# Determination of Surface Glass Transition Temperature of Monodisperse Polystyrene Based on Temperature-Dependent Scanning Viscoelasticity Microscopy

**Noriaki Satomi, Atsushi Takahara, and Tisato Kajiyama***

*Department of Materials Physics & Chemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

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**Introduction.** The structure and physical properties of polymeric solid surface are crucial for the various applications of polymer solids. The glass transition temperature, $T_g$, is the fundamental parameter of a polymer which is most closely related to the state of thermal molecular motion. The investigations of influence of the surface and confined states on $T_g$ have become one of the most fundamental interests in polymer surface science. In the cases of ultrathin polymer films, the glass transition behavior has been evaluated based on the spectroscopic ellipsometry,[1] the X-ray reflectivity,[2] the positron annihilation lifetime spectroscopy,[3] and the Brillouin light scattering.[4] These measurements revealed that the magnitude of $T_g$ for the ultrathin film depended on the film thickness and the state of interaction between polymer chain and substrate. Since these measurements were based on the changes in average physicochemical properties of polymer ultrathin films as a function of temperature, it is difficult to measure the molecular motion of polymer film at the outermost surface region. The outermost surface region is defined to be the region extending to twice the radius of gyration of an unperturbed chain, $2\langle S^2\rangle^{1/2}$ from the top surface into film. $\langle S^2\rangle^{1/2}$ is expressed by eq 1, where $N$ is the degree of polymerization and $b$ is the average statistical segment length.

$$\langle S^2\rangle^{1/2} = (Nb^2/6)^{1/2} \tag{1}$$

Scanning force microscopy (SFM) is a novel tool used to evaluate the surface structure and the surface molecular motion of polymeric solids.[5] SFM can directly evaluate the physicochemical properties at the outermost surface region on the basis of the deflection and torsion of the cantilever, which reflects atomic force, adhesion, friction, and magnetic or chemical interaction between the tip and the polymer surface. In our previous study, the surface relaxation process for monodisperse polystyrene (PS) films with different number-average molecular weights, $M_n$, has been investigated on the basis of lateral force microscopy (LFM)[6] and scanning viscoelasticity microscopy (SVM).[7] SVM measurements revealed that, in the case of the monodisperse PS films with $M_n$ less than ca. 30k, the film surface was in a glass−rubber transition state or in a rubbery state at room temperature, even though the bulk $T_g$, $T_{g,b}$, was far above room temperature.[7] Also, it was revealed from the temperature-dependent LFM that the magnitude of activation energy for the surface $\alpha_a$-relaxation process of the monodisperse PS film is almost half as much as that for the bulk one.[8] However, a temperature-dependent LFM measurement cannot directly evaluate the magnitude of surface $T_g$, $T_{g,s}$, from the scanning rate−lateral force relationship as a function of measuring temperature. The purpose of this study is to evaluate directly the magnitude of $T_g$ of the outermost surface for the monodisperse PS films with different $M_n$s on the basis of temperature-dependent SVM.

**Table 1. Characterizations of Monodisperse PSs Used in This Study**

| $M_n$ | $M_w/M_n$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| 4.9k | 1.09 | 90k | 1.05 |
| 30k | 1.08 | 250k | 1.03 |
| 54k | 1.03 | 1,450k[a] | 1.06 |

[a] Purchased from Pressure Chemical Co., Ltd.

**Experimental Section.** Monodisperse PSs used in this study were synthesized by a living anionic polymerization at 293 K using *sec*-butyllithium as an initiator. The end groups of the PSs used in this study are *sec*-butyl and $-CH_2-CH_2(C_6H_5)$ groups. Table 1 tabulates the $M_n$ and molecular weight dispersity, $M_w/M_n$, for the monodisperse PSs used in this study. The magnitudes of these were determined via gel permeation chromatography (GPC) with polystyrene standards. The monodisperse PS was used in order to avoid the influence of surface migration of the lower $M_n$ in polydisperse PSs. The PS films were coated from a toluene solution onto cleaned silicon wafer by a spin-coating method at the spin-speed of 2 krpm. These films were annealed at 423 K for 24 h in vacuo in order to achieve the thermal equilibrium state. The film thicknesses evaluated by the ellipsometric measurement were ca. 200 nm. Atomic force microscopic (AFM) observation before and after SVM scanning revealed that the surface of PS films were smooth in a scanning area of $\sim 1\ \mu m^2$.

