

SURFACE RHEOLOGY OF POLYMERIC SOLIDS

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Abstract Surface molecular motions of amorphous polymeric solids have been directly measured on the basis of scanning viscoelasticity microscopic (SVM) and lateral force microscopic (LFM) measurements. SVM and LFM measurements were carried out for films of conventional monodisperse polystyrene (PS) with *sec*-butyl and proton-terminated end groups at room temperature. In the case of the number-average molecular weight, M_n , less than ca. 4.0×10^4 , the surface was in a glass-rubber transition state even though the bulk glass transition temperature, T_g , was far above room temperature, meaning that the surface molecular motion was fairly active compared with that in the bulk. LFM measurements of the monodisperse PS films at various scanning rates and temperatures revealed that the time-temperature superposition was applicable to the surface mechanical relaxation behavior and also that the surface glass transition temperature, T_g^σ , was depressed in comparison with the bulk one even though the magnitude of M_n was fairly high at 1.40×10^5 . The surface molecular motion of monodisperse PS with various chain end groups was investigated on the basis of temperature-dependent scanning viscoelasticity microscopy (TDSVM). The T_g^σ s for the PS films with M_n of 4.9×10^3 to 1.45×10^6 measured by TDSVM were smaller than those for the bulk one, with corresponding M_n s, and the T_g^σ s for M_n s smaller than ca. 4.0×10^4 were lower than room temperature (293 K). The active thermal molecular motion at the polymeric solid surface can be interpreted in terms of an excess free volume near the surface region induced by the surface localization of chain end groups. In the case of $M_n = \text{ca. } 5.0 \times 10^4$, the T_g^σ s for the α,ω -diamino-terminated PS (α,ω -PS(NH₂)₂) and α,ω -dicarboxy-terminated PS (α,ω -PS(COOH)₂) films were higher than that of the PS film. The change of T_g^σ for the PS film with various chain end groups can be explained in terms of the depth distribution of chain end groups at the surface region depending on the relative hydrophobicity.

Keywords Surface rheology, Chain end groups, Scanning force microscope

INTRODUCTION

Surface structure and surface molecular motion of polymeric solids play an important role in various practical applications. The surface structure of polymers has been extensively studied^[1, 2], however, little work has been done on the surface molecular motion of polymeric solids. In order to design highly functionalized polymer surfaces, it is necessary both to control the surface structure and to clarify the state of thermal molecular motion in the surface region.

The glass transition behavior in thin polymer films has attracted great attention. Since the thin film has a large surface to volume ratio, the influence of surface on the glass transition temperature, T_g , might be prominent. In the case of ultrathin amorphous polymer films, spectroscopic ellipsometry^[3], X-ray reflectivity^[4], positron annihilation lifetime spectroscopy^[5] and Brillouin light scattering^[6] studies have revealed that T_g is a function of the film thickness and also depends on whether the film is free-standing or in contact with a substrate. Depending on the extent of polymer/substrate interaction, T_g of ultrathin films increases or decreases in comparison with that

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for a bulk region^[3-6]. However, little study has been done on the direct measurement of glass transition behavior at the free surface of bulk polymers. The molecular dynamics simulation of atactic polypropylene on graphite predicted a decrease in density at the air/polymer interfacial region^[7]. Also, the Monte Carlo simulation of amorphous polyethylene revealed that the mobility increased toward the free surface due to the decrease in density^[8].

Scanning force microscopy (SFM) is one of the family of scanning probe microscopy techniques and has proven to be useful for investigation of the surface morphology of materials with high resolution^[9, 10]. SFM images were created on the basis of the various forces acting between cantilever tip and sample surface such as van der Waals, electrostatic, frictional, magnetic forces, *etc.* The atomic force microscope (AFM) is becoming a widely used instrument for the observation of surface topography, which is obtained by detecting the normal force acting between the sample surface and the probe tip. The magnitude of the modulus for the generally used silicon or silicon nitride probe tip is ca. 300 GPa, which is higher than that of the polymer surface. Therefore, when the observation is carried out in a repulsive force region, the sample surface can be deformed due to the indentation of the probe tip.

