

POLYMER CHAIN DIFFUSION AT A TEMPERATURE BELOW ITS BULK GLASS TRANSITION TEMPERATURE*

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Abstract In this study, it was examined whether the dynamics of polymer chains at a surface is different from that in the bulk, and if so, to what extent they differ in terms of surface glass transition temperature and diffusion coefficient. Obtained results clearly indicate that surface chains can travel for a relatively large distance in comparison with the characteristic length scale of usual segmental motion even at a temperature below its bulk glass transition temperature, T_g^b . This is consistent with our previous results that the surface glass transition temperature is much lower than the corresponding T_g^b . Also, it was experimentally revealed that there was a gradient of molecular motion in the surface region.

Keywords Surface molecular motion, Surface glass transition temperature, Polystyrene, Poly(styrene-*block*-methyl methacrylate)

INTRODUCTION

Surfaces and interfaces of polymeric materials play an important role in many technological applications such as lubrication, adhesion, biomaterials, *etc.*^[1]. In order to design highly functionalized materials, understanding aggregation states and physical properties in the vicinity of surface and interfacial layers, which are mostly different from those in the interior bulk region, is quite important.

So far, authors have systematically studied surface molecular motion of monodisperse polystyrene (PS) films based on scanning force microscopy^[2]. As our main results, in the case of the PS film with a number-average molecular weight, M_n , smaller than 40,000, the surface was in a glass-rubber transition state or a rubbery one at room temperature even though the bulk glass transition temperature, T_g^b , was far above room temperature. This peculiar molecular motion at the surface has been explained in terms of chain end effect and reduced cooperativity. Also, chain conformation and entanglement at the surface would be different from those in the bulk^[3, 4] and thus, such factors might affect surface molecular motion as well^[5]. Based on the above-mentioned experimental results, it seems reasonable to infer that surface chains are movable over a relatively large distance compared with the characteristic length scale for segmental motion even at a temperature below the T_g^b as long as the temperature is higher than the T_g^s . The objective here is to reveal directly chain diffusion at temperatures below T_g^b . Two independent experiments are performed in this study. The first is the time evolution of the interfacial width of PS bilayers, and the second is the surface composition change of poly(styrene-*block*-methyl methacrylate) P(St-*b*-MMA) diblock copolymer films.

* This work was in part supported by a Grant-in-Aid for Scientific Research (A) (#13355034) from the Ministry of Education, Science, Sports, and Culture, Japan.

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Invited lecture presented at the International Symposium on Polymer Physics, 2002, Qingdao, China

Received August 31, 2002

EXPERIMENTAL SECTION

Interfacial Evolution of (hPS/dPS) Bilayers

Monodisperse PS (hPS) and deuterated PS (dPS) were used to prepare bilayer films. hPS with M_n of 29,000 and molecular weight dispersity M_w/M_n of 1.07 was synthesized by a living anionic polymerization using *sec*-butyllithium and methanol as an initiator and a terminator, respectively. M_w denotes the weight-average molecular weight. dPS with M_n of 29,000 and M_w/M_n of 1.03 was purchased from Polymer Source Inc. T_g^b s 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 the PS film with M_n of 29,000 was 264 K^[2]. 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. (hPS/dPS) bilayer films were prepared by a floating method, which has been described elsewhere^[6]. The bilayer interface was built up by two original surfaces of the hPS and dPS films. The bilayers were annealed under nitrogen atmosphere at two different temperatures, 365 and 393 K. The annealing temperature of 365 K was midway between the T_g^s and the T_g^b , whereas 393 K was well above the T_g^b . After annealing for a given time, the bilayer was rapidly quenched by immersing it into liquid nitrogen. The interfacial broadening of the bilayer by annealing was examined on the basis of the depth profiling of dynamic secondary ion mass spectroscopic (DSIMS, SIMS 4000, Seiko Instruments Inc. — Atomika Analysetechnik GmbH) measurement. To achieve a stable sputtering during the DSIMS measurement, the buffer dPS layer was also laminated onto the (hPS/dPS) bilayer by the floating technique. The incident beam of oxygen ions with 4 keV and ca. 30 nA was focused onto a $200 \times 200 \mu\text{m}^2$ area of the specimen surface. The incident angle was 45 deg. A gold layer of 20 nm thickness was sputter-coated onto the specimen surface to avoid charging of the specimen during the measurement.

