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Surface Thermal Molecular Motion of Chain End-Modified Polystyrenes

Tisato Kajiyama, Keiji Tanaka, Atsushi Takahara*

Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka 812-8581, Japan

Summary: Surface glass transition temperature, T_g^s, of three classes of monodisperse polystyrene, proton-terminated (PS-H), α,ω-diamino-terminated (α,ω-PS(NH$_2$)$_2$) and α,ω-dicarboxy-terminated (α,ω-PS(COOH)$_2$), were studied by scanning force microscopy. T_g^s of all samples was discernibly lower than the corresponding bulk glass transition temperature, T_g^b. Also, T_g^s value was strongly dependent on what the chemical structure of chain end groups was. Based on the time-temperature superposition principle, apparent activation energy of the α_a-relaxation process corresponding to surface segmental motion was evaluated to be approximately 230 kJ•mol^{-1}. This value was much smaller than the reported bulk ones, and was independent of the chemical structure of chain ends. This result implies that the cooperativity for the α_a-relaxation process at the PS surface is reduced in comparison with the bulk due probably to an existence of the free space presented to polymer segments at the surface. Hence, it was concluded that the surface α_a-relaxation process was activated by not only the chain end effect but also the reduced cooperativity at the surface.

Introduction

Molecular mobility of polymer chains at the surface has received a great deal of attention recently because of its importance in various functional applications such as permselective membranes, biomaterials, lubricant, adhesives, corrosion-resistant coatings, etc. Systematical understanding of surface properties, which are totally different from bulk ones, is crucial so that the performance of functional polymeric materials can be promisingly improved. This issue is also of importance and interest in the field as fundamentals of polymer science.

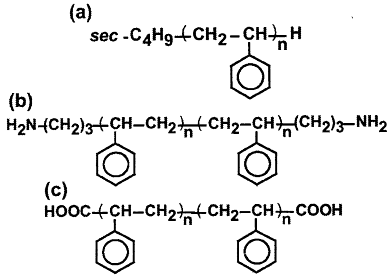

Figure 1. Chemical structures of PSs used; (a) PS-H, (b) α,ω-PS(NH$_2$)$_2$, (c) α,ω-PS(COOH)$_2$.

Since 1994, we have studied surface molecular motion of monodisperse proton-terminated polystyrene (PS-H) films based on scanning viscoelasticity microscopy (SVM) and lateral force microscopy (LFM).[1-3] SVM enables one to gain direct access to viscoelastic properties on solid surfaces by measuring an amplitude change in response force, and detecting a phase lag between a stimulus displacement and a response force. LFM relies on a measure of lateral force between a sample surface and a probe tip, and has been demonstrated to be a powerful tool to investigate viscoelasticity of various polymer surfaces as well. Based on both techniques, we have claimed that surface glass transition temperature, T_g^s, was much lower than the corresponding bulk glass transition temperature, T_g^b.[1-5] Although our conclusion has already emerged, it still opens why such active molecular motion takes place at the surface. For the moment, we have proposed the following two reasons to rationalize it; end group effect and reduced cooperativity of surface segmental motion. If the chain end effect is one of responsible factors on surface molecular motion, as we claim, the T_g^s value should be strongly dependent on what the chemical structure of chain end groups is. To strengthen our notion, surface glass transition behavior of PSs with hydrophilic chain ends, which might be depleted at the film surface so as to minimize the air/polymer interfacial free energy, is examined in this study.

Experimental

Proton-terminated polystyrene (PS-H), α,ω-diamino-terminated PS (α,ω-PS$(NH_2)_2$), and α,ω-dicarboxy-terminated PS (α,ω-PS$(COOH)_2$) were used as materials. Figure 1 shows the chemical structures of PS-H, α,ω-PS$(NH_2)_2$ and α,ω-PS$(COOH)_2$. PS films for SVM and LFM measurements were coated from toluene solutions onto cleaned silicon wafers with native oxide layer by a spin-coating method. The PS films were dried at room temperature for more than 24 h in air, and then annealed at 423 K for 24 h in vacuum. The film thickness evaluated by ellipsometric measurement was approximately 200 nm. T_g^s in PS films with various chain ends was evaluated by using SVM and LFM. The detail for both measurements has been reported elsewhere.[4-5]

Results & Discussion

To evaluate T_g^s, surface phase lag, δ^s, between imposed stimulus displacement signal and detected response force one was measured by SVM. Figure 2 shows a typical temperature dependence of δ^s for the PS-H film. The data was for PS-H film with number-average molecular weight, M_n of 140k. A peak observed in Figure 2 can be assigned to the α_a-relaxation corresponding to segmental motion at the surface. Following an empirical way, T_g^s was defined as an onset temperature, at which δ^s started to increase.