Lateral force microscopy (LFM) creates an image of lateral forces acting between the sliding cantilever tip and the surface^[11]. Since the frictional behavior of polymeric solids is closely related to their dynamic viscoelastic properties^[12], it is possible to investigate surface molecular motions of the polymeric solids by using LFM^[13]. The modulation of tip indentation leads to that of the force acting between the sample surface and the tip. If the sinusoidal modulation of tip indentation is applied to the sample surface (stimulation strain), the dynamic viscoelastic properties at the sample surface can be evaluated by measuring both the amplitude of the modulated response stress signal and the phase lag between stimulation strain and modulated deformation signal (response stress)^[14, 15]. A forced modulation AFM device, called a "scanning viscoelasticity microscope (SVM)", was designed by remodeling a commercially available AFM^[16]. The purpose of this study is to reveal the surface rheological properties of polymeric solids on the basis of SVM and LFM measurements.

SVM Studies on the Surface Molecular Motion of Monodisperse Polystyrene Films with Various Molecular Weights

SVM was first applied to the measurement of surface modulus and surface $\tan\delta$ of the monodisperse PS films at room temperature^[17]. The monodisperse sample was used to avoid the influence of low M_n components, which migrate to the surface region in polydisperse samples. Monodisperse PSs were synthesized by a living anionic polymerization at 293 K using *sec*-butyllithium as an initiator. The polymerization was terminated by the addition of methanol. The magnitudes of the number-average molecular weight, M_n , and the polydispersity index, M_w/M_n where M_w denotes the weight-average molecular weight, were determined via gel permeation chromatography (GPC) with polystyrene standards. Bulk T_g was evaluated on the basis of differential scanning calorimetric (DSC 8230, Rigaku Co., Ltd.) measurements at a heating rate of 10 K $\cdot$ min⁻¹ under dry nitrogen purge. The PS films of ca. 200 nm thickness were obtained by film casting from a toluene solution onto a silicon wafer with native oxide layer. The surface dynamic viscoelastic properties of the PS films were evaluated on the basis of SVM measurements, which were performed at 293 K in air in a repulsive force region. A commercially available silicon nitride (Si₃N₄) cantilever with integrated tips was used. The nominal spring constant of the cantilever was 0.09 N $\cdot$ m⁻¹. The modulation frequency and amplitude at the supporting part of the cantilever were 4 kHz and 1.0 nm, respectively.

The SFM apparatus used in this study is a SPA 300 (Seiko Instruments Industry Co., Ltd.) with an SPI 3700 controller. The cantilever is mounted on the piezoelectric transducer which has a resonance frequency of 1 ~ 10 kHz depending on the magnitude of an applied electric field. The cantilever position in the *z*-direction is sinusoidally modulated by applying an a.c. electric field to the piezoelectric transducer. The deflection of the cantilever is measured by a position-sensitive photodiode (PSD) and feeds into the feedback loop that controls the distance between tip and sample surface. The modulated force is also detected by the deflection of the cantilever. The deflection signal obtained with the PSD is filtered by a band-pass filter (BPF) in order to remove

the high- and low-frequency noises and feeds into a two-phase lock-in amplifier. The reference signal used is the sinusoidal signal from the frequency generator, which corresponds to the dynamic strain signal.

The surface dynamic viscoelastic functions of the monodisperse PS films were evaluated on the basis of SVM measurements. Figure 1 shows the molecular weight dependence of the surface dynamic storage modulus, E' , and surface $\tan\delta$ for the monodisperse PS films as well as the bulk $\tan\delta$ and bulk T_g values. Since, in a higher M_n range from 4.04×10^4 to 1.8×10^6 , there is only a slight M_n influence on the magnitude of the surface E' , it seems reasonable to consider that the influence of the chain end groups is negligible with respect to the magnitude of the surface E' . Especially in the case of the PS film with M_n of 1.8×10^6 , since the concentration of chain end group is extremely low, it can be assumed that the thermal molecular motion at the film surface is the same as that for the bulk sample even if the chain end groups are preferentially segregated at the film surface. Then, on the assumption that the magnitude of the surface E' is the same as that of the bulk E' at 293 K, the instrumental calibration constant was determined. In a M_n range higher than 4.04×10^4 , the magnitudes of the surface E' and surface $\tan\delta$ were constant and their magnitudes were ca. 4.5 GPa and 0.01, respectively, as shown in Fig. 1. This apparently indicates that the surface is in a glassy state at 293 K for a PS film with M_n larger than 4.04×10^4 , judging from the magnitudes of the surface E' and surface $\tan\delta$. Also, in the case of M_n smaller than 2.66×10^4 , the magnitudes of the surface E' and surface $\tan\delta$ decreased and increased with a decrease in M_n , respectively. The magnitudes of the surface E' and surface $\tan\delta$ indicate that the surface of the PS film with M_n lower than 2.66×10^4 is in a glass-rubber transition state even at 293 K. The bulk dynamic viscoelastic properties of the monodisperse PS sample were measured in order to compare them with those at the surface. Since, in the case of M_n smaller than 4.04×10^4 , the PS film was very fragile, dynamic spring analysis was applied to evaluate the bulk $\tan\delta$ ^[18]. In the case of M_n smaller than 2.66×10^4 , the magnitude of surface $\tan\delta$ was much higher than that of bulk $\tan\delta$, as shown in Fig. 1. This indicates that the M_n dependence of surface T_g for the PS film is more prominent than the bulk T_g , because the chain end effect on the molecular motion at the film surface is more distinct than that for in the bulk due to the surface localization of chain end groups, which will be discussed in later section. The absence of permanent deformation after the measurement was confirmed by AFM imaging. This means that the deformation has been done in the nearly linear viscoelastic region. From the results obtained here, it seems reasonable to conclude that the thermal molecular motion at the film surface is more active in comparison with that for the bulk sample especially in the case of M_n smaller than ca. 4.0×10^4 .

