Surface Relaxation Process of Monodisperse Polystyrene Film Based on Lateral Force Microscopic Measurements

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Introduction. Recently, thermal molecular motion of polymer chains existing in extraordinary environments such as in an ultrathin film and at an interfacial region has been paid great attention since these properties are quite important for the design of ultimate functional materials as well as scientific interests.[1] The thermal behavior of the polymeric thin films has been investigated by means of various methods, and then, it has been revealed that the glass transition temperature, T_g, in the thin films is quite different from that of the thick ones due to the difference in the chain conformation between thin and thick films.[2] However, a little study has been done on the thermal molecular motion at the air−polymer interface of the thick film.[3]

Authors have investigated the surface molecular motion of polystyrene (PS) films at 293 K by using scanning viscoelasticity microscopy (SVM) and lateral force microscopy (LFM).[4] On the basis of SVM and LFM measurements, the surface of the monodisperse PS films with the number-average molecular weight, M_n lower than ca. 30k was in a glass−rubber transition state even at 293 K, even though the bulk T_g was far above 293 K.[4] Active thermal molecular motion at the surface of PS films was explained by an excess free volume induced by the surface localization of chain end groups. At present, however, it has not yet been revealed how the mobility of polymer chains existing at the surface behave with varying temperature. Also, there is not any experimental evidence that the surface T_g of the monodisperse PS film with M_n higher than ca. 30k is depressed compared with the bulk one. The purpose of this study is to understand the surface relaxation process of the monodisperse PS film with M_n of 140k based on the temperature-dependent LFM measurements.

Experimental Section. Monodisperse PS with M_n of 140k and M_w/M_n of 1.06, where M_w denotes the weight-average molecular weight, was prepared by a living anionic polymerization at 293 K using *sec*-butyllithium as an initiator. The PS film was coated from a toluene solution onto a cleaned silicon wafer by a spin-coating method. The film was dried at 293 K for more than 72 h and annealed at 393 K for 24 h under vacuum. The film thickness evaluated by ellipsometric measurement was ca. 200 nm.

The surface molecular relaxation behavior of the PS film was evaluated by using LFM (SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. LFM measurement was carried out at various temperatures in vacuo in order to avoid the surface oxidation and a capillary force effect induced by surface-adsorbed water. A piezoscanner was thermally insulated from the heating stage. When the cantilever was heated or cooled, the cantilever was bent due to the difference of thermal expansion coefficient between the substrate and gold. Thus, the double gold coated cantilever with the bending spring constant of 0.09 N·m^{-1} (Olympus Co., Ltd.) was used.

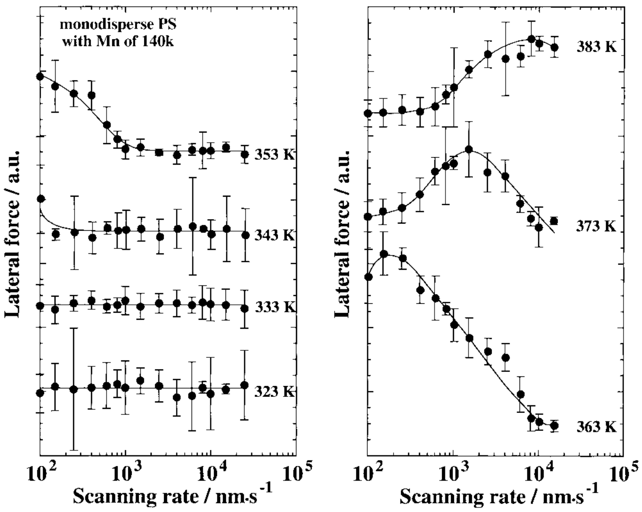

Figure 1. Scanning rate dependence of the lateral force with various temperatures for the monodisperse PS film with M_n of 140k.

Results and Discussion. Since the frictional behavior of polymeric solids is closely related to their viscoelastic properties,[5] it is possible to investigate the surface molecular motion of the polymeric solids by using LFM, which can detect the lateral force between the solid surface and sliding cantilever tip on a nanometer scale. In both cases of the glassy surface or rubbery one, no distinct scanning rate dependence of the lateral force is observed, whereas, in the case of the surface being in a glass−rubber transition state, the maximum peak with the scanning rate might be clearly observed. Thus, if the magnitude of lateral force increases or decreases with the scanning rate, it can be concluded that the surface is in a glass−rubber transition state. More detailed explanation of the scanning rate−lateral force relationship was published elsewhere.[4] Since our LFM apparatus cannot cover the whole scanning rate range corresponding to the transition from a glassy state to a rubbery one at only a certain measuring temperature, such as room temperature, the scanning rate dependence of the lateral force was evaluated at various temperatures.

