Surface Mobility in Monodisperse Polystyrene Films

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Summary: Surface dynamics in monodisperse polystyrene films was examined by lateral force microscopy in conjunction with dynamic secondary ion mass spectroscopy. Glass transition temperature, T_g, at the surface was markedly lower than the corresponding bulk T_g. Also, it was shown that polymer chains present at the surface could diffuse even at a temperature below the bulk T_g. The surface depth, in which molecular motion was activated, was of the order of 5 nm.

Keywords: dynamic secondary ion mass spectroscopy, diffusion, glass transition temperature, lateral force microscopy, surface, polystyrenes

Introduction

Surfaces and interfaces of polymeric materials play an important role in many technological applications such as lubrication, adhesion, biomaterials, etc. To design highly functionalized polymeric materials, the systematical understanding of aggregation states and physical properties in the vicinity of surface and interfacial layers, which differs from those in the interior bulk region, is quite important. However, surface physical properties, especially molecular motion, has been far from clear for the moment.

So far we have systematically studied surface molecular motion in monodisperse polystyrene (PS) films by mainly using scanning force microscopy.[1,2] As a main result, it was elucidated that molecular motion at the film surface was activated in comparison with that in the interior bulk region. This activation of surface mobility has been explained in terms of chain end effect[3] and reduced cooperativity.[4] Based on the aforementioned situation, it seems reasonable to infer that surface chains are movable in a relatively large distance even at a temperature below the bulk glass transition temperature, T_g^b, as long as the temperature is higher than the surface glass transition temperature, T_g^s. However, a little information about such has been known. The objective of this study is to reveal directly chain diffusion at the surface, based on the time evolution of the interfacial width of PS bilayers.

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Experimental

Monodisperse PSs were synthesized by an anionic polymerization using *sec*-butyllithium and methanol as an initiator and a terminator, respectively. PS films were coated from toluene solutions onto silicon wafers by a spin-coating method. The film was dried at 296 K for more than 24 h and then annealed at 393 K for 24 h under vacuum. The film thickness evaluated by ellipsometric measurement was approximately 200 nm. The surface relaxation behavior of the PS film was examined by using lateral force microscopy (LFM; SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. The applied force to the cantilever was set to be 10 nN in a repulsive force region. T_g^b was determined by differential scanning calorimetry (DSC8230, Rigaku Co., Ltd.). For interdiffusion experiment, bilayer films composed of monodisperse PS and deuterated PS (dPS) were prepared by a floating method.[5] The interfacial broadening of the bilayers by annealing was examined by dynamic secondary ion mass spectroscopy (DSIMS; SIMS 4000, Atomika Analysetechnik GmbH). The incident beam of oxygen ions with 4keV and ca. 30 nA was focused onto a 200 μm x 200 μm area of the specimen surface. The incident angle was 45 deg.

Results and Discussion

First of all, to discuss about surface molecular motion with the segmental scale, T_g^s in the PS films was examined. Since the manifestation of frictional force of polymeric solids is closely related to their viscoelastic properties, it is possible to examine surface molecular motion of the polymeric solids by using LFM.[2,6] That is, when the energy dissipation increases at the surface due to molecular motion, lateral force increases. Hence, it can be postulated that lateral force alteration with measuring temperature is essentially similar to the temperature dependence of dynamic loss modulus or mechanical loss tangent.

Figure 1 shows the lateral force versus temperature curves for the PS films with number-average molecular weight, M_n, of 4.9k and 140k at the scanning rate, v, of 1 $\mu m \cdot s^{-1}$. The ordinate is normalized by the peak value of lateral force to show how the lateral force varies with temperature in the vicinity of a transition region. The lateral force-temperature curves shown in Figure 1 make it clear that each surface transition temperature for the PS films with M_n of 4.9k and 140k is much lower than the corresponding T_g^b of 348 and 376 K, respectively, based on the onset of DSC curves. Thus, it seems reasonable to conclude that the segmental motions at PS film surfaces are more activated than that in the internal bulk phase.