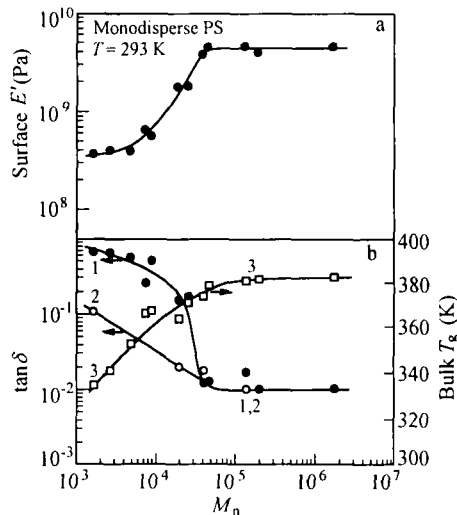


Fig. 1 a) Molecular weight dependence of surface E' and surface $\tan\delta$ for the monodisperse PS films at 293 K; b) bulk $\tan\delta$ and bulk T_g values were evaluated by using Rheovibron and DSC, respectively

● surface $\tan\delta$, ○ bulk $\tan\delta$, □ bulk T_g

Temperature Dependence of Lateral Force for Monodisperse Polystyrene Films

LFM is a useful tool for the scanning rate and temperature dependent two-dimensional measurements of lateral force. The lateral force between solid surface and sliding cantilever tip on a nanometer scale can be evaluated by detecting the torsion of the sliding cantilever. Figure 2 shows schematic representation of the lateral force-scanning rate curve evaluated by LFM. The scanning rate dependence of lateral force corresponds well to the frequency dependence of the dynamic loss modulus, E'' . In the cases of the glassy surface or the rubbery one, no distinct scanning rate dependence of lateral force is observed, whereas in the case of the surface in a glass-rubber transition state a maximum peak of frictional (lateral) force with the scanning rate is generally observed due to the appearance of the E'' maximum in a transition region. Therefore, when the magnitude of lateral force evaluated by LFM exhibits an apparent scanning rate dependence, it can be concluded that the surface is in a glass-rubber transition state.

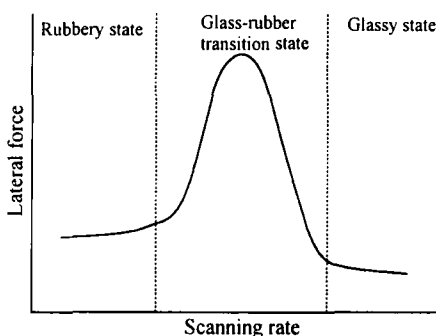


Fig. 2 Schematic representation of the lateral force-scanning rate curve evaluated by LFM

The scanning rate dependence of lateral force was measured with SFM. The tip indent depth evaluated by Hertz's elastic theory^[19] was ca. 1.1 nm. Also, the scanning rate, v , of LFM measurement can be converted to the frequency, f , of SVM measurement based on Hertz's elastic theory as given by Eq. (1).

