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Effect of End Group Chemistry on Surface Molecular Motion of Monodisperse Polystyrene Films

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SUMMARY : The surface molecular motion of monodisperse polystyrene (PS) with various chain end groups was investigated on the basis of temperature-dependent scanning viscoelasticity microscope (TDSVM). The surface glass transition temperatures, T_g^ss for the proton-terminated PS (PS-H) films with number-average molecular weight, M_n of 4.9k - 1,450k measured by TDSVM measurement were smaller than those for the bulk one, with corresponding M_ns, and the T_g^ss for M_n smaller than ca. 50k were lower than room temperature (293 K). In the case of M_n = ca. 50k, the T_g^ss for the α,ω-diamino-terminated PS (α,ω-PS$(NH_2)_2$) and α,ω-dicarboxy-terminated PS (α,ω-PS$(COOH)_2$) films were higher than that of the PS-H film. On the other hand, the T_g^s for the α,ω-perfluoroalkylsilyl-terminated PS (α,ω-PS$(SiC_2C^F{}_6)_2$) film with the same M_n was much lower than those for the PS films with all other chain ends. The change of T_g^s for the PS film with various chain end groups can be explained in terms of the depth distribution of chain end groups at the surface region.

Introduction

Glass transition temperature, T_g is the fundamental parameter of polymeric solids which is closely related to the state of thermal molecular motion. In the case of ultrathin polymer films, the glass transition behavior has been evaluated based on spectroscopic ellipsometry1), X-ray reflectivity2), and Brillouin light scattering3). These measurements revealed that the magnitude of T_g for the ultrathin film depended on the film thickness and the state of interaction between polymer chain and substrate. Since these measurements were based on the temperature change in average physicochemical properties of polymer ultrathin films, it is difficult to measure the molecular motion of polymer film at the outermost surface region.

Scanning force microscopy (SFM) can directly evaluate the physicochemical properties at the outermost surface region on the basis of the deflection and torsion of the cantilever which reflect atomic force, adhesion, friction, magnetic or chemical

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interaction between tip and polymer surface. In our previous study, the surface relaxation process for the monodisperse polystyrene (PS) films with different number-average molecular weights, M_ns had been investigated by lateral force microscopy (LFM)[4)] and scanning viscoelasticity microscopy (SVM)[5)]. From the temperature change in the shift factors used in the formation of the master curve, the apparent activation energy for the surface α_a-relaxation process of the monodisperse PS film was found to be approximately half that for the bulk one[6)]. The purpose of this study is to evaluate the influence of the chain end chemistry on the magnitude of surface T_g, T_g^s for the monodisperse PS films with various M_ns on the basis of temperature-dependent SVM (TDSVM)[7)].

Experimental

The polymers used in this study were monodisperse four kinds of PSs with various chain end chemistry, and were synthesized by a living anionic polymerization. Table I tabulates the M_n, the molecular weight dispersity, M_w/M_n, and the bulk T_g, T_g^b for four kinds of PSs. The T_g^b was evaluated on the basis of differential scanning calorimetric (DSC) measurement at a heating rate of 10 K min^{-1} under a dry nitrogen purge. The monodisperse sample was used in order to avoid the influence on

Table I. Characterizations of four kinds of PSs used in this study.

Sample	M_n	M_w/M_n	T_g^b / K
PS-H	4.9k	1.09	362
	30k	1.08	374
	54k	1.03	377
	90k	1.05	378
	250k	1.03	379
	1,450k$^{a)}$	1.06	380
α,ω - $PS(NH_2)_2$	23k	1.08	375
	52k	1.08	378
α,ω - $PS(COOH)_2$	12k$^{b)}$	1.09	385
	52k$^{b)}$	1.08	382
α,ω - $PS(SiC_2C^F{}_6)_2$	25k	1.12	373
	48k	1.17	377
	93k	1.17	379

^{a}Purchased from Pressure Chemical Co., Ltd.
^{b}Purchased from Polymer Source. Inc.