Surface Reorganization of P(St-*b*-MMA) Films

Symmetric P(St-*b*-MMA) copolymer was purchased from Polymer Laboratories Co. Ltd. M_n , M_w/M_n and PS fraction of copolymer, f_{PS} , was 45.5 k, 1.10, 48.7 wt%, respectively. Since the χN value of the P(St-*b*-MMA) used, where χ and N are the Flory-Huggins interaction parameter and the total degree of polymerization, respectively, was 18.3, it is anticipated that the P(St-*b*-MMA) is in a phase-separated state^[7]. Surface free energy for PS and PMMA at 298 K are 40.7 and 41.2 mJ m⁻², respectively^[8]. The copolymer thin films with a thickness of ca. 50 nm were prepared on gold substrates by a dip-coating method. The DSC curve of the bulk P(St-*b*-MMA) copolymer showed two base line shifts corresponding to T_g^b of PS and PMMA segments, 380.5 K and 394.2 K. The surface chemical composition of the P(St-*b*-MMA) films was examined by X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained with an ESCA 750 X-ray photoelectron spectrometer (Shimadzu Co. Ltd.). The XPS measurement was made under conventional conditions with MgK α X-ray source. The analytical depth of XPS, d , from the outermost surface is defined by

$$d = 3\lambda \cdot \sin \theta \quad (1)$$

where λ is the inelastic mean-free path of photoelectrons in the solids and θ is the emission angle of photoelectrons^[9]. The d of polymeric materials generally ranges from 2.7 to 10.5 nm according to Ashley's equation^[10]. Annealing treatment of the films was carried out in the XPS chamber at various temperatures with 5 K intervals. The specimen was held at each temperature for 8 h.

RESULTS AND DISCUSSION

Interfacial Evolution of (hPS/dPS) Bilayers

Based on inter-diffusion experiments using (hPS/dPS) bilayers, it is first examined whether surface chains can discernibly diffuse even at a temperature below T_g^b .

Figure 1 shows a typical DSIMS profile of H⁺, D⁺ and C⁺ for the (hPS/dPS) bilayer. Since the intensity of 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 can be simply converted to the depth from the surface on the

assumption of a constant sputtering rate through the bilayer, which was pre-examined using a *d*PS film of known thickness. In general, the concentration profile measured by DSIMS is broadened from an ideal one owing to an instrument function mainly originated from an atomic mixing effect. The broadening of the measured profile was corrected by following the procedure reported by Whitlow and Wool^[11]. Assuming that the derivative of D^+ intensity, I_{D^+} , is expressed by a Gaussian function, the interfacial thickness was defined as twice the standard deviation of the Gaussian, corresponding to the depth range where I_{D^+} rises from 16 to 84 % of the maximum value.

Figure 2 shows the time evolution of the interfacial thickness for the (*h*PS/*d*PS) bilayer by annealing at two different temperatures. At 393 K above T_g^b , the interfacial thickness proportionally increased to a half power of the annealing time, t , meaning that the diffusion proceeds in the context of Fick's law. On the other hand, at 365 K, which was above the T_g^s and below the T_g^b , the interfacial thickness remained constant at 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 clearly indicates that chains move across the bilayer interface even at a temperature below T_g^b . Since the bilayer interface was originally composed of two film surfaces, a 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 the surface layer of 4.8 nm thickness is enhanced in comparison with that in the interior region. 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^[12].

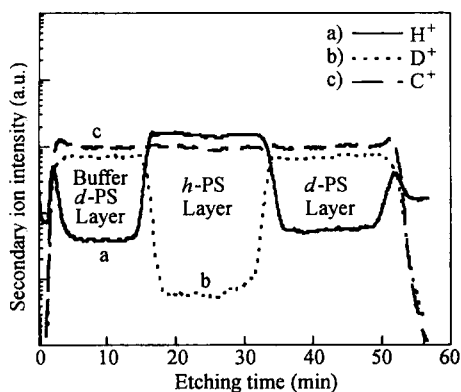


Fig. 1 Typical DSIMS profile of proton and deuterium and carbon ions for the (*h*PS/*d*PS) bilayer

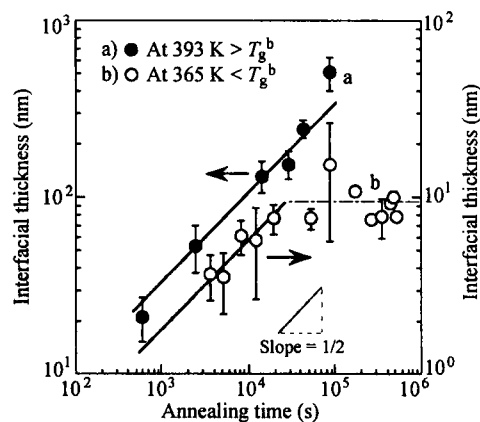


Fig. 2 Double-logarithmic plots of interfacial thickness vs. annealing time for the (*h*PS/*d*PS) bilayer annealed at 393 K and 365 K