$$v = 2f \left[\frac{3}{4} \left(\frac{1 - \mu_{\text{tip}}^2}{E_{\text{tip}}} + \frac{1 - \mu_{\text{polymer}}^2}{E_{\text{polymer}}} \right) RF_c \right]^{1/3} \quad (1)$$

where μ , E , R and F_c are the Poisson ratio, modulus, the tip radius, and contact force, respectively. The scanning rate of our LFM measurement was in the range from $10^2 \text{ nm} \cdot \text{s}^{-1}$ to $10^5 \text{ nm} \cdot \text{s}^{-1}$. It might be impossible to obtain the lateral force-scanning rate curve over a very wide range of scanning rate from a glassy to a rubbery state, as shown in Fig. 2, at a given temperature of 293 K. Then, the scanning rate dependence of lateral force was measured at various temperatures in order to apply the rheological time-temperature superposition principle. A scanning stage of LFM was heated to a certain measuring temperature under vacuum. A piezoscanner was thermally insulated from the heating stage. LFM measurements were carried out in vacuo in order to reduce a capillary force effect induced by surface-adsorbed water. The double gold coated cantilever with the bending spring constant of $0.09 \text{ N} \cdot \text{m}^{-1}$ was used in order to reduce cantilever deflection due to the difference in thermal expansion constants between Si_3N_4 and gold.

Figure 3 shows the scanning rate dependence of lateral force as a function of temperature for the monodisperse PS film with $M_n = 1.4 \times 10^5$ ^[20]. In a lower temperature range at 333 K, the scanning rate dependence of lateral force was apparently not observed. This indicates that the surface of the monodisperse PS film with $M_n = 1.4 \times 10^5$ is in a glassy state and the surface T_g is higher than 333 K. On the other hand, in a temperature range from 343 K to 353 K, the magnitude of the lateral force increased with decreasing scanning rate, especially in a lower scanning rate region. The scanning rate, at which the magnitude of lateral force starts to increase with decreasing scanning rate, was shifted to the higher scanning rate with an increase in measuring

temperature from 343 K to 363 K. The scanning rate dependent behavior of the lateral force at 343 K to 363 K clearly indicates that the surface is in a glass-rubber transition state in a lower scanning rate region. Since the bulk T_g of PS with $M_n = 1.4 \times 10^5$ evaluated by DSC was 380 K, it seems reasonable to conclude that the surface T_g was depressed compared with the bulk one even though the molecular weight of the monodisperse PS is fairly high at 1.4×10^5 . Also, in a temperature range from 363 K to 383 K, a distinct peak was observed on the scanning rate-lateral force curve. At 383 K the magnitude of the lateral force decreased over a wide scanning rate region with a decrease in the scanning rate. This indicates that the PS surface turns into a rubbery state.

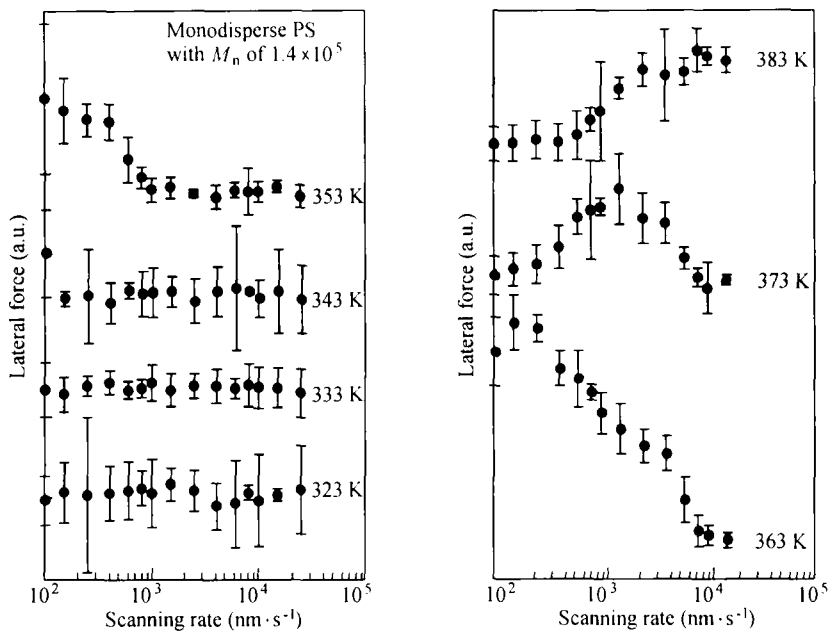


Fig. 3 Scanning rate dependence of lateral force for the monodisperse PS film with $M_n = 1.4 \times 10^5$ as a function of temperature