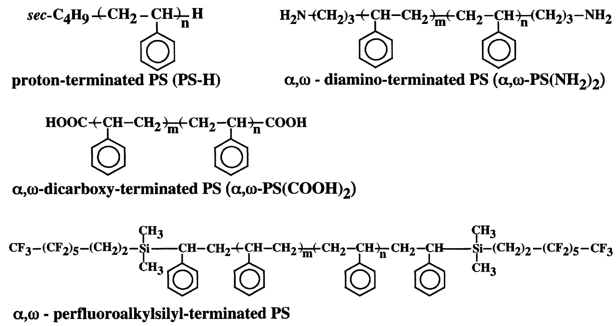

Fig. 1: Chemical structure of PSs with various chain end groups.

surface migration of lower M_n in polydisperse sample. Fig. 1 shows the chemical structure of the PSs with various chain end groups. The PS films were coated from a toluene solution onto cleaned silicon wafer by a spin-coating method. The film thickness evaluated by ellipsometric measurement was ca. 200 nm. These films were annealed at 423 K for 24 hrs under vacuum to achieve the thermal equilibrium state. In order to investigate the surface molecular motion of these PS films, the surface dynamic viscoelastic function, in other words, the surface phase lag between dynamic deformation and force signals was measured as a function of temperature based on TDSVM. TDSVM equipment was SPA 300HV (Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. TDSVM measurement was carried out at various temperatures in vacuo under a reference force of ~1 nN (repulsive force). The modulation frequency and the modulation amplitude at the supporting part of the cantilever were 4 kHz and 1.0 nm, respectively. A commercially available silicon nitride (Si_3N_4) tip on a rectangular cantilever with the bending spring constant of 0.09 N m^{-1} (Olympus Co., Ltd.) was used.

Results and Discussion

Fig. 2 shows the temperature dependence of the surface phase lag, δ^s between imposed stimulation displacement and detected response force signals, and the bulk tanδ for the monodisperse proton-terminated PS (PS-H) films with M_ns of 4.9k, 30k, 54k, 90k, 250k, and 1,450k. The temperature dependence of bulk tanδ was obtained by Rheovibron (DDV-01FP, Orientec A&D Co., Ltd.) at 3.5 Hz. Though it might be possible that the measured δ_s contains the contribution of the phase lag from the mechanical vibration system[8)], the calibration has not been done at the

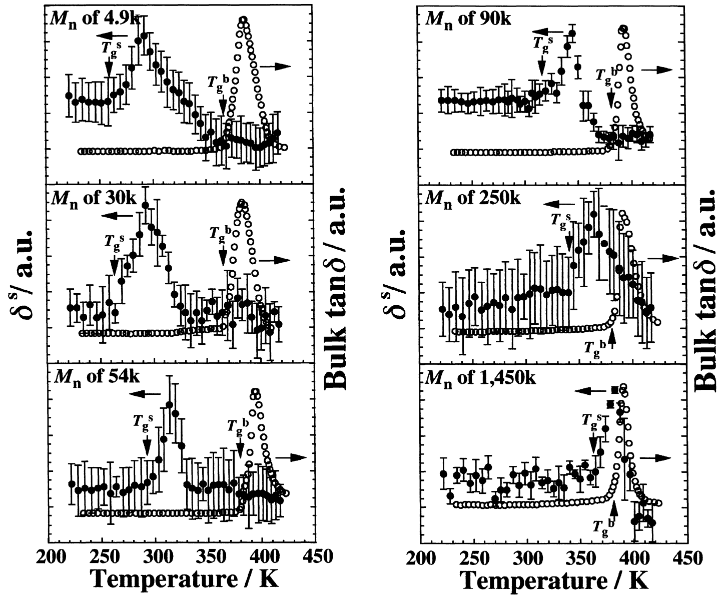

Fig. 2: Temperature dependence of surface phase lag, δ^s and bulk tanδ for the PS-H films with different M_ns.

