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Molecular Weight Dependence of Surface Dynamic Viscoelastic Properties for the Monodisperse Polystyrene Film

Keiji Tanaka, Aki Taura, Shou-Ren Ge,
Atsushi Takahara, and Tisato Kajiyama*

Department of Chemical Science & Technology,
Faculty of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-81, Japan

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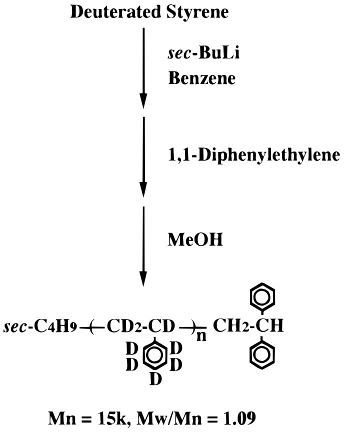
Introduction. Surface molecular motion has received a great amount of attention recently,[1−6] due to its importance in practical applications such as permselective membranes, biomaterials, adhesives, and so on. The authors investigated the depth dependence of the surface glass transition temperature, T_g, for the poly(styrene-*block*-methyl methacrylate) diblock copolymer film on the basis of the temperature- and angular-dependent X-ray photoelectron spectroscopic (XPS) measurements.[6] It was revealed that the surface T_g was much lower than that of the bulk sample and also that the surface T_g gradually increased to the bulk T_g with an increase in the depth from the air−polymer interface. The depression of T_g at the top surface region could be explained by the localization of chain end groups at the air−polymer interface.[4,6] In this paper, “surface” is defined as the region from the air−polymer interface to the depth of twice the radius of gyration of an unperturbed chain, $2R_g$.

The atomic force microscope (AFM)[7] is widely used for the observation of surface topography, which is achieved by detecting the force acting between the sample surface and the probe tip. When the observation is carried out in a repulsive force region of the force curve, the sample surface might be deformed by the indentation of the tip. The modulation of the indented tip leads to modulation of the force between the sample surface and the tip. If the modulation is applied sinusoidally, the dynamic viscoelastic properties at the sample surface can be evaluated by measuring the amplitude of the modulated deformation for the sample (response stress) and the phase lag between the modulation signal (stimulation strain) and the modulated deformation for the sample. The forced oscillation AFM equipment, the so-called “scanning viscoelasticity microscope” (SVM), was designed by modification of a commercially available AFM.[5] The two-dimensional mapping of dynamic mechanical properties for the phase-separated surface was performed by utilizing the SVM.[8] The purpose of this study is to evaluate the surface dynamic viscoelastic properties of the monodisperse polystyrene (PS) film on the basis of SVM measurement.

Experimental Section. Materials and Film Preparation. The monodisperse PS used in this study was prepared by a living anionic polymerization at 293 K using *sec*-butyllithium as an initiator. The number-average molecular weight, M_n, and the molecular weight distribution, M_w/M_n, were determined via gel permeation chromatography (GPC) with polystyrene standards. The monodisperse PS film $\sim$200 nm thick was coated from toluene solution onto a cleaned silicon wafer by spin-coating at 2 krpm.

Scheme 1



Evaluation of Surface Dynamic Viscoelastic Properties of the Monodisperse PS Film. The surface dynamic viscoelastic functions of the monodisperse PS film were evaluated on the basis of SVM measurement. The details for the experimental setup were published elsewhere.[5] The measurement was performed at 293 K in air under a repulsive force of $\sim$25 nN. The modulation frequency and the modulation amplitude were 4 kHz and 1.0 nm, respectively. The cantilever used was microfabricated from Si_3N_4, and its spring constant was 0.09 N m^{-1}. The electrical and mechanical phase lags of the instruments were calibrated by using a silicon wafer as a standard with a phase lag of zero. Quantitative measurement of the surface modulus was achieved by utilizing a standard sample, such as ultrahigh molecular weight PS of which the end group contribution to the T_g can be negligible. The details of the quantitative analysis method for the surface modulus will be published elsewhere.[9]

Investigation of Surface Localization of Chain End Groups. Depth profiling of the deuterated polystyrene (dPS) film, of which the chain end groups were labeled with protonated groups, was carried out with a dynamic secondary ion mass spectroscopic (DSIMS) measurement. Scheme 1 shows the method of preparation of end-labeled dPS used in this study. End-labeled dPS was prepared by a living anionic polymerization. Each end portion was labeled with a proton. The DSIMS analysis was performed using SIMS 4000 (Seiko Instruments Inc., Atomika Analysetechnik GmbH). The incident beam of oxygen ions, at 3.0 keV and with a current measured at the ion beam of 6−7 nA, was focused onto a 100 μm × 100 μm area of the specimen surface. A platinum layer 10 nm thick was sputter-coated on the surface of the end-labeled dPS film in order to avoid a charging of the specimen during SIMS measurement.

