Effect of Chain End Chemistry on Surface Molecular Motion of Polystyrene Films

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Introduction. Recently, studies on thermal molecular motions in polymeric thin films[1−3] and at the polymeric solid surface[4,5] have remarkably progressed in major research fields due to technological importance as well as scientific interests. The glass transition behavior in polystyrene (PS) thin films is fairly different from that of the bulk sample due to both an increase in the ratio of interfacial area to its volume and the hydrophobic end group localization at the surface, resulting in a striking depression on its glass transition temperature, T_g.

We have investigated surface molecular motions of the monodisperse and polydisperse PS films by using scanning viscoelasticity microscopy (SVM) and lateral force microscopy (LFM).[6,7] In the case of the monodisperse PS film with the number-average molecular weight, M_n, smaller than ca. 30k, synthesized by a living anionic polymerization using *sec*-butyllithium and methanol as an initiator and a termination reagent, respectively, the surface was in a glass−rubber transition state even at room temperature.[6] This active surface molecular motion can be interpreted in terms of an excess free volume induced by the surface localization of chain end groups due to its smaller surface free energy compared with that of the main chain part. On the other hand, in the case of commercially available polydisperse PS film with polar chain ends containing the M_n component smaller than ca. 30k, no remarkable active surface molecular motion was observed at 293 K due to a depletion of chain ends from the outermost surface. However, since the chain end structure of polydisperse PS used in our previous experiment is not fully known, the surface molecular motions of the PS films with well-defined polar chain ends should be investigated. In this study, the surface molecular motions of α,ω-dicarboxy-terminated PS (α,ω-PS-$(COOH)_2$) and α,ω-diamino-terminated PS (α,ω-PS-$(NH_2)_2$) are investigated by using LFM at 293 K, and also, proton-terminated PS (H-PS) is used as a reference material.

Experimental Section. Monodisperse PSs with various chain ends such as H-PS, α,ω-PS$(COOH)_2$, and α,ω-PS$(NH_2)_2$ were used as materials. Table 1 shows the characteristics of three kinds of PSs. H-PS was synthesized by a living anionic polymerization using *sec*-butyllithium as an initiator. Thus, both chain end portions are composed of a *sec*-butyl group and a proton-terminated styrene unit, respectively. α,ω-PS$(COOH)_2$ was purchased from Polymer Source, Inc. The initiator used for the preparation of α,ω-PS$(COOH)_2$ was lithium naphthalene. The carboxyl end groups were introduced by reacting the living end with highly purified CO_2 gas. The functionality of α,ω-PS$(COOH)_2$ was determined by acid−base titration in toluene/methanol with NaOH, using phenolphthalein as the indicator. Also, α,ω-PS-$(NH_2)_2$ was synthesized by a living anionic polymerization using potassium naphthalene and 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane as an initiator and termination reagent, respectively.[8] The protecting group for the amino function was removed by reprecipitation using methanol-added hydrochloric acid. The functionality of α,ω-PS$(NH_2)_2$ was determined on the basis of thin-layer chromatography.[8] The M_w and M_n were evaluated from gel permeation chromatography (GPC).

Table 1. Characterizations of Polystyrenes Used in This Study

sample	$10^{-3}M_n$[a]	M_w/M_n[a]	functionality	bulk T_g[b]/K
H-PS	9.0	1.09		368.4
α,ω-PS$(COOH)_2$	12.0	1.09	1.98	383.0
α,ω-PS$(NH_2)_2$	7.9	1.10	1.95	365.9

[a] By GPC. [b] By DSC.

Table 2. Surface Compositions of PSs

	O/C		N/C	
sample	surface	bulk	surface	bulk
α,ω-PS$(COOH)_2$	0.0028	0.0044		
α,ω-PS$(NH_2)_2$			0.0013	0.0033

The surface chemical compositions of the PS films were investigated on the basis of X-ray photoelectron spectroscopic (XPS) measurement. The XPS spectra were obtained with an ESCA 850 X-ray photoelectron spectrometer (Shimadzu Co. Ltd.). The XPS measurement was performed under conventional conditions with a Mg Kα X-ray source at 8 kV and 30 mA. All C_{1s} peaks corresponding to the neutral carbon were calibrated at a binding energy of 285.0 eV to correct for the charging energy shift. Since the magnitude of the emission angle of the photoelectron was 30°, the magnitude of the analytical depth from the outermost surface was ca. 5.3 nm.

In order to investigate the surface molecular motions of these PS films, LFM measurements were carried out at 293 K in air under a repulsive force of ca. 10−25 nN. The LFM equipment used in this study was a SPA 300 (Seiko Instruments Industry Co., Ltd.) with an SPI 3700 controller. A commercially available silicon nitride (Si_3N_4) cantilever with integrated tips (Olympus Co., Ltd.) was used. The nominal spring constant of the cantilever was 0.09 $N\cdot m^{-1}$.