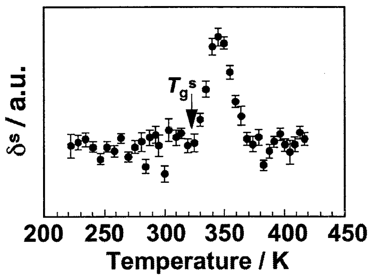

Figure 2. Temperature dependence of δ^s for PS-H with M_n of 140k.

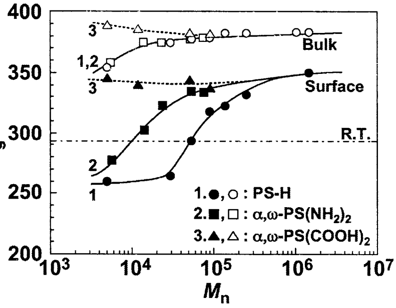

Figure 3. M_n dependence of T_g^s and T_g^b for the PS-H, α,ω-PS$(NH_2)_2$ and α,ω-PS$(COOH)_2$ films.

Figure 3 shows the M_n dependence of T_g^s and T_g^b for the PS-H, α,ω-PS$(NH_2)_2$ and α,ω-PS$(COOH)_2$ films. T_g^b was measured by differential scanning calorimetry (DSC). As a general trend, T_g^s was lower than the corresponding T_g^b. This result implies that thermal molecular motion at the surface is more active than that in the bulk, independent of chain end chemistry. However, the T_g^s value was strongly dependent on the chain end species at a given M_n. Hence, it seems reasonable to consider that the chain end effect is one of the responsible determining factors on the magnitude of T_g^s. In the case of the PS-H, the M_n dependence of T_g^s was more remarkable than that of T_g^b. Thus far, characteristic thermal molecular motion at the PS-H surface has been explained in terms of the chain end effect and the reduced cooperativity.[1-5] The chain end groups of the PS-H are preferentially segregated at the surface due to its lower surface free energy than the main chain part. Since the chain end groups have the larger freedom than the main chain part, an excess free volume is induced at the surface. Also, a segment existing at the surface is supposed to have a fewer neighbor segments to move cooperatively owing to the free space on the polymer phase. Thus, active molecular motion takes place at the PS-H surface. In the case of the α,ω-PS$(NH_2)_2$, the surface free energy of the chain end is relatively larger than that of the main chain part. Thus, it is inferred that the chain ends are depleted at the surface. Actually, angular-dependent X-ray photoelectron spectroscopic measurement revealed that this prediction would be true. This means that an excess free volume at the surface induced by chain end localization may not be counted for the α,ω-PS$(NH_2)_2$ films. Nevertheless, T_g^s was much lower than T_g^b, and the M_n dependence of T_g^s was clear, as shown in Figure 3. Therefore, it seems most likely that thermal molecular motion at the surface is activated by other factors in addition to the chain end effect, such as the reduced cooperativity. In contrast to the PS-H and α,ω-PS$(NH_2)_2$, neither distinct M_n dependence of T_g^s nor T_g^b was observed for the α,ω-PS$(COOH)_2$ film. Since the α,ω-PS$(COOH)_2$ are intermolecularly associated between chain ends via hydrogen bonding, the apparent M_n of the α,ω-PS$(COOH)_2$ increases in comparison with its own M_n.[6] Hence, it is difficult to discuss about the M_n dependence of T_g^s and T_g^b for the α,ω-PS$(COOH)_2$. In any event, it can be envisaged that the chain end chemistry is one of the responsible factors determining on the T_g^s value.

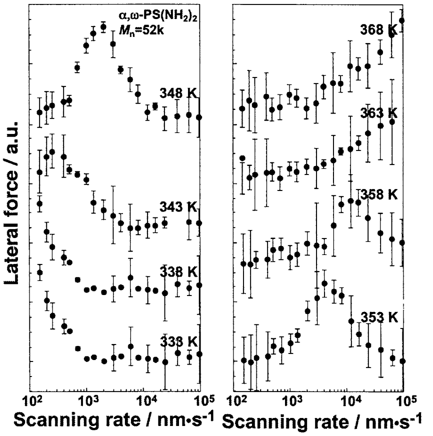

Figure 4. Scanning rate dependence of lateral force for the α,ω-PS$(NH_2)_2$ film with M_n of 52k at the temperature range of 333 to 368 K.