Figure 4 shows a master curve drawn by horizontal and vertical shifts of each of the curves shown in Fig. 3. The reference temperature was 363 K for $M_n = 1.4 \times 10^5$. Since the plot in Fig. 4 is very similar to the schematic curve shown in Fig. 2, it seems reasonable to consider as a general concept or trend that the scanning rate dependence of the lateral force exhibits a peak in a glass-rubber transition and also that is not observed in a glassy region and a rubbery one. Figure 4 clearly indicates that the time-temperature superposition, which is characteristic of amorphous bulk polymeric materials at around T_g , can also be applied to the surface rheological analysis of an α_a -relaxation process corresponding to glass transition behavior. The relationships between horizontal shift factor, a_T and reciprocal measuring temperature followed the Arrhenius type equation. Then, the magnitude of the activation energy for the surface α_a -relaxation process (surface micro-Brownian motion) calculated from the slope of the a_T versus $1/T$ plot was $220 \text{ kJ} \cdot \text{mol}^{-1}$. This magnitude is lower than that for the reported bulk value of $360 \text{ kJ} \cdot \text{mol}^{-1}$ [21]. At the air-polymer interface, an excess free volume is induced by the surface localization of the chain end groups, and also the degree of freedom of polymeric segments in contact with the air might be greater than that in the bulk state. Then, it can be predicted from the magnitude of the activation energy that the energy barrier and/or the size of thermal molecular motion for the α_a -relaxation process at the film surface might be depressed in comparison with those for the bulk one.

Molecular Weight Dependence of Lateral Force of Monodisperse Polystyrene Films

Figure 5 shows the scanning rate dependence of lateral force as a function of M_n for the monodisperse PS film. Since no distinct scanning rate dependence of the lateral force was observed for the monodisperse PS with $M_n = 1.4 \times 10^5$, it seems reasonable to consider that the surface is in a glassy state. On the other hand, the magnitude of

the lateral force for a monodisperse PS film surfaces with M_n lower than 4.04×10^4 was apparently dependent on the scanning rate. In the case of monodisperse PS with $M_n = 4.04 \times 10^4$, although the scanning rate dependence of the lateral force was not observed in a higher scanning rate region, the lateral force increased with a decrease in the scanning rate in a lower scanning rate region. Then, this result indicates that the surface of the monodisperse PS film with $M_n = 4.04 \times 10^4$ is in a glass-rubber transition state and a glassy one in low and high scanning rate regions, respectively. Therefore, the curve b in Fig. 5 indicates that the surface measured by using SVM at 4 kHz is in a glassy state. Since the lateral force continuously increased with a decrease in the scanning rate for the PSs with M_n of 2.66×10^4 and 1.97×10^4 , it can be concluded that the surface is in a glass-rubber transition state at 293 K. Moreover, in the case of PSs with $M_n = 9.0 \times 10^3$ and 4.9×10^3 , the peak was clearly observed on the lateral force-scanning rate curve. This indicates that the surface of the monodisperse PS films with $M_n = 9.0 \times 10^3$ and 4.9×10^3 is already in a glass-rubber transition state at 293 K, even though the bulk T_g is around 360 K as shown in Fig. 1. Since the peak on the lateral force-scanning rate curve for the monodisperse PS film with $M_n = 9.0 \times 10^3$ appears in a lower scanning rate region in comparison with that for $M_n = 4.9 \times 10^3$, it is envisaged that the surface T_g for the monodisperse PS film with $M_n = 9.0 \times 10^3$ is higher than that with $M_n = 4.9 \times 10^3$. The above-mentioned LFM results agreed well with SVM ones.

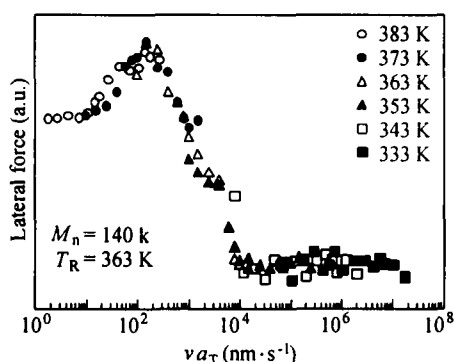


Fig. 4 Master curve of PS with $M_n = 1.4 \times 10^5$ drawn by horizontal and vertical shifts of each curve shown in Fig. 3 as a reference temperature of 363 K