Results and Discussion. Table 2 summarizes the surface chemical composition of α,ω-bifunctional PS in a depth range of ~5.3 nm. In the cases of α,ω-PS-$(COOH)_2$ and α,ω-PS$(NH_2)_2$, the elemental ratio of oxygen/carbon and nitrogen/carbon can be used for the measure of the surface concentration of a chain end group. The elemental ratios in the bulk state were calculated from the chemical structure. As the surface

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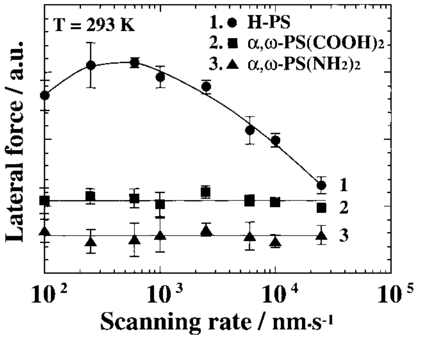

Figure 1. Scanning rate dependence of lateral force for the H-PS, α,ω-PS(COOH)$_2$, and α,ω-PS(NH$_2$)$_2$ films at 293 K.

elemental ratios for O/C for α,ω-PS(COOH)$_2$ and N/C for α,ω-PS(NH$_2$)$_2$ were similar than those in bulk, it can be concluded that the hydrophilic end groups are depleted from the outermost surface in order to minimize the interfacial free energy at the air/solid interface. On the other hand, the end group localization at the surface of H-PS has been confirmed by dynamic secondary ion mass spectroscopic measurement.[6]

In order to investigate an effect of chain end structure on surface molecular motions, lateral forces of three kinds of PS films with various chain end groups were evaluated at 293 K by LFM. Figure 1 shows the scanning late dependence of the lateral force for the H-PS, α,ω-PS(COOH)$_2$, and α,ω-PS(NH$_2$)$_2$ films. As discussed in our previous paper, the scanning rate dependence of the lateral force corresponds well to the frequency dependence of the loss modulus, E''.[7] Thus, it can be concluded that the polymeric solid surface is in a glass−rubber transition state, if the magnitude of the lateral force depends on the scanning rate. As shown in Figure 1, the magnitude of the lateral force for the H-PS film was strongly dependent on the scanning rate and the peak of the lateral force was clearly observed on the lateral force−scanning rate curve. This result indicates that surface E'' has the maximum value in the scanning rate region employed here; that is, the surface of the H-PS film is in a glass−rubber transition state at 293 K, even though the bulk T_g evaluated by differential scanning calorimetry (DSC) is far above 293 K. Since chain end groups of H-PS are preferentially segregated at the surface due to its lower surface free energy compared with that of the main chain part, an excess free volume is induced at the surface by the chain end terminus. Thus, the surface molecular motion of the PS film becomes fairly active in comparison with the bulk one.

On the other hand, in the case of α,ω-PS(COOH)$_2$ film, no distinct scanning rate dependence of the lateral force was observed, as shown in Figure 1. This result clearly indicates that the surface of the α,ω-PS(COOH)$_2$ films is in a glassy state at 293 K. Since both chain end groups for α,ω-PS(COOH)$_2$ have a higher surface free energy in comparison with the main chain part, chain end groups are depleted from the surface region,[9] resulting in an excess free volume at the surface. Also, because α,ω-PS(COOH)$_2$s are intermolecularly associated by hydrogen bonding, the apparent molecular weight of α,ω-PS(COOH)$_2$ increases, resulting in a decrease in the chain end group concentration. Thus, it seems reasonable to conclude that the surface of the α,ω-PS(COOH)$_2$ film is in a glassy state at 293 K. The intermolecular association of α,ω-PS(COOH)$_2$ was confirmed on the basis of Fourier transform-infrared spectroscopic measurements.[10]

In order to reduce the intermolecular association effect, that is, to investigate only the effect of depletion of chain ends from the surface, the scanning rate dependence of the lateral force for the α,ω-PS(NH$_2$)$_2$ film, which could not form a strong intermolecular association, was evaluated at 293 K. The magnitude of the lateral force was independent of the scanning rate in fashion similar to that of the α,ω-PS(COOH)$_2$ film. It was confirmed by XPS measurement that chain end groups migrated into the surface internal region owing to its higher surface free energy compared with the main chain part. Thus, it seems reasonable to conclude that the surface molecular motion is not activated in comparison with the bulk region at 293 K if chain end groups cannot be preferentially segregated at the surface even though M_n is as small as ca. 10k.

In conclusion, XPS measurements revealed that the hydrophilic end groups of α,ω-bifunctional PSs were depleted from the outermost surface. The effect of chain end chemistry on the surface molecular motion was investigated on the basis of the LFM measurement at 293 K using the monodisperse PS films with various chain end groups. It was found that the surface molecular motion was not activated in comparison with the bulk one at 293 K, if chain end groups migrated deeply into the bulk region.

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