present time because of the difficulty in determination of the calibration constant. However, it seems reasonable to compare quantitatively the temperature dependence of the δ^s and the bulk tanδ to decide the T_g^s and the T_g^b since the calibration constant might not change so much in the temperature range around these T_g^ss. Fig. 2 shows the α_a loss peaks corresponding to the surface and bulk micro-Brownian motion of polymeric chains, respectively. The peaks of δ^ss appeared in a lower temperature region than those bulk tanδs, though the δ^s and the bulk tanδ were measured at 4 kHz and 3.5 Hz, respectively. The threshold temperature, that is, the temperature at which the magnitude of δ^s or bulk tanδ starts to increase, can be empirically used as the surface or bulk T_gs[9]. Then, in this study, this threshold temperatures of the δ^s and the bulk tanδ were defined as T_g^s and T_g^b, respectively. The T_g^s and T_g^b are shown by arrows in Fig. 2. The T_g^ss were more apparently shifted to a higher temperature with an increase in M_n than T_g^bs, as shown in Fig. 2. Therefore, it seems reasonable to conclude that the surface thermal molecular motion is more activated in comparison with the bulk one. Also, the T_g^s for the PS-H film was strongly dependent on the M_n as compared with the bulk one. These results indicate that the surface molecular motion of the monodisperse PS-H film is closely related to the concentration of chain end groups at the film surface. Since the magnitudes of the T_g^s for the PS-H films with M_n lower than ca. 50k were below 293 K, it seems reasonable to conclude that the PS-H films surface with M_n lower than ca. 50k is in a glass-rubber transition state or a rubbery state, even at room temperature, 293 K. The T_g^s asymptotically approaches the bulk one with an increase in M_n and the T_g^s for high M_n of ca. 1,000k was slightly lower than the bulk one. Therefore, these results apparently indicate that a reduction of T_g^s of PS-H in comparison with T_g^b may be caused by an increased free volume at the surface due to the preferential surface enrichment of chain end groups as well as the decrease in number of chain entanglement density10). Also, these results support our previous result that the magnitude of activation energy for the surface α_a-relaxation process at the air-polymer interface was almost half as much as that for the bulk one, maybe due to an extra freedom for the active thermal segmental motion of PS chains at the air-polymer interface6).

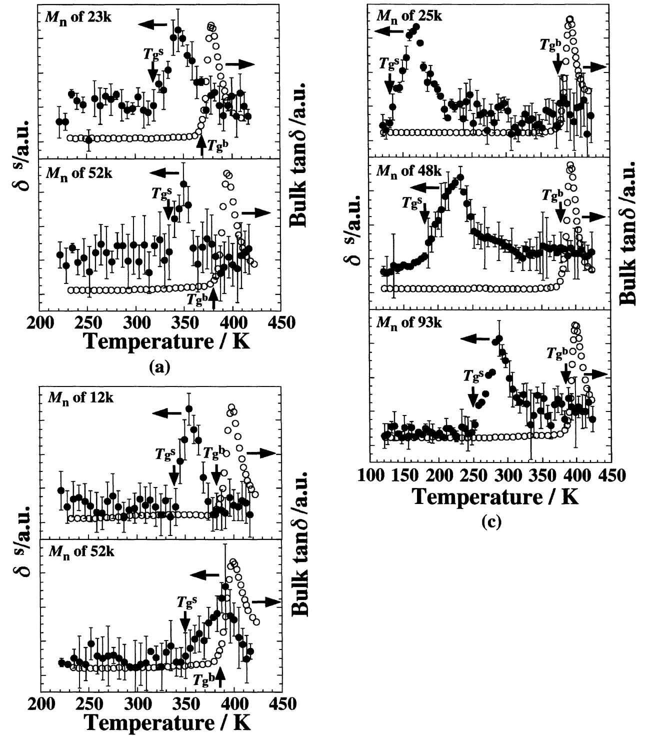

Fig. 3: Temperature dependence of δ^s and bulk tanδ for (a) α,ω-PS(NH$_2$)$_2$, (b) α,ω-PS(COOH)$_2$ and (c) α,ω-PS(SiC$_2$C$^F_6$)$_2$ films.

