Scientific Research (A) (#13355034) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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MA034001Y