Depth Dependence of the Surface Glass Transition Temperature of a Poly(styrene-*block*-methyl methacrylate) Diblock Copolymer Film on the Basis of Temperature-Dependent X-ray Photoelectron Spectroscopy

Tisato Kajiyama,* Keiji Tanaka, and Atsushi Takahara

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

Received November 30, 1994

Introduction. Surface structure and surface molecular motion of multiphase polymer films play an important role in many functional applications.[1] In order to design the highly functionalized surface, it is necessary to control surface structure and to reveal the molecular motion at the surface region.

Studies on the surface phase-separated structure of block copolymers have been done extensively by several groups.[2-5] Most works revealed that the component with lower surface free energy compared with that of the other component was preferentially concentrated at the air–polymer interface.

DeKoven and co-workers casted the question "is the molecular surface of polystyrene really glassy?"[6] They concluded that the outermost surface of the PS film with a molecular weight less than 24K was in a rubbery state from the recovery characteristics of the scratched pattern formed by a cantilever tip on the basis of atomic force microscopic (AFM) observation. The authors designed a scanning viscoelasticity microscope (SVM) and studied the two-dimensional mapping of moduli for multiphase polymers.[7] SVM observation of the polymer surface revealed that the magnitude of tan δ at the surface region was higher than that in the bulk sample. In this paper, the terms "bulk sample" and "bulk" are defined as the whole sample and the inside of the specimen, respectively. However, the systematic measurement of glass transition temperature, T_g, at the surface of solid polymers has not been reported yet.

The purpose of this study is to evaluate T_g at the film surface of a symmetric poly(styrene-*block*-methyl methacrylate) diblock copolymer [P(St-*b*-MMA)] on the basis of the temperature-dependent X-ray photoelectron spectroscopic (TDXPS) and the angular-dependent XPS (ADXPS) measurements.

Experimental Section. The symmetric P(St-*b*-MMA) copolymer was purchased from Polymer Laboratories Co., Ltd. The total number-average molecular weight, M_n, and the polydispersity of P(St-*b*-MMA) was 45.5K and 1.10, respectively. Also, the PS weight fraction of copolymer was 48.7%. The magnitudes of the surface free energy for PS and PMMA at 298 K are 40.7 and 41.2 mJ·m^{-2}, respectively.[8] The copolymer thin film with a thickness of ca. 50 nm was prepared by a dip-coating method.

Differential scanning calorimetry (DSC; Rigaku thermoflex 8230) was used to evaluate T_g of the bulk P(St-*b*-MMA) copolymer and PS and PMMA homopolymers. The specimen was heated up to 423 K at a heating rate of 10 K·min^{-1} under a dried nitrogen purge.

The surface chemical composition of the P(St-*b*-MMA) film was investigated on the basis of TDXPS and ADXPS measurements. The XPS spectra were obtained with a ESCA 750 X-ray photoelectron spectrometer (Shimadzu Co., Ltd.). The XPS measurement was performed under conventional conditions with a Mg Kα X-ray source. The main chamber of XPS was maintained at ~10^{-6} Pa. The analytical depth of XPS, d, from the outermost surface is defined by

$$d = 3\lambda \sin\theta \qquad (1)$$

where λ is the inelastic mean-free path of the photoelectron in the solids and θ is emission angle of the photoelectron.[9] The magnitude of d of polymeric materials ranges from 2.7 to 10.5 nm by using the value of λ evaluated from Ashley's equation.[10] The surface composition change owing to the annealing-induced surface reorganization process was measured by using a temperature-controlled heating stage of XPS. The annealing of the specimen was carried out from 293 to 373 K at 5 K intervals. The specimen was held at each temperature for 8 h.

Results and Discussion. The DSC thermogram of P(St-*b*-MMA) showed two base-line shifts which indicated two T_gs. This result indicates that the bulk P(St-*b*-MMA) is in a microphase-separated state. The temperature at the midpoint of the base-line shift was defined as T_g. In a comparison of P(St-*b*-MMA) with the PS and PMMA homopolymers, it was revealed that the lower and higher T_g corresponded to the PS and PMMA components, respectively. $T_{g,PS}$ and $T_{g,PMMA}$ for the bulk P(St-*b*-MMA) were 380.5 and 394.2 K, respectively.

Figure 1 shows the schematic representation of the surface ordering process for the segregated symmetric P(St-*b*-MMA). The as-cast film of P(St-*b*-MMA) formed randomly oriented microphase-separated domains at the surface region, since the solvent was evaporated fairly fast from the film before attainment of an equilibrium state, and then P(St-*b*-MMA) molecular chains were frozen in a non-equilibrium state. With annealing of the as-cast film of P(St-*b*-MMA), the reorganization at the film surface proceeded, and then the well-defined lamellar structure parallel to the film surface was formed in a quasi-equilibrium state.

