

NOTES

Further Study of Chain End Effect on Surface Mobility in Monodisperse Polystyrene Films

Keiji TANAKA[†], Fumi ARIURA, Toshihiko NAGAMURA, and Tisato KAJIYAMA^{*,††}

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

*Kyushu University, Fukuoka 812-8581, Japan

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Surfaces of polymeric materials play important roles in many technological applications.¹ Hence, to design highly functionalized polymeric materials, the systematical understanding of aggregation states and physical properties in the surface region, which are sometimes quite different from the bulk ones, is of pivotal importance as the first benchmark.

In the last decade, surface mobility in polymer films, especially polystyrene (PS), has been extensively explored by many research groups. Consequently, major conclusion emerged is that surface dynamics in PS films is much more enhanced than the internal bulk dynamics,^{2–15} although some contradict arguments are still going on.^{16–18} Even if a notion of enhanced surface dynamics is accepted, it is far from clear for the moment why molecular motion at the PS surface must be activated.

So far, we have examined surface glass transition temperature (T_g^s) in films of monodisperse α,ω -diamino-terminated PS, which possesses end groups with higher surface free energy than the main chain part.¹⁹ Since the end groups deeply migrated into the bulk to minimize the interfacial free energy, the difference of glass transition temperature between surface and bulk was not so remarkable as that for PS, synthesized by *sec*-butyllithium and methanol as an initiator and a terminator, respectively (*sec*-Bu-PS-H). In the case of the *sec*-Bu-PS-H, end groups would be partitioned to the surface.^{2b,c} These results clearly show that the chain end concentration at the surface is closely related to T_g^s value.^{20–22} Hence, further discussion about a chain end effect on surface dynamics should be made so that a whole picture of peculiar surface dynamics can be rationalized. Of course, many factors such as reduced cooperativity,^{2c,23} chain orientation,²³ and loose entanglement¹³ should be simultaneously stud-

ied in addition to the chain end effect.

In general, as a monodisperse PS, *sec*-Bu-PS-H has been used in most researches related to surface phenomenon. However, *sec*-Bu-PS-H possesses an asymmetric structure in terms of chain ends, and this would lead to ambiguous understanding to the chain end effect. Hence, in this study, two kinds of PS with symmetric chain ends, α,ω -di-*sec*-butyl-terminated and α,ω -diproton-terminated polystyrene (α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂), are synthesized. Our interest is whether T_g^s in films of α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂ is different, and is to what extent the T_g^s value is dependent on chain end structure, if any.

EXPERIMENTAL

Figure 1 illustrates synthetic routes of α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂. α,ω -PS(*sec*-Bu)₂, **1**, was synthesized by coupling two living styryl anions, initiated by *sec*-butyllithium, with 1,3-bis(1-phenylethenyl)-benzene (MDDPE), **2**. **2** was prepared by Wittig reaction of 1,3-dibenzoylbenzene under the presence of

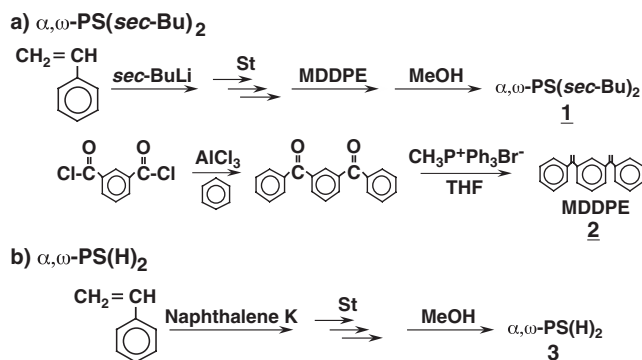


Figure 1. Synthetic routes for (a) α,ω -PS(*sec*-Bu)₂ and (b) α,ω -PS(H)₂.

[†]To whom correspondence should be addressed (TEL: +81-92-642-3560, Fax: +81-92-651-5606, E-mail: k-tanaka@cstf.kyushu-u.ac.jp).

^{††}To whom correspondence should be addressed (TEL: +81-92-642-2100, E-mail: kajiyama@cstf.kyushu-u.ac.jp).