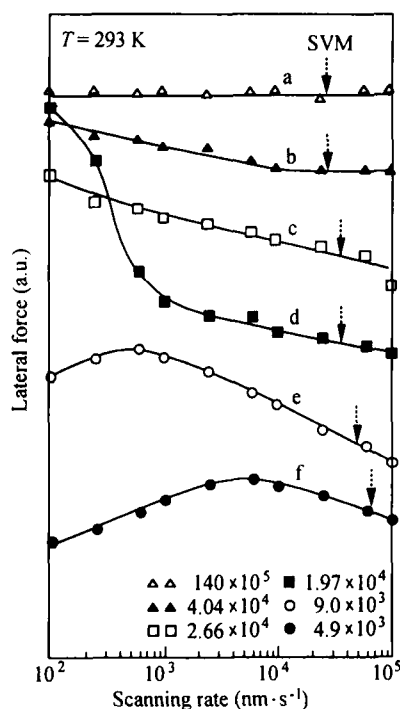


Fig. 5 Scanning rate dependence of lateral force for the monodisperse PS film at 293 K as a function of M_n

As shown in Fig. 1, the magnitude of the surface E' decreases with a decrease in M_n at 293 K and also, in general, it decreases with a rise in measuring temperature. Therefore, from the point of view of a variation of surface E' , the M_n dependence of the surface E' at 293 K qualitatively corresponds to the measuring temperature dependence of the surface E' by using the monodisperse PS film with a certain M_n . Then, it is reasonably expected that a master curve based on scanning rate-lateral force superposition can be obtained from Fig. 5. This master curve may be similar to the master curve based on time-temperature superposition. Figure 6 shows the scanning rate dependence of lateral force for the monodisperse PS films with different M_n s at 293 K. Figure 6

suggests that the lateral force-scanning rate master curve can be constructed on the basis of the lateral force measurement of the monodisperse PS films with various M_n s at a certain temperature.

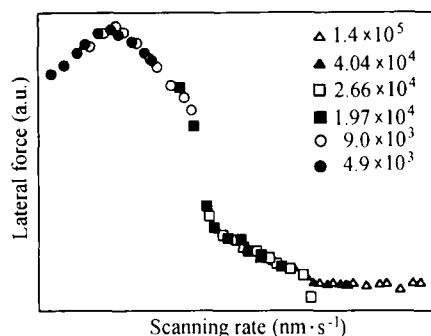


Fig. 6 Master lateral force-scanning rate curve for the monodisperse PS films with various M_n s at 293 K drawn from the results in Fig. 5

Temperature-Dependent SVM Study of Monodisperse Polystyrene Films

The purpose of this section is to evaluate the influence of the chain end chemistry on the magnitude of surface T_g , T_g^σ for the monodisperse PS films with various M_n s on the basis of temperature-dependent SVM (TDSVM)^[22].

The polymers used in this study were monodisperse PSs with various chain end chemistries, and were synthesized by a living anionic polymerization. α,ω -Diamino-terminated PS (α,ω -PS(NH₂)₂) and α,ω -dicarboxy-terminated PS (α,ω -PS(COOH)₂) were synthesized using a bifunctional initiator. In order to investigate the surface molecular motion of these PS films, the surface dynamic viscoelastic function, in other words, the surface phase lag between dynamic deformation and force signals, were measured as a function of temperature.

Figure 7 shows the temperature dependence of the surface phase lag, δ^σ between imposed stimulation displacement and detected response force signals, and the bulk $\tan\delta$ for the monodisperse PS films with M_n = 4.9×10^3 , 30×10^4 , 2.5×10^5 and 1.45×10^6 . The temperature dependence of bulk $\tan\delta$ was obtained by dynamic spring analysis at 3.5 Hz. Though it might be possible that the measured δ^σ contains the contribution of the phase lag from the mechanical vibration system^[23], the calibration has not been done at the present time because of the difficulty in the determination of the calibration constant. Figure 7 shows the α_a loss peaks corresponding to the surface and bulk micro-Brownian motion of polymeric chains, respectively. The peaks of δ^σ s appeared in a lower temperature region than those of bulk $\tan\delta$ s, though the δ^σ and the bulk $\tan\delta$ were measured at 4 kHz and 3.5 Hz, respectively. The threshold temperature, that is, the temperature at which the magnitude of δ^σ or bulk $\tan\delta$ starts to increase, can be empirically used as the surface or bulk T_g s^[24]. Then, in this study, these threshold temperatures of the δ^σ and the bulk $\tan\delta$ were defined as T_g^σ and bulk T_g , respectively. The T_g^σ and bulk T_g are marked by arrows in Fig. 7. The T_g s were more apparently shifted to a higher temperature with an increase in M_n than bulk T_g s, as shown in Fig. 7. Therefore, it seems reasonable to conclude that the surface thermal molecular motion is more activated in comparison with the bulk one. Also, the T_g^σ for the PS film was strongly dependent on the M_n as compared with the bulk one. These results indicate that the surface molecular motion of the monodisperse PS film is closely related to the concentration of chain end groups at the film surface. Since the magnitudes of the T_g^σ for the PS films with M_n lower than ca. 4.0×10^4 were below 293 K, it seems reasonable to conclude that the PS films surface with M_n lower than ca. 4.0×10^4 is in a glass-rubber transition state or a rubbery state, even at room temperature. The T_g^σ asymptotically approaches the bulk one with an increase in M_n and the T_g^σ for high M_n of ca. 1.5 M was slightly lower than the bulk one. Therefore, these results apparently indicate that a reduction of T_g^σ of PS in comparison with bulk T_g may be caused by an increased free volume at the surface due to the preferential surface enrichment of chain end groups^[25] as well as the decrease in number of chain entanglement density^[26]. Also, these results support our previous result that the magnitude of the activation energy for the