Results and Discussion. Molecular Weight Dependence of Surface Dynamic Viscoelasticity for the Monodisperse PS Film. Figure 1 shows the molecular weight dependence of the dynamic storage modulus, E', and the loss tangent, tan δ, at the monodisperse PS film surface as well as the tan δ values for the bulk sample. In the case of $M_n > 40.4$K, the magnitudes of surface E' and surface tan δ were constant at $\sim$4.5 GPa and 0.01, respectively. These magnitudes of surface E' and surface tan δ agreed with those for the bulk sample, which was in a glassy state at 293 K. Thus, it seems reasonable to conclude from the magnitudes of surface E' and surface tan δ that the

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* Author to whom correspondence should be addressed.

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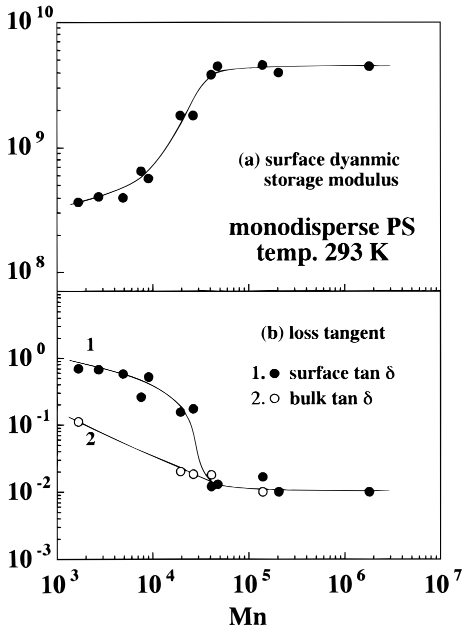

Figure 1. Molecular weight dependence of (a) surface dynamic storage modulus, E', and (b) surface loss tangent, tan δ, for monodisperse PS. The open circles in (b) show bulk tan δ. The measurement was carried out at a temperature of 293 K, and the modulation frequency and amplitude were 4 kHz and 1.0 nm, respectively.

surface of the monodisperse PS film with $M_n > 40.4$K is in a glassy state. On the other hand, in the case of $M_n < 26.6$K, the magnitudes of surface E' and surface tan δ decreased and increased, respectively, with a decrease in M_n. It is generally accepted that the onsets for the α_a-absorption on the tan δ−temperature curve and for the α_a-dispersion on the E'−temperature curve correspond well to T_g.[10] Thus, it can be concluded from the magnitudes of surface E' and surface tan δ that the surface of the monodisperse PS film with $M_n < 26.6$K is in a glass−rubber transition state or in a rubbery state, even at room temperature. These results indicate that the T_g of the monodisperse PS film surface decreases with a decrease in M_n, and then, in the case of $M_n < 26.6$K, the surface T_g decreases below 293 K.

Dynamic viscoelastic properties of the bulk PS sample with monodisperse M_n were measured in order to compare the bulk E' with the surface E'. The bulk E' was measured by using Rheovibron (DDV-01FP, Orientec Inc.). Since, in the case of $M_n < 40.4$K, the film was very fragile, the dynamic spring analysis technique was applied.[11] The open circles in Figure 1b show tan δ of the bulk sample. The magnitudes of bulk tan δ were almost 0.01, except for the case of $M_n = 1.7$K, and its magnitude was much smaller than that of surface tan δ. In the case of $M_n = 1.7$K, although the magnitude of bulk tan δ was 0.1, its magnitude was also much smaller than that of surface tan δ. Thus, it seems reasonable to conclude that molecular motion at the film surface is more active in comparison with that for the bulk sample in the case of $M_n < 26.6$K. Since SVM measurement was carried out at 293 K, in the case that the surface T_g is higher than room temperature of 293 K, it is impossible to reveal the discrepancy of molecular motion between surface and bulk regions on the basis of SVM measurement at 293 K. The temperature dependence of surface viscoelastic functions will be discussed in the future.