Table I. Characterization of PS after fractionation

Polymer	M_n	M_w/M_n	T_g^b /K
α,ω -PS(<i>sec</i> -Bu) ₂	17k	1.04	370
	67k	1.06	372
α,ω -PS(H) ₂	19k	1.04	362
	77k	1.06	376

triphenylmethylphosphonium bromide.²⁴ 1,3-Dibenzoylbenzene was obtained by Friedel Crafts reaction of benzene with isophthaloyl dichloride in the presence of AlCl₃, as shown in Figure 1.²⁵ Since the coupling reaction was not perfect, the product after the polymerization was fractionated to obtain α,ω -PS(*sec*-Bu)₂ with high purity. α,ω -PS(H)₂, **3**, was synthesized using naphthalene potassium and methanol as an initiator and a terminator, respectively.

Table I shows number-average molecular weight (M_n), molecular weight dispersity (M_w/M_n), where M_w is weight-average molecular weight, and T_g^b for α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂. T_g^b was measured by differential scanning calorimetry (DSC) under dry nitrogen purge at the heating rate of 10 K·min⁻¹. α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂ films with the thickness of approximately 200 nm were spin-coated from toluene solutions onto silicon wafers with a native oxide layer. The thickness was sufficient to avoid any ultrathinning effects on surface dynamics in this M_n range.²⁶ To remove residual solvent molecules and eliminate residual stress imposed by the spin coating procedure, the films were dried at 296 K for more than 24 h, and then, annealed at 423 K for 24 h *in vacuo*. After annealing, the films were cooled down to room temperature at the rate of 0.5 K·min⁻¹.

Surface relaxation behavior of the films was examined by using an LFM (SPA 300 HV, Seiko Instruments Industry Co., Ltd.) with an SPI 3800 controller. A cantilever used was fabricated from Si₃N₄, of which both sides were uncoated, and possessed the bending spring constant of 0.1 N·m⁻¹. The normal force onto the cantilever was set to be 10 nN in a repulsive force region. It was pre-confirmed that the sample surface was not damaged by scanning a tip under the current condition. Lateral force was acquired as a function of temperature at the heating rate of 0.4 K·min⁻¹ under vacuum.

RESULTS AND DISCUSSION

Frictional behavior of polymeric materials is closely related to their viscoelastic properties.²⁷ Hence, it is possible to examine relaxation processes at the polymer surface by using LFM.^{2,4} That is, when mechanical energy at the surface imposed by a sliding tip starts to dissipate due to the release of molecular mo-

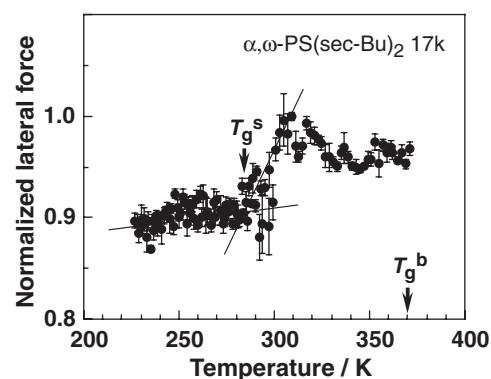


Figure 2. Typical lateral force–temperature curve at the scanning rate of 1 $\mu\text{m}\cdot\text{s}^{-1}$. The data is from α,ω -PS(*sec*-Bu)₂ with M_n of 17k.

tion, lateral force increases. Thus, it can be postulated that a change of lateral force with measuring temperature is essentially similar to temperature dependence of dynamic loss modulus or loss tangent.

Figure 2 shows a typical temperature dependence of lateral force. The data was obtained from α,ω -PS(*sec*-Bu)₂ with M_n of 17k under the fixed scanning rate of 1 $\mu\text{m}\cdot\text{s}^{-1}$. A lateral force peak was clearly observed at around 310 K. Based on our previous study,^{2d} this peak is assignable to surface α_a -relaxation process corresponding to segmental motion, namely, glass-rubber transition at the surface. An onset temperature on the lateral force–temperature curve, that is, the temperature at which the lateral force starts to increase, can be empirically defined as T_g^s .^{2d,f} In this case, the value was evaluated to be 283 K on the basis of the intercept of two straight lines, as shown in the figure, and was much lower than the T_g^b of 370 K. This result makes it clear that surface molecular motion is more active than the corresponding bulk motion.