Figure 2 shows the XPS C_{1s} spectra of the as-cast P(St-*b*-MMA) film and also PS and PMMA homopolymer films at an emission angle of the photoelectron of 15°. 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 $\pi-\pi^*$ of the benzene ring (291.5–292.0 eV) by a standard nonlinear 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 3 shows the annealing temperature dependence of the PS weight fraction for the P(St-*b*-MMA) film at the surface region as a function of the analytical depth. Using Paynter's algorithm,[11] surface compositions within the ranges of 2.7–5.3 and 5.3–7.4 nm were calculated on the basis of ADXPS measurement. Since the initial PS weight fraction at all analytical depths was ca. 50%, it was apparent that both PS and PMMA domains were almost equally present at the surface region in 7.4 nm deep. Field-emission scanning electron microscopic observation for the as-cast P(St-*b*-MMA) film revealed the presence of randomly oriented domains on the film surface. In the case of the analytical

---

* Author to whom correspondence should be addressed.

0024-9297/95/2228-3482$09.00/0

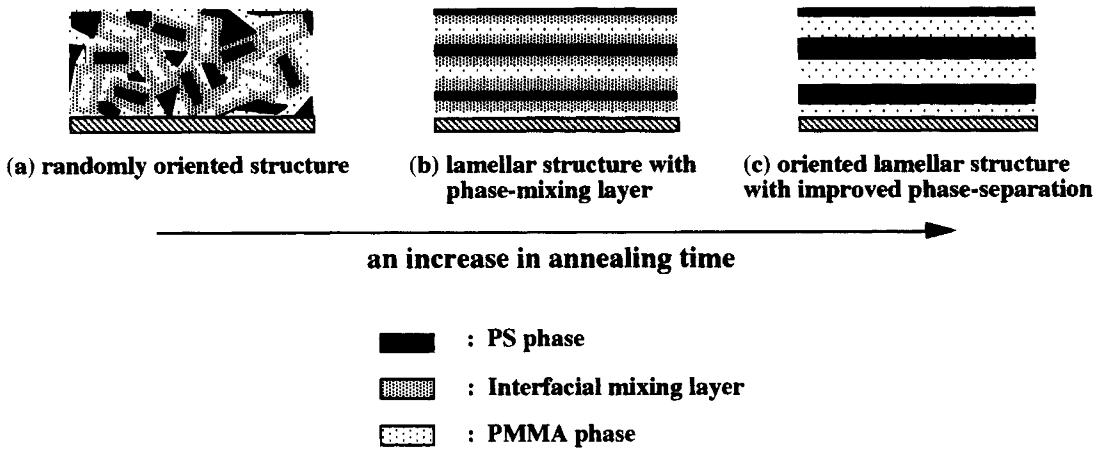

Figure 1. Schematic representation of the surface reorganization of the strong segregated symmetric P(St-*b*-MMA) diblock copolymer. The orientation of lamellae accompanying a decrease in the interfacial phase-mixing layer occurred when the strong segregated P(St-*b*-MMA) film on the hydrophilic substrate was annealed at $T_g < T < T_{MST}$. The reorganization process consists of forming a PS thin overlayer and proceeding with microphase separation.

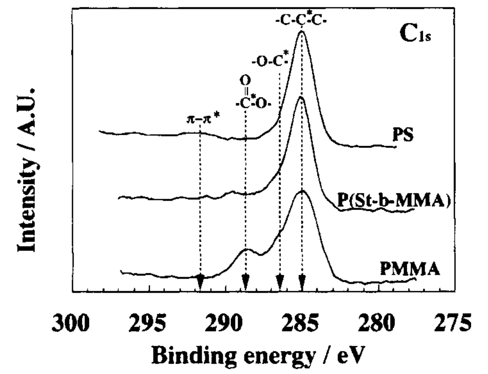

Figure 2. XPS C_{1s} core-level spectra of the as-cast P(St-*b*-MMA) film and also PS and PMMA films.