The temperature dependence of the surface dynamic viscoelastic function, in other words, the surface phase lag between imposed stimulation displacement and detected response force signals for the monodisperse PS films was measured on the basis of temperature-dependent SVM in order to evaluate the $T_{g,s}$. The temperature-dependent SVM equipment was SPA 300HV (Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. Temperature-dependent SVM measurement was carried out at various temperatures in vacuo under a reference force of ~1 nN (repulsive force). The modulation frequency and the modulation amplitude at the supporting part of the cantilever were 4 kHz and 1.0 nm, respectively. A commercially available silicon nitride ($Si_3N_4$) tip on a rectangular cantilever with the bending spring constant of 0.09 $N \cdot m^{-1}$ (Olympus Co., Ltd.) was used. Both sides of the cantilever were coated with gold in order to reduce the temperature-induced bending of the cantilever due to the difference in the thermal expansion coefficients between $Si_3N_4$ and gold as small as possible. No damage on the surface was observed after temperature-dependent SVM measurement by AFM.

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* To whom correspondence should be addressed. Telephone: +81-92-642-3558. Fax: +81-92-651-5606. E-mail: tkajitcf@mbox.nc.kyushu-u.ac.jp.

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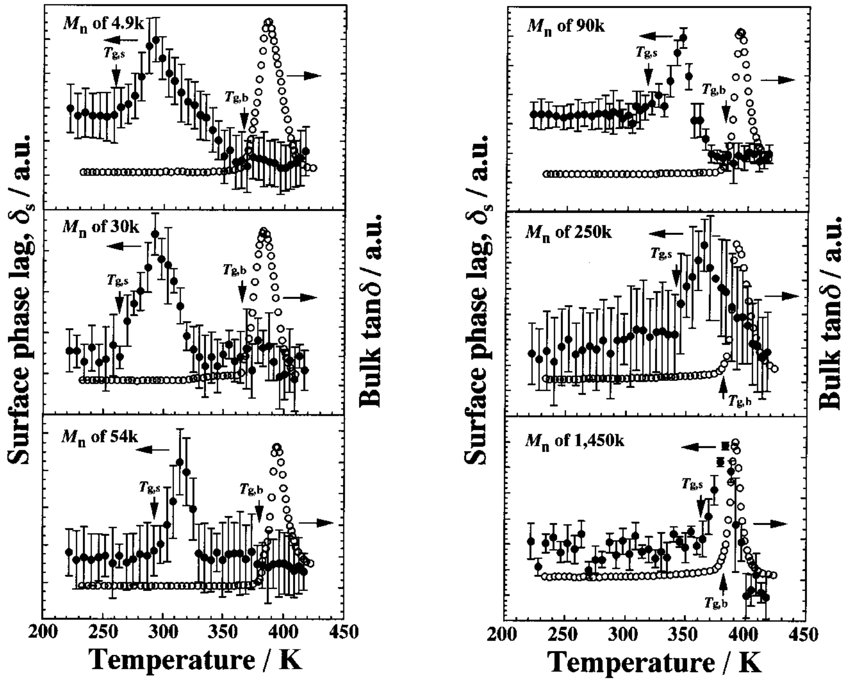

**Figure 1.** Temperature dependence of $\delta_s$ and bulk tan $\delta$ for the monodisperse PS films.

To compare the surface molecular motion with the bulk one, the bulk loss tangent, tan $\delta$ was measured with Rheovibron (DDV-01FP, Orientec A&D Co., Ltd.). Similar samples were run separately in SVM and Rheovibron measurements to determine the surface and bulk $T_g$s. The PS film was supported on the copper spiral spring by the solvent-casting method, since a PS film with low $M_n$, which had sufficient strength to withstand the applied dynamic displacement, could not be prepared. Since the toluene solution of PS with 3 wt % is coated on the copper spiral spring repeatedly in the process of solvent-casting method, the PS film thickness is thick enough to neglect the effect of substrate/film interface. The sample for Rheovibron measurement was dried at 423 K for 5 days under vacuum.