surface α_a -relaxation process at the air-polymer interface was almost half as much as that for the bulk one, maybe due to an extra freedom for the active thermal segmental motion of PS chains at the air-polymer interface^[20].

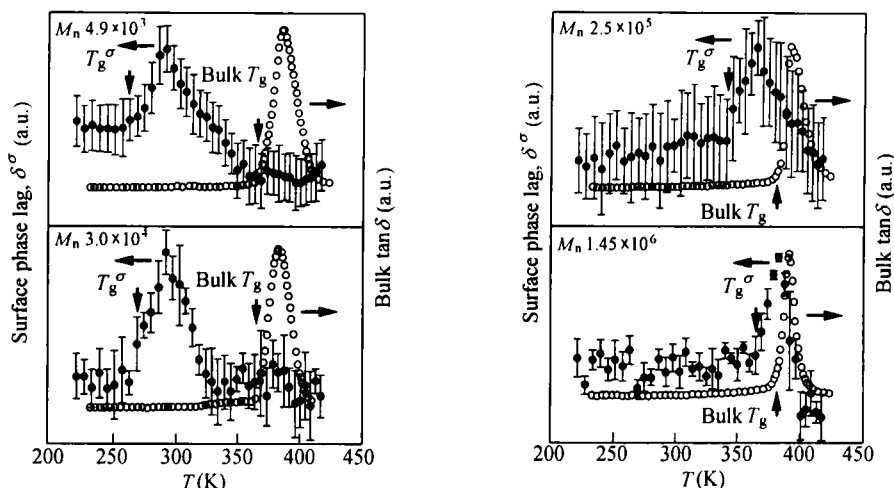


Fig. 7 Temperature dependence of the surface phase lag, δ^σ between imposed stimulation displacement and detected response force signals, and the bulk $\tan\delta$ for the PS films with M_n s = 4.9×10^3 , 3.0×10^4 , 2.5×10^5 , and 1.45×10^6

The previous results revealed that the surface molecular motion of the monodisperse PS film was closely related to the distribution of chain end groups at the outermost surface. However, the surface molecular motion of the PS film with different kind of chain end groups has not been evaluated yet. PSs with both chain end groups of amino and carboxyl groups were prepared, and the T_g^σ s of these PSs were measured based on TDSVM. Figure 8 shows the temperature dependence of the δ^σ and the bulk $\tan\delta$ for a) the α,ω -diamino-terminated PS (α,ω -PS(NH₂)₂) films with M_n s = 2.3×10^4 and 5.2×10^4 and b) the α,ω -dicarboxy-terminated PS (α,ω -PS(COOH)₂) films with M_n s = 1.2×10^4 and 5.2×10^4 . The peaks of δ^σ due to the surface α_a -relaxation process were observed for all δ^σ -temperature curves and appeared in a lower temperature region than those of bulk $\tan\delta$ s, as shown in Figs. 8a) and b). As mentioned above, it is empirically accepted that the threshold temperatures of δ^σ and bulk $\tan\delta$ were decided as T_g^σ and bulk T_g , respectively. In the same manner as PS, the magnitude of the T_g^σ s for the α,ω -PS(NH₂)₂, α,ω -PS(COOH)₂, was lower than the bulk one. However, these T_g^σ s were strongly dependent on the end group chemistry. At the same M_n , the T_g^σ s for the α,ω -PS(NH₂)₂, and α,ω -PS(COOH)₂ films were higher than that for the PS film.

