Surface Mobile Layer of Polystyrene Film below Bulk Glass Transition Temperature

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Received January 2, 2001
Revised Manuscript Received May 7, 2001

Introduction. The aggregation states and physical properties at a polymeric solid surface are completely different from those in the interior region on account of the free energy difference between the surface and the bulk.[1] The authors have systematically studied surface molecular motion for monodisperse polystyrene (PS) films using scanning force microscopy and revealed its peculiarity in comparison with the bulk region.[2−4] For instance, the surface glass transition temperature, T_g^s, of a PS film with a number-average molecular weight, M_n, $\leq$40k is lower than room temperature, although the corresponding bulk glass transition temperature, T_g^b, is far above 293 K.[4,5] The depression of T_g^s in comparison with T_g^b has been explained in terms of an excess free volume resulting from the surface localization of chain end groups and a reduced cooperativity for the surface α-relaxation process because of the existence of the free space on the polymer surface.[5] However, little information is known about the depth range of such active surface molecular motion of the PS film.

Judging from the above-mentioned experimental results, it seems reasonable to infer that the chains at the surface move, laterally and perpendicularly even at temperatures below T_g^b as long as the temperature is higher than T_g^s. The perpendicular diffusion in the surface region can be examined by using a bilayer film composed of two different components in which the two surfaces stand face-to-face.[6−10] Boiko and Prud'homme studied the annealing time dependence of the (PS/PS) interfacial shear strength at temperatures below T_g^b.[9] They found that the shear strength increased with time even though the annealing temperature was well below T_g^b.[9] This time evolution of the interfacial shear strength below T_g^b was accounted for by considering that the mobility of chains at the interface, which used to be the surface, was much enhanced in comparison with that in the bulk region. Although their results correspond well with our findings, specifically regarding the active surface molecular motion, the depth range of the vigorous molecular motion in the surface region of PS films is still an open question. The objective of this study is to give a direct answer to this problem.

Experimental Section. The polymers used in this study were monodisperse PS (hPS) and monodisperse deuterated PS (dPS). hPS with a M_n of 29k and a molecular weight dispersity, M_w/M_n, of 1.07 was synthesized by a living anionic polymerization using *sec*-butyllithium and methanol as the initiator and terminator, respectively. M_w denotes the weight-average molecular weight. dPS with a M_n of 29k and a M_w/M_n of 1.03 was purchased from Polymer Source Inc. The T_g^bs of hPS and dPS measured by differential scanning calorimetry (DSC) were 376 and 373 K, respectively. The choice of this M_n was based on our previous result that the T_g^s of a PS film with a M_n of 29k was 264 K.[4] Because the discrepancy between T_g^b and T_g^s is relatively large, it is easy to regulate the polymer diffusion only into the surface region.

Figure 1 schematically shows how the (hPS/dPS) bilayer film was constructed. First, the bottom dPS layer for the bilayer was coated from a toluene solution onto a silicon wafer by the spin-coating method at a speed of 1.5k rpm, as shown in Figure 1, part 1. The thickness of this layer was approximately 300 nm. The top hPS film with almost the same thickness was independently coated onto a microscope slide glass in a similar manner. Both films were annealed at 393 K for at least 36 h in vacuo to remove the residual solvent and the strain imposed by the film preparation process. The (hPS/dPS) bilayer was prepared by applying the floating technique as follows: The perimeter of the hPS film was scored with a blade and then floated off onto the surface of a 2.7 wt % 1-hydro-2-fluoro ammonium solution,[11] as shown in Figure 1, part 2. Then, the hPS film was picked up onto the dPS film by attaching the dPS film from the air side, as shown in the bottom part of Figure 1. In other words, the bilayer interface was built from two original surfaces of hPS and dPS films. It was confirmed by atomic force microscopy that the bilayer was uniform enough for dynamic secondary ion mass spectroscopic (DSIMS) measurements. The bilayers were annealed under nitrogen atmosphere at two different temperatures, 365 and 393 K. The annealing temperature of 365 K was in the middle between T_g^s and T_g^b, whereas 393 K was well above T_g^b. After a given time, the annealing was rapidly quenched by immersing the bilayer into liquid nitrogen.