**Results and Discussion.** Figure 1 shows the temperature dependence of the surface phase lag, $\delta_s$, between imposed stimulation displacement and detected response force signals and the bulk tan $\delta$ for the monodisperse PS films with $M_n$s of 4.9k, 30k, 54k, 90k, 250k, and 1,450k. The temperature dependence of bulk tan $\delta$ was obtained by Rheovibron at 3.5 Hz. Though it might be possible that the measured $\delta_s$ contains the contribution of the phase lag from the mechanical vibration system, the calibration has not been done at the present time, because of the difficulty in determination of the calibration constant. However, it seems reasonable to compare qualitatively the temperature dependence of the $\delta_s$ and the bulk tan $\delta$ to decide the $T_{g,s}$ and the bulk one since the calibration constant might not change so much in the temperature range around these $T_{g,s}$s. Figure 1 shows the $\alpha_a$ loss peaks corresponding to the surface and bulk micro-Brownian motion of polymeric chains, respectively. The peaks of $\delta_s$s appeared in a lower temperature region than those bulk tan $\delta$s, though $\delta_s$ and bulk tan $\delta$ were measured at 4 kHz and 3.5 Hz, respectively. The onset temperature, that is, the temperature at which the magnitude of $\delta_s$ or bulk tan $\delta$ starts to increase, can be empirically used as the surface or bulk $T_g$s.[9] $T_{g,s}$ and $T_{g,b}$ are shown by the arrows in Figure 1. $T_{g,s}$s were more apparently shifted to a higher temperature region with an increase in $M_n$ than $T_{g,b}$s, as shown in Figure 1. Therefore, it seems reasonable to conclude that the surface thermal molecular motion is more activated in comparison with the bulk one.

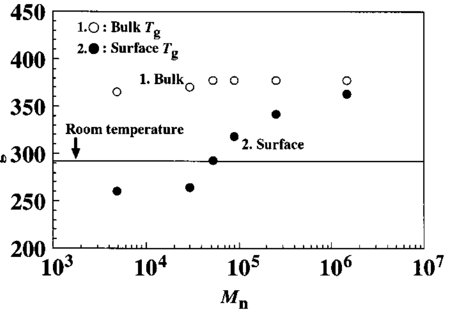

**Figure 2.** Molecular weight dependence of $T_{g,s}$ and $T_{g,b}$ for the monodisperse PS films.

Figure 2 shows the molecular weight dependence of the surface and bulk $T_g$s for the monodisperse PS films. As mentioned above, the onset of an increase in the $\delta_s$ and the bulk tan $\delta$, shown by arrows in Figure 1, can be empirically defined as the surface and bulk $T_g$s, respectively. The $T_{g,s}$ for the PS film was strongly dependent on the $M_n$ as compared with the bulk one and was lower than that for the bulk one. Since the magnitudes of the $T_{g,s}$ for the PS films with $M_n$ lower than ca. 50k were below 293 K. It seems reasonable to conclude that the PS film surface with $M_n$ lower than ca. 50k is in a glass–rubber transition state or a rubbery state, even at room temperature, 293 K. The $T_{g,s}$ approaches the bulk one with an increase in $M_n$ and the $T_{g,s}$ for high $M_n$ of ca. 1,000k was slightly lower than the bulk one, as shown in Figure 2. Therefore, Figure 2 apparently indicates that the reduction of $T_{g,s}$ in comparison with $T_{g,b}$ may be caused by the effect of increased free volume at the surface due to a preferential surface enrichment of chain end groups[6] as well as the effect that surface micro-Brownian motion of polymer chains at the air–polymer interface has an extra freedom compared with bulk one. Also, Figure 2 supports our previous result that the magnitude of activation energy for the surface $\alpha_a$-relaxation process at the air–polymer interface was almost half as much as that for the bulk one, maybe due to the extra freedom for the active thermal segmental motion of PS chains at the air–polymer interface.[8]

In conclusion, the thermal molecular motion at the outermost surface of the PS film was successfully measured directly on the basis of temperature-dependent SVM. Then, it became possible to compare directly the surface and bulk thermal molecular motions of the polymeric solid film, based on the temperature dependences of the $\delta_s$ and the bulk tan $\delta$. It was revealed that the $T_{g,s}$ was depressed in comparison with the $T_{g,b}$, even though $M_n$ was as high as 1450k, perhaps due to the extra freedom at the air–polymer interface with respect to the surface micro-Brownian motion. Since the $T_{g,s}$ for the PS films with $M_n$ lower than ca. 50k was below 293 K, it seems reasonable to conclude that the surface is in a glass–rubber transition state or a rubbery state even at room temperature.

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