The previous results revealed that the surface molecular motion of the monodisperse PS-H film was closely related to the distribution of chain end groups at the outermost surface [4-6]. However, the surface molecular motion of the PS film with different kind of chain end groups has not been evaluated yet[11]. PSs with both chain end groups of amino, carboxyl, and fluoroalkylsilyl groups were prepared, and the T_g^ss of these PSs were measured based on TDSVM. Fig. 3 shows the temperature dependence of the δ^s and the bulk tanδ for (a) the α,ω-diamino-terminated PS (α,ω-$PS(NH_2)_2$) films with M_ns of 23k and 52k, (b) the α,ω-dicarboxy-terminated PS (α,ω-$PS(COOH)_2$) films with M_ns of 12k and 52k, and (c) the α,ω-perfluoroalkylsilyl-terminated PS (α,ω-$PS(SiC_2C^F{}_6)_2$) films with M_ns of 25k, 48k and 93k. The peaks of δ^s, which correspond to the surface α_a-relaxation process, were similarly observed on the δ^s-temperature curves of all kinds of PSs and appeared in a lower temperature region than those of bulk tanδs, as shown in Fig. 3 (a), (b) and (c). As mentioned above, it is empirically accepted that the threshold temperature of δ^s and bulk tanδ were decided as T_g^s and T_g^b, respectively. In the same manner as PS-H, the magnitude of the T_g^ss for the α,ω-$PS(NH_2)_2$, α,ω-$PS(COOH)_2$ and α,ω-$PS(SiC_2C^F{}_6)_2$ films was lower than the bulk one. However, these T_g^ss at the same M_n (M_n = ca. 50k) were strongly depended on the end group chemistry. At the same M_n, the T_g^ss for the α,ω-$PS(NH_2)_2$ and α,ω-$PS(COOH)_2$ films were higher than that for the PS-H film. On the other hand, a larger depression of T_g^s for the α,ω-$PS(SiC_2C^F{}_6)_2$ film than those of PSs with other chain end groups was observed.

Fig. 4 shows the molecular weight dependence of the surface and bulk T_gs for the monodisperse PS films with various chain end groups. The T_g^ss of α,ω-$PS(NH_2)_2$ and α,ω-$PS(COOH)_2$ were higher than those of PS-H with corresponding M_n. Since both chain end groups for α,ω-$PS(NH_2)_2$ and α,ω-$PS(COOH)_2$ have higher surface free energy in comparison with the main chain part, the chain end groups are depleted from the surface region. 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 or the networks of PS chains were formed, resulting in a decrease in surface molecular motion. Thus, it seems reasonable to conclude that the T_g^ss of α,ω-$PS(COOH)_2$ were higher than those of α,ω-$PS(NH_2)_2$ and PS-H at the same M_n. On the other hand, the T_g^ss of α,ω-$PS(SiC_2C^F{}_6)_2$ film with all M_ns were much lower than the bulk one and that for the PS-H film. Since the fluoroalkylsilyl end group is more hydrophobic than the main chain part and the *sec*-butyl and $-CH_2-CH_2(C_6H_5)$ groups, which are the chain end group of PS-H, the surface free energy of fluoroalkylsilyl end group is lower than that of PS-H.

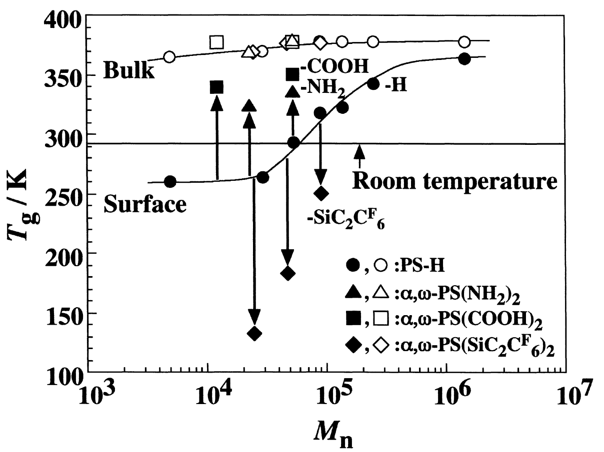

Fig. 4: Molecular weight dependence of surface and bulk T_gs for the PS films with various chain end groups. The filled and open symbols denote the data for the T_g^s and T_g^b, respectively.

Therefore, a larger depression of T_g^s for the α,ω-PS($\mathrm{SiC_2C^F_6}$)$_2$ film than that of PS-H was explained by the intensive surface localization of fluoroalkylsilyl end group compared with other kind of PSs. In the case of the α,ω-PS($\mathrm{SiC_2C^F_6}$)$_2$ film, this intensive surface localization of fluoroalkylsilyl end group in the surface layer less than ~ 1 nm was confirmed on the basis of angular-dependent X-ray photoelectron spectroscopic (ADXPS) measurement.

Conclusion

The molecular weight dependences of the T_g^s for the monodisperse PS film with various chain end groups were evaluated by TDSVM measurement. The T_g^s's for the various chain end group terminated PS film were much lower than the bulk ones, and the T_g^s was strongly dependent on a difference of surface free energy between chain end group and main chain. The difference of T_g^s was explained by the surface concentration of chain end groups which is closely related to the free volume fraction.

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