Figure 9 shows the molecular weight dependence of the surface and bulk T_g s for the monodisperse PS films with various chain end groups. The T_g^σ s of α,ω -PS(NH₂)₂ and α,ω -PS(COOH)₂ were higher than that of PS with corresponding M_n . Since both chain end groups for α,ω -PS(NH₂)₂ and α,ω -PS(COOH)₂ have higher surface free energy in comparison with the main chain part, the chain end groups are depleted from the outermost surface region. Also, because α,ω -PS(COOH)₂ are intermolecularly associated via hydrogen bonding, the apparent molecular weight of α,ω -PS(COOH)₂ increases. Thus, it seems reasonable to conclude that the T_g^σ s of α,ω -PS(COOH)₂ were higher than those of α,ω -PS(NH₂)₂ and PS at the same M_n .

CONCLUSION

SVM and LFM measurements for the monodisperse PS films were carried out in order to investigate the surface molecular motion. It was revealed that the monodisperse PS film surface with M_n less than ca. 4.0×10^4 was in a glass-rubber transition state even at 293 K due to an excess free volume at the air/polymer interface induced by the surface localization of chain end groups. Also, temperature dependent LFM measurements of the monodisperse PS films revealed that the time-temperature superposition was applicable to the surface relaxation

behavior and the T_g^σ was lower than the bulk one even though M_n was as high as 1.4×10^5 .

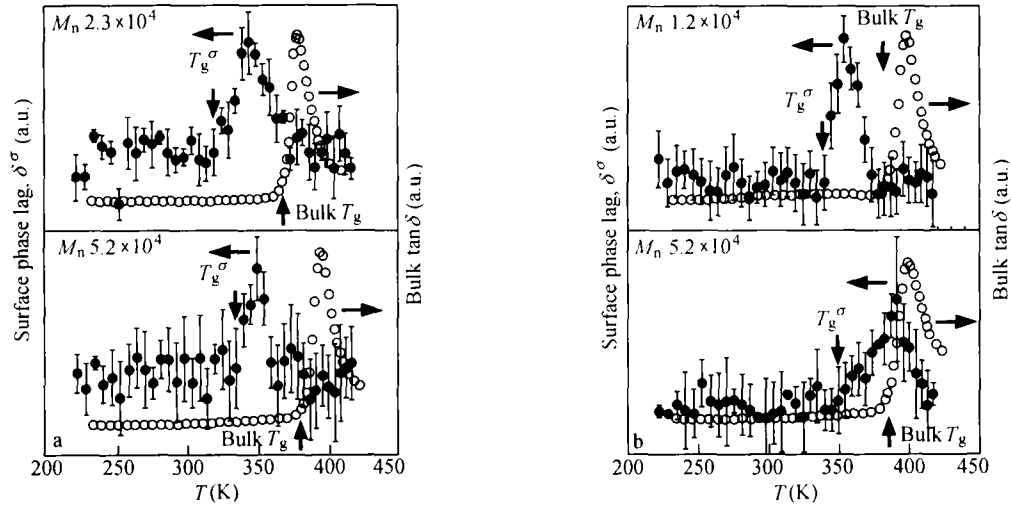


Fig. 8 Temperature dependence of the δ^σ and the bulk $\tan \delta$ for a) the α,ω -diamino-terminated PS (α,ω -PS(NH₂)₂) films with M_n s of 2.3×10^4 and 5.2×10^4 , and b) the α,ω -dicarboxy-terminated PS (α,ω -PS(COOH)₂) films with M_n s of 1.2×10^4 and 5.2×10^4

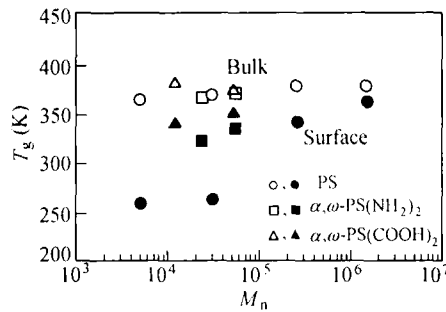


Fig. 9 Molecular weight dependence of the surface and bulk T_g s for the monodisperse PS films with various chain end groups
The filled and open symbols denote the data for T_g^σ and bulk T_g , respectively

The molecular weight dependences of T_g^σ for the monodisperse PS films with various chain end groups were evaluated by TDSVM measurements. The T_g^σ s for the various chain end group terminated PS films were considerably lower than the bulk ones, and the T_g^σ was strongly dependent on a difference of surface free energy between chain end group and main chain part. The difference of T_g^σ was explained by the surface concentration of chain end groups, which is closely related to the free volume fraction.

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