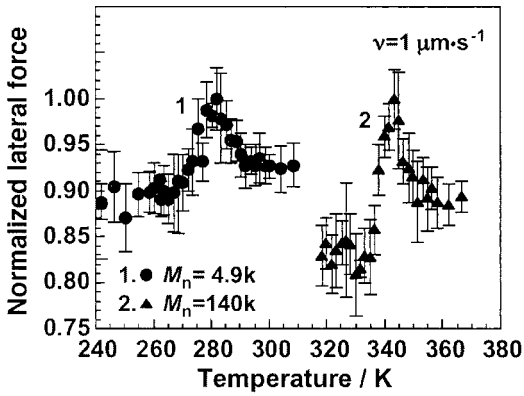

Fig. 1. Temperature dependence of lateral force for the PS films with M_n of 4.9k and 140k at the scanning rate of 1 μm•s^{-1}.

An onset temperature on the lateral force-temperature curve, that is, the temperature at which the magnitude of lateral force starts to increase, can be empirically defined as T_g^s.[4] Figure 2 shows T_g^s so obtained as a function of M_n, and T_g^b determined by DSC are also plotted for a comparison. The arrow beside the ordinate denotes our room temperature, which is abbreviated as "R.T.". It is clear that T_g^s exhibits the stronger M_n dependence than T_g^b. It is of interest to note that the surface is already in a glass-rubber transition or rubbery state at room temperature in case of a M_n smaller than approximately 40k.

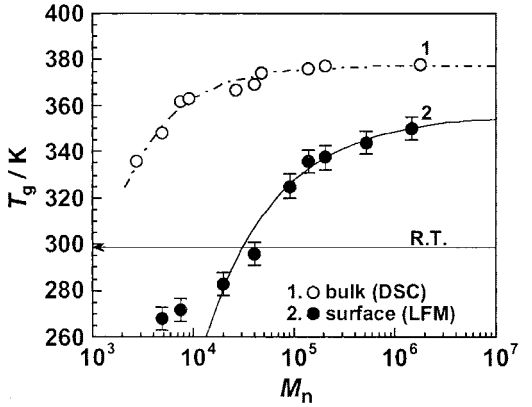

Fig. 2. Molecular weight dependences of T_g^b and T_g^s for the PS films. The broken and solid curves are drawn in the context of the power law analysis.

We now turn to surface perpendicular diffusion in PS films. This can be examined by using a bilayer film composed of two different components, in which both surfaces stand face-to-face. Figure 3 shows the typical DSIMS profile of proton and deuterium and carbon ions for the (PS/dPS) bilayer. Here, one component of the bilayer was labeled by deuterium to detect experimentally where the interface was. Since the intensity of the carbon ion C^+ was almost constant through the bilayer, it is clear that the steady-state etching proceeded during the measurement. The abscissa of the etching time was simply converted to the depth from the surface on the assumption of a constant sputtering rate through the bilayer, which was pre-examined using the dPS film with a known thickness.

A measured concentration profile by DSIMS is generally broadened from an ideal one owing to an atomic mixing effect. The broadening of the measured SIMS profile was quantified by the instrument function Δz_g corresponding to the depth resolution. Figure 4 shows our definition of the interfacial thickness; (a) the deuterium ion intensity profile $I_{D+}(z)$ through the interface and (b) the derivative of $I_{D+}(z)$ by the distance from the center of the interface. Assuming that the $dI_{D+}(z)/dz$ can be expressed by Gaussian function, the Δz_i (i = g or m), where the Δz_m denotes the measured

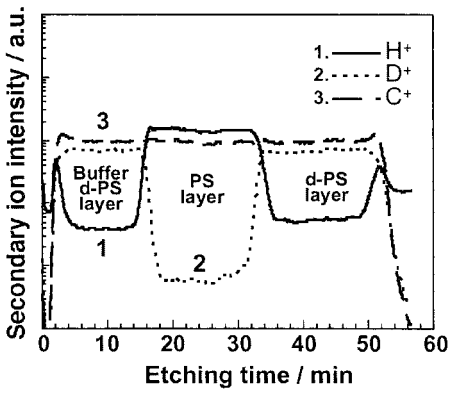

Fig. 3. Typical DSIMS profile of proton and deuterium and carbon ions for the (PS/dPS) bilayer.