Surface Localization of Chain End Groups. A depression in T_g at the film surface compared with that for the bulk sample can be explained by the surface localization of chain end groups.[4,6] However, the surface localization of chain end groups has not been experimentally confirmed in relation to surface molecular motion. Using deuterated polystyrene of which the chain end groups were labeled with protonated groups, SIMS depth profiling was performed in order to reveal the surface segregation of the chain end groups. Figure 2 shows the SIMS depth profile of the end-labeled dPS film. The dashed vertical line corresponds to the air−polymer interface. Figure 2 shows the respective increase and the decrease in concentration of protons and deuterium ions at the air−polymer interface. Since the styrene molecule was deuterated, protons were present only in both chain end portions. Thus, the SIMS depth profile apparently shows an enrichment of chain end groups in the depth range from the outermost surface to R_g. Since the surface localization of chain end groups induces a larger free volume fraction at the film surface compared with that in a bulk phase, it seems reasonable to conclude that surface molecular motion at the film surface is fairly active in comparison with that for the bulk sample.

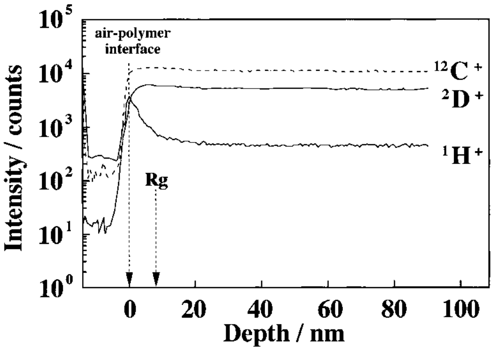

Figure 2. SIMS depth profile of protons and deuterium ions for the end-labeled deuterated PS film. M_n and the radius of gyration of an unperturbed chain, R_g, for end-labeled deuterated PS were 15K and 8.1 nm, respectively.

Conclusion. The molecular weight dependence of the surface viscoelasticity function for the monodisperse PS film was investigated on the basis of SVM measurement. In the case of $M_n < 26.6$K, it was revealed that the film surface was in a glass−rubber transition state or a rubbery state, even at 293 K. A depression of the surface T_g compared with that of the bulk sample was explained on the basis of the surface localization of chain end groups. SIMS measurement revealed that chain end groups were enriched in the depth range from the outermost surface to R_g.

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References and Notes

(1) Meyers, G. F.; DeKoven, B. M.; Seitz, J. T. *Langmuir* **1992**, *8*, 2330.
(2) (a) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1993**, *23*, 579. (b) Keddie, J. L.; Jones, R. A. L. *Isr. J. Chem.* **1995**, *35*, 21.
(3) (a) Reiter, G. *Langmuir* **1993**, *9*, 1344. (b) Reiter, G. *Macromolecules* **1994**, *27*, 3046.
(4) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.
(5) Kajiyama, T.; Tanaka, K.; Ohki, I.; Ge, S.-R.; Yoon, J.-S.; Takahara, A. *Macromolecules* **1994**, *27*, 7932.
(6) (a) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1995**, *28*, 3482. (b) Tanaka, K.; Takahara, A.; Kajiyama, T. *Acta Polym.* **1995**, *46*, 476.

(7) Binnig, G.; Quate, C. F.; Gerber, C. G. *Phys. Rev. Lett.* **1986**, *56*, 930.

(8) (a) Tanaka, K.; Yoon, J.-S.; Takahara, A.; Kajiyama, T. *Macromolecules* **1995**, *28*, 934. (b) Ge, S.-R.; Takahara, A.; Kajiyama, T. *J. Vac. Sci. Technol.* **1994**, *A12* (4), 2530. (c) Ge, S.-R.; Takahara, A.; Kajiyama, T. *Langmuir* **1995**, *11*, 1341.

(9) Tanaka, K.; Takahara, A.; Kajiyama, T., manuscript in preparation.

(10) Takayanagi, M.; Manabe, S. *Tech. Rep. Kyushu Univ.* **1965**, *37*, 362.

(11) Naganuma, S.; Sakurai, T.; Takahashi, Y.; Takahashi, S. *Kobunshi Kagaku* **1972**, *29*, 105.

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