Next, the diffusion coefficients at 393 and 365 K are discussed. The concentration profile $C(z')$ of deuterium ion along the direction normal to the surface is given by^[13]

$$C(z') = 0.5 \left[1 - \operatorname{erf} \left\{ \frac{z'}{\sqrt{4Dt}} \right\} \right] \quad (2)$$

where D and z' are diffusion coefficient and distance from the center of the interface, respectively. However, the general DSIMS profile obtained by experiment is convoluted with the instrument function, as mentioned before. In that case, the apparent concentration profile can be expressed as follows^[13]:

$$C_{app}(z') = 0.5 \left[1 - \operatorname{erf} \left\{ \frac{z'}{\sqrt{a^2 + 4Dt}} \right\} \right] \quad (3)$$

where a is an apparent broadening factor and thus the instrument function of 7.4 nm was used for the a . The D values at 393 and 365 K evaluated by Eq. (3) were $(1.8 \pm 0.7) \times 10^{-7}$ and $(7.5 \pm 5.8) \times 10^{-10} \mu\text{m}^2 \cdot \text{s}^{-1}$, respectively, which were much larger than the corresponding bulk diffusion coefficients.

Surface Reorganization of P(St-*b*-MMA) Films

The next step is to study chain diffusion by monitoring the surface reorganization process of the P(St-*b*-MMA) film, from a non-equilibrium state to a quasi-equilibrium state, at a temperature below T_g^b . A structural change on a relatively large scale can only be attained by chain diffusion.

Figure 3 shows the schematic representation of the surface ordering process for the segregated symmetric P(St-*b*-MMA). The as-cast P(St-*b*-MMA) film formed randomly oriented microphase-separated domains, since the solvent was evaporated fairly fast from the film before reaching a quasi-equilibrium state, with the result in that the chains were frozen in a non-equilibrium state. With annealing of the film, the surface reorganization started to proceed, and eventually, the well-defined lamellar structure parallel to the film surface was formed in a quasi-equilibrium state.

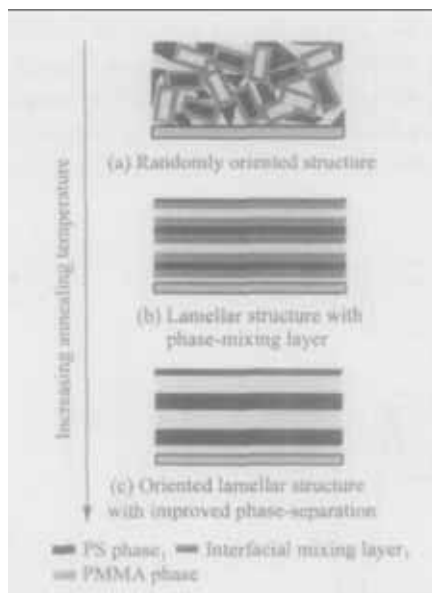


Fig. 3 Schematic representation of surface ordering for the strong segregated symmetric P(St-*b*-MMA) diblock copolymer film upon annealing

Figure 4 shows the XPS C_{1s} spectra of the as-cast P(St-*b*-MMA) film and also PS and PMMA homopolymer films at the emission angle of photoelectrons of 15 deg. The C_{1s} spectra for the P(St-*b*-MMA) films were deconvoluted into four peaks corresponding to neutral carbon (285.0 eV), ether carbon (286.5 eV), carbonyl carbon (288.8 eV) and the shake-up of π - π^* of benzene ring (291.5–292.0 eV) by a standard non-linear curve-fitting. Then, the surface PS weight fraction was evaluated on the basis of the ratio of the XPS peak intensities for the neutral, ether and carbonyl carbons.