The interfacial broadening of the bilayer by annealing was examined on the basis of depth profiling by DSIMS (SIMS 4000, Seiko Instruments Inc.−Atomika Analysetechnik GmbH) measurement. Because a hPS film with a M_n of 29k is very fragile, it is almost impossible to construct a well-defined bilayer film with a large area. Hence, neutron reflectivity (NR), which has depth resolution superior to that of DSIMS, could not be applied in this experiment. To gain access to stable sputtering during the DSIMS measurements, a buffer dPS layer was also laminated onto the (hPS/dPS) bilayer by the floating technique. The thickness of the buffer dPS layer was approximately 200 nm. An incident beam of oxygen ions with an energy of 4 keV and a current of ca. 30 nA was focused onto a 200 × 200 μm^2 area of the specimen surface. The incident angle was 45°. A gold layer of 20-nm thickness was sputter-coated onto the specimen surface to avoid charging of the specimen during DSIMS measurements.

Results and Discussion. Figure 2 shows a typical DSIMS profile of protons and deuterium and carbon ions for the (hPS/dPS) bilayer. Because the intensity of the carbon ion, C^+, was almost constant through the bilayer, it is clear that steady-state etching proceeded during the measurements. The abscissa of the etching time can be simply converted to the depth from the surface on the assumption of a constant sputtering rate through the bilayer, which was pretested using a dPS film with a known thickness.

The concentration profile measured by DSIMS is generally broadened from the ideal as a result of an instrument function that mainly originates from an atomic mixing effect. The broadening of the measured SIMS profile was subtracted by following the procedure reported by Whitlow and Wool.[7] Assuming that the derivative of secondary D^+ intensity, I_{D+}, can be expressed by a Gaussian function, the interfacial thickness

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10.1021/ma010012k CCC: $20.00

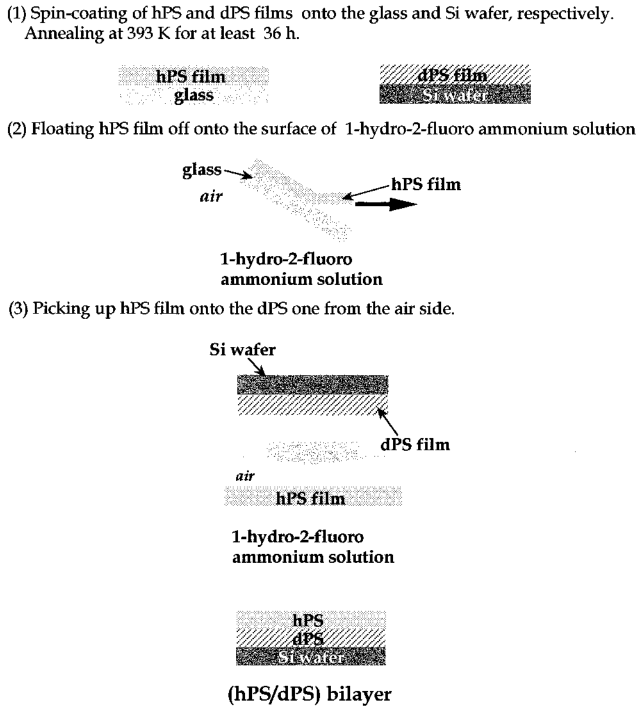

Figure 1. Schematic representation of how the (hPS/dPS) bilayer was constructed. See text for detail.

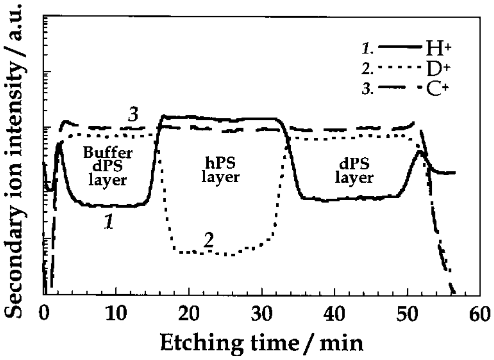

Figure 2. Typical DSIMS profile of protons and deuterium and carbon ions for the (hPS/dPS) bilayer.