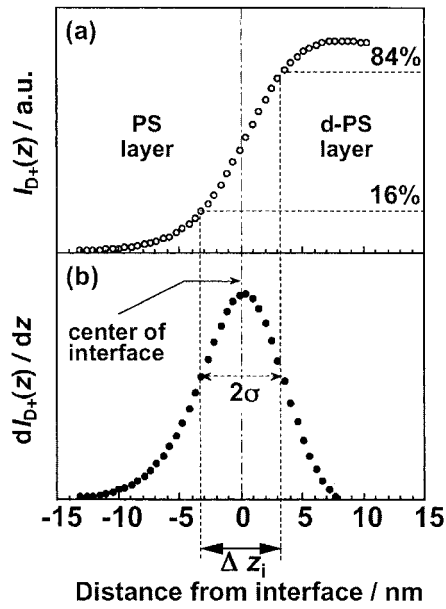

Fig. 4. Our definition of the interfacial thickness, Δz_i (i=g or m) from DSIMS profile; (a) the deuterium ion intensity profile, $I_{D+}(z)$, through the interface, and (b) the derivative of $I_{D+}(z)$ by the distance from the center of the interface. The Δz_g and the Δz_m were defined as twice the standard deviation of Gaussian function.

apparent width of the bilayer interface, is defined as twice the standard deviation of Gaussian function, corresponding to the depth range where I_{D+} arises from 16 to 84 % of the maximum value. Given that the measured and ideal profiles are expressed by Gaussian functions as shown in Figure 4, the real interfacial thickness Δz is given in terms of the Δz_m and the Δz_g.[7]

$$\Delta z = (\Delta z_m^2 - \Delta z_g^2)^{1/2} \qquad (1)$$

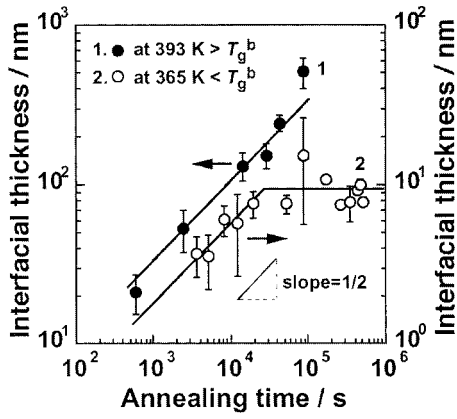

Fig. 5. Double-logarithmic plots of interfacial thickness versus annealing time for (PS/dPS) bilayer annealed at 393 K and 365 K. Slope of 1/2 is drawn in the context of the Fickian diffusion.

Figure 5 shows the time evolution of the interfacial thickness for the (PS/dPS) bilayer by annealing as a function of temperature. Each elemental film possesses M_n of 29k. The choice of this M_n was based on Figure 2, showing that the T_g^s of the PS film with M_n of 29k was approximately 290 K. Since the discrepancy between the T_g^b and the T_g^s is relatively large, it is easy to regulate the polymer diffusion only into the surface region. At 393 K above the T_g^b, the interfacial thickness proportionally increased to the 1/2 power of the annealing time, t. This result is in good accordance with the Fickian diffusion, because the calculated reptation time is approximately 120 s. On the other hand, at 365 K, which was above the T_g^s and below the T_g^b, the interfacial thickness reached a constant value of (9.6±2.5) nm after $t = 2 \times 10^4$ s, although the initial interfacial evolution could be described in terms of Fickian diffusion. This result implies that there is a gradient of the glass transition temperature in the surface region, and makes it clear that the polymer interdiffusion across the bilayer interface definitely occurs even at a temperature below its T_g^b. Since the bilayer interface was originally composed of two film surfaces, a half of the evolved interfacial width corresponds to the

surface region of one film, in which polymer diffusion was attained. Thus, it seems reasonable to claim that the surface layer of 4.8 nm thick is in a glass-rubber transition state or even in a rubbery one at 365 K. It is of interest to note that the thickness of this surface layer is almost the same as the radius of gyration of an unperturbed PS chain with M_n of 29k, 4.5 nm. The thickness of the surface layer being in the glass-rubber transition state should strongly depend on the temperature and the molecular weight. A more conclusive study based on this point of view will be reported shortly.

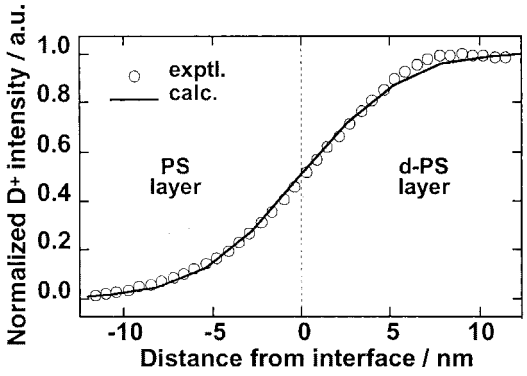

Fig. 6. Depth profile of deuterium ion, D^+, at the bilayer interface annealed at 365 K and for 72 h. The ordinate is normalized by the maximum intensity of D^+ ion. The solid curve indicates the best fitted one by using eq. (3) with the D_{eff} of 1.8 x 10^{-7} $\mu m^2 \cdot s^{-1}$ as a fitting parameter.