Figure 1 shows the scanning rate dependence of the lateral force as a function of temperature for the monodisperse PS film with M_n of 140k. In the temperature range from 293 to 333 K, no scanning rate dependence of the lateral force was observed. This apparently indicates that the surface T_g of the monodisperse PS with M_n of 140k is higher than 333 K. In the temperature range from 343 to 353 K, the magnitude of the lateral force increased with a decrease in the scanning rate, especially at a lower scanning rate

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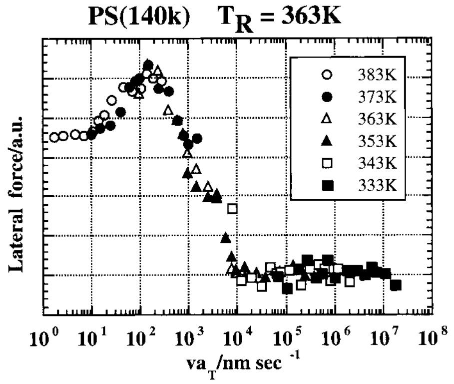

Figure 2. Master curve of the scanning rate−lateral force relationship for the monodisperse PS film with M_n of 140k drawn from the each curve in Figure 1. A reference temperature of 363 K was used.

region. The scanning rate, at which the magnitude of lateral force starts to increase with a decrease in the scanning rate, was shifted to the higher scanning rate region with an increase in measuring temperature from 343 to 353 K. The existence of the scanning rate dependence of the lateral force clearly indicates that the surface is in a glass−rubber transition state at a lower scanning rate region. Since the bulk T_g of PS with M_n of 140k evaluated by differential scanning calorimetry was 381.5 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 was fairly high at 140k. Also, in the temperature range from 363 to 383 K, the peak was clearly observed on the scanning rate−lateral force curve. At 383 K above bulk T_g, the magnitude of the lateral force decreased with a decrease in the scanning rate in a wide scanning rate region. This means that the PS surface is almost in a rubbery state. The shape of each curve in Figure 1 suggests that the master curve can be obtained by the horizontal and vertical shifts. Since the magnitude of the lateral force showed a large error bar, only the magnitude of the horizontal shift, a_T was evaluated.

Figure 2 shows the master curve drawn by horizontal and vertical shifts of each curve shown in Figure 1 as a reference temperature of 363 K. Since the master curve obtained from the experimental result in Figure 1 is very similar to the scanning rate dependence of the lateral force, 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 it is not observed in a glassy region and a fully rubbery one. Figure 2 clearly indicates that the time−temperature superposition, which is characteristic of viscoelastic bulk polymeric materials, can be applied to the surface relaxation process.

Figure 3 shows the relationship between a_T and reciprocal measuring temperature. Figure 3 corresponds to the Arrhenius plot. The magnitude of activation energy for the surface α-relaxation process calculated from the slope of the log a_T vs $1/T$ plot was 220 kJ·mol^{-1}. This magnitude is a little smaller than that for the bulk one of 360−430 kJ·mol^{-1}.[6] At the air−polymer interface, an excess free volume is induced by the surface localization of the chain end groups and, also, the polymeric segment density at the air interface is less than that in the bulk on the basis of a simulation study.[7] Then, it can be predicted from the magnitude of the activation energy that the energy barrier and/or the segment size of thermal molecular motion for the α-relaxation process at the film surface might be decreased in comparison with those for the bulk one.

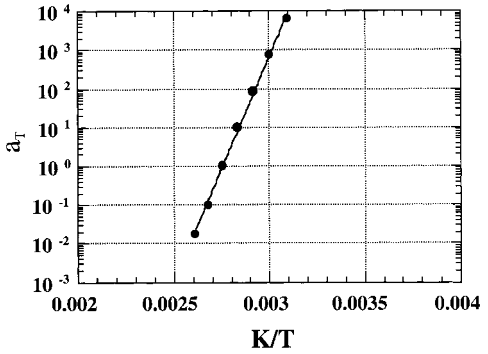

Figure 3. Relationship between the a_T and the reciprocal measuring temperature.

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References and Notes

(1) Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surfaces from Physics to Technology*; John Wiley & Sons: New York, 1994.

(2) (a) Keddie, J. L.; Jones, R. A. L.; Coury, R. A. *Europhys. Lett.* **1994**, *27*, 59. (b) van Zanten, J. H.; Wallace, W. E.; Wu, W.-I. *Phys. Rev. E* **1996**, *53*, R2053. (c) Forest, J. A.; Dlnoski-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002. (d) De Maggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1997**, *78*, 1524. (e) Hall, D. B.; Hooker, J. C.; Torkelson, J. M. *Macromoleules* **1997**, *30*, 667.

(3) (a) Kajiyama, T.; Tanaka, K.; Ohki, I.; Ge, S.-R.; Yoon, J.-S.; Takahara, A. *Macromolecules* **1994**, *27*, 7932. (b) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1995**, *28*, 3482. (c) Tanaka, K.; Takahara, A.; Kajiyama, T. *Acta Polym.* **1995**, *46*, 476. (d) Liu, Y.; Russell, T. P.; Samant, M. G.; Stohr, J.; Brown, H. R.; Cossy-Favre, A.; Diaz, J. *Macromolecules* **1997**, *30*, 7768.

(4) (a) Tanaka, K.; Taura, A.; Ge, S.-R.; Takahara, A.; Kajiyama, T. *Macromolecules* **1996**, *29*, 3040. (b) Kajiyama, T.; Tanaka, K.; Takahara, A. *Macromolecules* **1997**, *30*, 280.

(5) (a) Grosch, K. A. *Proc. R. Soc. London A* **1963**, *274*, 21. (b) Minato, K.; Takemura, T. *Jpn. J. Appl. Phys.* **1967**, *6*, 719.

(6) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: New York, 1991.

(7) (a) Mansfield, K. F.; Theodorou, D. N *Macromolecules* **1991**, *24*, 6283. (b) Brown, H. R.; Russell, T. P. *Macromolecules* **1996**, *29*, 798.

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