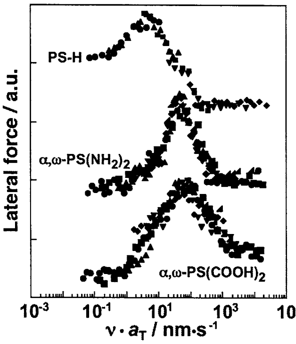

Figure 5. Master curves related to the scanning rate-lateral force relationship for the (1) PS-H with M_n of 140k, (2) α,ω-PS$(NH_2)_2$ with M_n of 52k and (3) α,ω-PS$(COOH)_2$ with M_n of 52k.

Next, apparent activation energy of the surface α_a-relaxation was examined on the basis of the time-temperature superposition principle. Since the measuring frequency of our SVM is limited in one decade at present, the complement technique, LFM, was applied. Figure 4 shows the scanning rate dependence of lateral force at various temperatures for the α,ω-PS$(NH_2)_2$ film with M_n of 52k. The lateral force was independent of the scanning rate at a temperature lower than 323 K. At higher temperatures, 343 to 358 K, a peak of lateral force was clearly observed. Then, the lateral force decreased with a decrease in the scanning rate at the higher temperature than 363 K. Eventually, the lateral force recovered the invariance with respect to the scanning rate. Thus, the overall profiles reflect a successive change of the surface molecular motion from the glassy state to the rubbery one via the transition with increasing temperature. Similar results were obtained for the PS-H and α,ω-PS(COOH)$_2$ films.

Figure 5 shows the master curves of the lateral force-scanning rate relation for the PS-H, α,ω-PS(NH$_2$)$_2$ and α,ω-PS(COOH)$_2$ films, and clearly indicates that the time-temperature superposition can be applied even to the surface α_a-relaxation process. Invoking that the relationship between shift factor, a_T, and measuring temperature is Arrhenius type, the apparent activation energy, $\Delta H^{\ddagger}$, of the surface α_a-relaxation process can be calculated from a linear slope in the plot of a_T against to reciprocal absolute temperature, as shown in Figure 6. The surface $\Delta H^{\ddagger}$ of the PS-H, α,ω-PS(NH$_2$)$_2$ and α,ω-PS(COOH)$_2$ films so obtained were 230±10, 230±10 and 220±10 kJ mol^{-1}, respectively. It is noteworthy here that the surface $\Delta H^{\ddagger}$ is much smaller than the reported values of the $\Delta H^{\ddagger}$ for bulk samples, ranging from 360 to 880 kJ mol^{-1}.[7] The discrepancy of $\Delta H^{\ddagger}$ between surface and bulk indicates that the size and/or energy barrier of the cooperative movement for the α_a-relaxation process are/is reduced at the surface in comparison with the bulk. The reduced cooperativity at the surface can be easily understood by taking into account a fact that the free space is presented to polymer segments at the surface. That is, the existence of the free space induces active micro-Brownian motion at the air/polymer interface. Thus, T_g^s was lower than T_g^b even in the case that the chain end effect can be negligible such as the α,ω-PS(NH$_2$)$_2$, α,ω-PS(COOH)$_2$ and PS-H films with infinite M_n, as shown in Figure 3. Finally, we conclude that the active thermal molecular motion occurs at the surface by the reduced cooperativity in addition to the chain end effect.

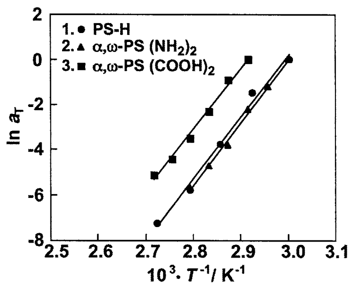

Figure 6. Semi-logarithmic plots of shift factor, a_T, versus reciprocal absolute temperature for the (1) PS-H, (2) α,ω-PS(NH$_2$)$_2$ and (3) α,ω–PS(COOH)$_2$ films.

Conclusions

Glass transition behaviors of the PS-H, α,ω-PS(NH$_2$)$_2$ and α,ω-PS(COOH)$_2$ films were studied by SVM in conjunction with LFM. It was found that T_g^s was lower than the corresponding T_g^b even in the case of the α,ω-PS(NH$_2$)$_2$ and α,ω-PS(COOH)$_2$ films. However, the T_g^s value was strongly dependent on chain end chemistry. The surface $\Delta H^{\ddagger}$ of PS-H, α,ω-PS$(NH_2)_2$ and α,ω-PS$(COOH)_2$ were 230±10, 230±10 and 220±10 kJ mol^{-1}, respectively. These values were well below the bulk $\Delta H^{\ddagger}$. It was concluded that the active thermal molecular motion at the surface was attained by the reduced cooperativity in addition to the chain end effect.

Acknowledgements

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