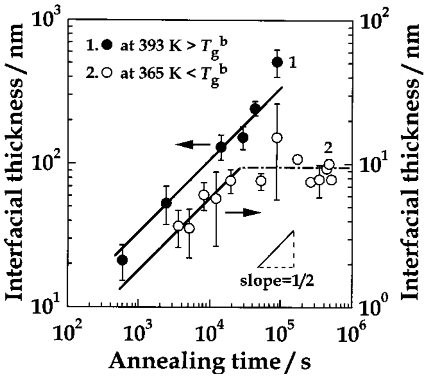

Figure 3. Double-logarithmic plot of interfacial thickness versus annealing time for (hPS/dPS) bilayer annealed at 393 and 365 K. The slope of 1/2 is drawn in the context of Fickian diffusion.

was defined as twice the standard deviation of the Gaussian function, corresponding to the depth range where I_{D+} rises from 16 to 84% of the maximum value. Figure 3 shows the time evolution of the interfacial thickness for the (hPS/dPS) bilayer during annealing at different two temperatures. At 393 K, above T_g^b, the interfacial thickness proportionally increased with the $^1/_2$ power of the annealing time, t. This result is in good accordance with Fickian diffusion, because the calculated reptation time is approximately 130 s. On the other hand, at 365 K, which is above T_g^s and below 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 apparently described in terms of Fickian diffusion. This result makes it clear that chains move across the bilayer interface even at a temperature below T_g^b. Because the bilayer interface was originally composed of two film surfaces, one-half of the evolved interfacial width might correspond to the surface region of one film in which polymer diffusion was attained. Thus, it seems most likely that the chain mobility in a surface layer of 4.8-nm thickness is enhanced in comparison with that in the interior region. Interfacial broadening of the PS bilayer was not observed when the annealing was performed at a temperature below T_g^s.[12] Also, it should be noted that the thickness of this surface layer is almost the same as the radius of gyration of an unperturbed chain with a M_n of 29k, 4.5 nm. Hence, it is hard to conclude for the moment whether this chain movement is based on interdiffusion across the bilayer or some sort of relaxation of the surface chains. The thickness of the surface layer in which the chain mobility is enhanced in comparison with the bulk should strongly depend on the temperature and the molecular weight. A more conclusive study based on this point of view will be reported shortly.[13]

Finally, we turn to the diffusion coefficients at 393 and 365 K. The concentration profile $C(z')$ of deuterium ions along the direction normal to the surface is given by[14]

$$C(z') = 0.5\left[1 - \mathrm{erf}\left(\frac{z'}{\sqrt{4Dt}}\right)\right] \tag{1}$$

where D and z' are the diffusion coefficient and distance from the center of the interface, respectively. However, the general DSIMS profile obtained in the experiment is convoluted with the instrument function, as mentioned before. In that case, the apparent concentration profile can be expressed as[14]

$$C_{\mathrm{app}}(z') = 0.5\left[1 - \mathrm{erf}\left(\frac{z'}{\sqrt{a^2 + 4Dt}}\right)\right] \tag{2}$$

where a is the apparent broadening factor; thus our instrument function of 7.4 nm was used for the a. The D values at 393 and 365 K evaluated using eq 2 were $(1.8 \pm 0.7) \times 10^{-7}$ and $(7.5 \pm 5.8) \times 10^{-10}$ $\mu\mathrm{m}^2\ \mathrm{s}^{-1}$, respectively.

In conclusion, the time evolution of the interfacial thickness of a PS bilayer 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 annealing time, obeying Fickian diffusion. In contrast, in the case of the annealing at 365 K, which is between T_g^s and T_g^b, the interfacial thickness remained constant after the initial interfacial evolution. This result clearly indicates that the mobility of chains in the vicinity of the surface is much enhanced in comparison with that in the bulk.

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research (A) (#13355034) and COE Research (#08CE2005) from the Ministry of Education, Science, and Culture, Japan.

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(11) In general, it might be impossible to float a spin-coated PS thin film that had been annealed at a temperature above T_g^b off onto the pristine water surface. However, it turns out to be possible using the surface of a 2.7 wt % 1-hydro-2-fluoro ammonium solution in lieu of water.

(12) In the case of a higher-molecular-weight bilayer, the area obtained is large enough for NR as well as DSIMS measurements. Both measurements revealed that the interfacial width of the bilayer could not be evolved unless the annealing was made at a temperature above T_g^s.

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MA010012K