Figure 5 shows the annealing temperature dependence of the PS weight fraction for the P(St-*b*-MMA) film in the surface region as a function of the analytical depth. Using Paynter's algorithm^[14], the surface composition within the range of 2.7 to 5.3 nm and 5.3 to 7.4 nm were extracted on the basis of the angular-dependent XPS measurements. Since the initial PS weight fraction at all analytical depths was approximately 50%, it is clear that both PS and PMMA domains were almost equally present in the surface region examined here. Field-emission scanning electron microscopic observation of the as-cast P(St-*b*-MMA) film revealed the presence of randomly oriented domains on the film surface. In the analytical depth ranges of 0.0–2.7 nm and 2.7–5.3 nm, the enrichment of PS segments was recognized more apparently with increasing annealing temperature. The enrichment of PS segments started at a temperature, as shown by the arrows in Fig. 5. This surface segregation of

PS segments results from the minimization of the air/polymer interfacial free energy. On the other hand, the enrichment of PMMA segments was recognized above a certain temperature in the depth range of 5.3–7.4 nm. Each enrichment of PS and PMMA segments in the depth ranges of 0.0–5.3 nm and 5.3–7.4 nm probably corresponds to the formation of the second PMMA layer beneath the first PS surface layer as shown in Fig. 3 because the symmetric diblock copolymer was used as the sample.

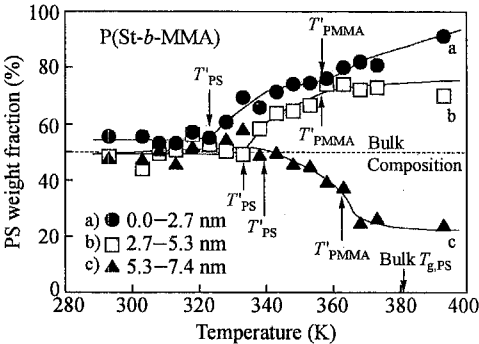
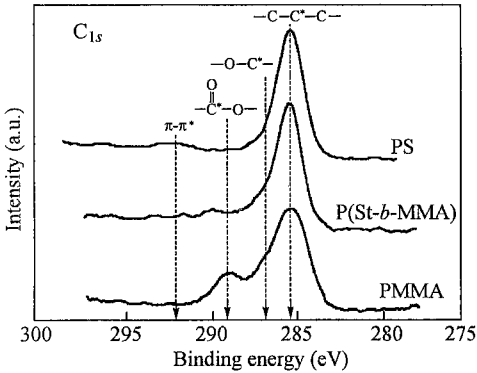


Fig. 4 XPS C_{1s} spectra of the as-cast P(St-*b*-MMA), PS and PMMA homopolymer films at an emission angle of photoelectrons of 15 deg

Fig. 5 Annealing temperature dependence of surface composition for the P(St-*b*-MMA) film as a function of the analytical depth

The surface reorganization can be only attained at a temperature, at which PS or PMMA segments can travel on a large scale, that is, their segmental motions start. Hence, the first and the second increases in the surface PS fraction as shown in Figure 5 might reflect T_g s of PS and PMMA segments. Table 1 summarizes the characteristic temperatures related to the surface reorganization for the P(St-*b*-MMA) film in the different depth ranges. These temperatures are much lower than the T_g^b for the bulk PS and PMMA samples. Here, it is noteworthy that the surface characteristic temperature decreased more strikingly as the analytical region became closer to the outermost surface. This result makes it clear that there is a gradient of molecular motion in the surface region.

Table 1. Temperatures, T' , at which surface composition starts to change, as a function of depth		
Depth range (nm)	T'_{PS} (K)	T'_{PMMA} (K)
0.0–2.7	322.5	356.5
2.7–5.3	332.5	356.5
5.3–7.4	339.4	362.5
Bulk	380.5	394.2

Fox and Flory defined T_g as a temperature, at which a free volume fraction attained a certain value such as 0.025, namely, the iso-free volume theory^[15]. According to this notion, Table 1 implies that more excess free volume exists in the surface region than in the interior bulk phase. The larger free volume at the surface would be due to the localized chain end groups at the surface^[2, 16] and/or just reduced density at the air/polymer interface^[17]. In a sense of the iso-entropy theory by Gibbs and Dimarzio^[18], the term of “free volume” can be replaced by “entropy”. Either way, however, the results presented clearly shows that chain mobility at the surface is enhanced in comparison with the bulk region.

CONCLUSIONS

The time evolution of the PS bilayer interfacial thickness 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 Fickian diffusion. In contrast, in the case of annealing at 365 K, being between the T_g^s and the T_g^b , the interfacial

thickness remained constant after the initial interfacial evolution. This result clearly indicates that surface chains can diffuse even at a temperature below the T_g^b , that is, the mobility of chains in the vicinity of the surface is much enhanced in comparison with the bulk. The enhanced chain mobility was also observed at the surface in the P(St-*b*-MMA) films via the annealing-induced surface reorganization process. In this experiment, it was clearly shown that there was a gradient of molecular motion in the surface region.

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