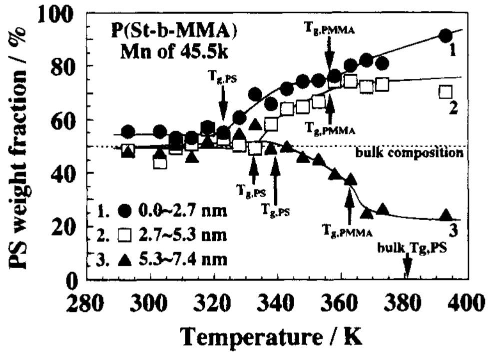

Figure 3. Annealing temperature dependence of the surface composition of a P(St-*b*-MMA) film as a function of the analytical depth.

depth ranges of 0.0−2.7 and 2.7−5.3 nm, the enrichment of PS segments was recognized more apparently with an increase in the annealing temperature. The enrichment of PS segments started at a certain annealing temperature, as shown by the arrows in Figure 3. This surface enrichment 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 annealing temperature in the case of the analytical depth range of 5.3−7.4 nm. Therefore, each enrichment of PS and PMMA segments in the depth ranges of 0.0−5.3 and 5.3−7.4 nm clearly indicates the formation of the second PMMA layer beneath the first PS surface layer as shown in parts b or c of Figure 2, since the symmetric diblock copolymer is used as the sample.

Table 1. T_g for P(St-*b*-MMA) with M_n of 45.5K in Different Depth Ranges

depth range/nm	$T_{g,PS}$/K	$T_{g,PMMA}$/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

The surface reorganization can be attained in the annealing temperature range at which PS or PMMA segments can change their conformation or aggregation state in a large scale, that is, their micro-Brownian motions start. Therefore, the first and the second increases in the PS weight fraction as shown in Figure 3 correspond to T_gs of PS and PMMA segments, because the PS and PMMA segments are present on the surface of the as-cast film. Table 1 summarizes T_gs for P(St-*b*-MMA) in different depth ranges. Table 1 apparently indicates that T_gs of PS and PMMA segments at the film surface are much lower than those for the bulk PS and PMMA samples. The magnitude of T_g decreased more strikingly as the analytical region became closer to the outermost surface. Fox and Flory defined that T_g was a temperature at which a free volume fraction attained a certain constant value.[12] Therefore, based on the iso-free-volume theory, Table 1 indicates that more excess free volume exists at the surface region in comparison with that in the bulk. The larger free volume at the surface region compared with that in the bulk sample would be due to the localized chain end groups at the surface region[13] and/or the presence of a geometrically unsymmetrical atmosphere at the air−polymer interface. Also, the temperature at which the excess entropy attained a certain constant value was defined as T_g by Gibbs and Di Marzio.[14] Thus, according to Gibbs' and Di Marzio's definition, the iso-entropy theory, Table 1 indicates that a polymer chain at the surface region has more excess entropy compared with that in the bulk. At the present time, it is hard to decide which contribution from excess free volume or excess entropy is the main reason for a decrease of T_g at the surface region.

In conclusion, the surface T_g for P(St-*b*-MMA) has been evaluated on the basis of TDXPS. It was revealed that the surface T_g for P(St-*b*-MMA) was much lower than that for its bulk sample. Also, the depth dependence of T_g for P(St-*b*-MMA) has been revealed on the basis of the combination of TDXPS and ADXPS. The great decrease in T_g for P(St-*b*-MMA) was observed for the depth closer to the outermost surface.

References and Notes

(1) Takahara, A. In *Modern Approaches to Wettability*; Schrader, M., Loeb, G., Eds.; Plenum Press: New York, 1992; Chapter 7, p 179.
(2) Takahara, A.; Takahashi, K.; Kajiyama, T. *J. Biomater. Sci., Polym. Ed.* **1993**, *5* (3), 183.
(3) Chen, X.; Gardella, J. A., Jr.; Kumler, P. L. *Macromolecules* **1993**, *26*, 3778.
(4) Lewis, K. B.; Ratner, B. D. *J. Colloid Interface Sci.* **1993**, *159*, 77.
(5) Green, P. F.; Christensen, T. M.; Russell, T. P.; Jérôme, R. *Macromolecules* **1989**, *22*, 2189.
(6) Meyers, G. F.; DeKoven, B. M.; Seitz, J. T. *Langmuir* **1992**, *8*, 2330.
(7) Kajiyama, T.; Tanaka, K.; Ohki, I.; Ge, S. R.; Yoon, J. S.; Takahara, A. *Macromolecules* **1994**, *27*, 7932.
(8) Wu, S., Paul, D. R., Eds. *Polymer Blends*; Academic Press: New York, 1978; Vol. 1.
(9) Andrade, J. D. In *Surface and Interfacial Aspects of Biomedical Polymers Vol. 1—Surface Chemistry and Physics*; Andrade, J. D., Ed.; Plenum Press: New York, 1985; Chapter 6, p 105.
(10) Ashley, J. C. *IEEE Trans. Nucl. Sci.* **1980**, *NS-27*, 1454.
(11) Paynter, R. W. *Surf. Interface Anal.* **1981**, *3*, 186.
(12) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(13) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.
(14) Gibbs, J. H.; Di Marzio, E. A. *J. Chem. Phys.* **1958**, *43*, 373.

MA9461411