Next, the effective diffusion coefficients D_{eff}s at 393 and 365 K are extracted from the SIMS depth profiles. The concentration profile $C(z')$ of deuterium ion along the direction normal to the surface is given by[8]

$$C(z') = 0.5[1 - erf\left\{\frac{z'}{\sqrt{4D_{eff}t}}\right\}] \quad (2)$$

where z' is the distance from the center of the interface. However, the DSIMS profile obtained by the experiment is convoluted with the instrument function, as mentioned before. In that case, the apparent concentration profile can be expressed as follows;[8]

$$C_{app}(z') = 0.5[1 - erf\left\{\frac{z'}{\sqrt{a^2 + 4D_{eff}t}}\right\}] \quad (3)$$

where a is the apparent broadening factor and thus the instrument function of 7.4 nm was used for the a. Figure 6 shows the typical depth profile of normalized deuterium ion at the bilayer

interface annealed at 365 K for 72 h. The solid curve is the best-fit one with a D_{eff} as a fitting parameter by using Eq. (3). The D_{eff}s at 393 and 365 K were estimated to be $(1.8 \pm 0.7) \times 10^{-7}$ and $(7.5 \pm 5.8) \times 10^{-10}$ $\mu m^2 \cdot s^{-1}$, respectively.

It has been widely accepted that the temperature dependence of D_{eff} follows the Vogel relationship.[9,10]

$$\log\left(\frac{D_{eff}}{T}\right) = A - \frac{B}{T - T_{\infty}} \qquad (4)$$

where A and B are constants, and besides T_{∞} is the temperature at which long-range motion of the polymer completely ceases, that is, (T_g-50) K. When eq. (4) is applied to our results, the determination of T_{∞} is somewhat complicated. What was examined in this study was the surface diffusion, and then it is not clear which T_g, T_g^s or T_g^b, should be taken. Since in the case of the annealing at 393 K, the chain diffusion could take place into the internal bulk phase, the T_g^b was used for the determination of T_{∞}, resulting in the T_{∞} of 326 K. Using Green and Kramer's equation and value for A and B,[10] respectively, the D_{eff} at 393 K was calculated to be 9.8×10^{-8} $\mu m^2 \cdot s^{-1}$. This value was in good agreement with the measured D_{eff} of $(1.8 \pm 0.7) \times 10^{-7}$ $\mu m^2 \cdot s^{-1}$ in this study. On the contrary, the annealing temperature of 365 K was below the T_g^b. Hence, the T_g^s of 264 K was used for the determination of the T_{∞}, namely, the T_{∞} of 214 K. In that case, the calculated D_{eff} at 365 K was 1.8×10^{-2} $\mu m^2 \cdot s^{-1}$, which was totally different from the D_{eff} by the experiment. For the moment, we have surmised that the inconsistency of the calculated value by eq. (4) with the experimental D_{eff} is based on the ill-chosen value of the T_{∞}, which might be underestimated. This explanation can be understood by taking into account that the T_{∞} is gradually increased along the direction normal to surface and then eventually reached the bulk value of 326 K due to the gradient of the glass transition temperature at the surface region.

Conclusions

Surface dynamics in the PS film was studied, from the segmental scale to center of mass diffusion, by LFM in conjunction with DSIMS. T_g^s in the PS films was much lower than the corresponding T_g^b, and ist M_n dependence was more remarkable at the surface. The time evolution of the PS bilayer interface was examined at temperatures below and above the T_g^b. At 393 K above the T_g^b, the interfacial thickness monotonically increased with the annealing time, obeying the Fickian diffusion. In contrast, in the case of the annealing at 365 K being between

the T_g^s and the T_g^b, the interfacial thickness was remained to be a constant after the initial interfacial evolution. This result apparently indicates that the polymer interdiffusion can be attained due to the enhanced molecular mobility in proximity to the interface, which used to be in the film surface region, even at a temperature lower than the T_g^b as long as the annealing temperature was higher than the T_g^s.

Acknowledgements

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