Figure 3 shows the relations of T_g^s and T_g^b to M_n for the α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂, denoted by squares and triangles, respectively. To discuss how chain end structure affects T_g^s , the data for *sec*-Bu-PS-H with the symbols of small circles are also presented.^{2d} An effect of chain end structure on T_g^b was not significant, and T_g^b value monotonically decreased with M_n , consistent with the equation established by Fox and Flory.²⁸ On the other hand, the M_n dependence of T_g^s seems to be somehow complicated. T_g^s vs. M_n for the *sec*-Bu-PS-H film was well expressed by a simple power law, $T_g^s = 356 - K \cdot M_n^{-0.6 \pm 0.03}$ where K is a constant, with the M_n range higher than $10^{3.4}$, as drawn by the thick curve in Figure 3.^{2d} At M_n of approximately 70k marked by shaded area, T_g^s for all PS films can be directly compared. T_g^s was strongly dependent on what the chain end structure was, and the order was α,ω -

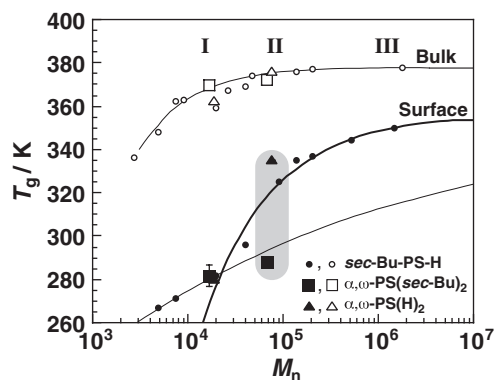


Figure 3. M_n dependences of T_g^s and T_g^b for α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂. For a comparison, data for *sec*-Bu-PS-H is also shown.^{2d} See text in detail.

PS(*sec*-Bu)₂ < *sec*-Bu-PS-H < α,ω -PS(H)₂. According to prediction for surface free energy (γ) based on the notion of group contribution,²⁹ the γ of a *sec*-butyl group is much smaller than that of a repeating styrene unit. Also, the γ of a styrene unit terminated by proton should be slightly lower than that of a repeating one on account of a larger freedom, namely, an entropic contribution, although the energetic difference between the two is trivial. This means that the end groups preferentially segregate at the surface to minimize the interfacial free energy with the air phase.^{2b,c} Since the end groups possess the larger freedom, an excess free volume is supposed to be induced at the surface, resulting in enhanced surface mobility. Of course, the depression of T_g^s from the corresponding bulk value is closely related to the extent of surface concentration of chain ends. Taking into account that the γ of a *sec*-butyl group is lower than that of a styrene unit terminated by proton, the aforementioned T_g^s order among the three PS films can be easily understood.

On the other hand, in the case of lower M_n region such as 20k, the chain end effect on T_g^s was not observed at all, as shown in Figure 3. Here, it is noteworthy that the T_g^s - M_n relation for the *sec*-Bu-PS-H film was deviated from the power law of $M_n^{-0.6}$. Instead, T_g^s was proportional to $M_n^{-0.13}$, as shown by the thin curve in Figure 3. Invoking that the M_n dependence of glass transition temperature is related to the number density of chain ends,²⁸ Figure 3 tells us that in the case of M_n smaller than 20k, the chain end concentration at the surface is not necessarily increased with decreasing M_n . A plausible explanation of this is that a chain conformation, of which the both ends are located at the surface, can be hardly realized due to its decreased internal freedom.

The M_n dependence of T_g^s can be roughly divided into three regimes. A clear chain end effect on T_g^s would be observed only for appropriate M_n region,

as marked by regime II in Figure 3. In the case of higher M_n region, the dependence will be not experimentally observed due to extremely low chain end concentration although the chain ends preferentially partitioned to the surface. We call this M_n region regime III. In addition, the dependence would not be seen either for lower M_n region because of the above-mentioned reason. Based on Figure 3, it seems reasonable to conclude that chain end chemistry is definitely one of responsible factors for the reduction of glass transition temperature at the film surface. In a sense, however, it is also clear from Figure 3 that the chain end effect cannot fully account for the enhanced mobility in the surface region. Therefore, more systematic studies taking into account other factors should be made in the future.

CONCLUSIONS

α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂ were synthesized by anionic polymerization, and T_g^s in films of α,ω -PS(*sec*-Bu)₂ and α,ω -PS(H)₂ was examined by LFM. T_g^s for the films was much smaller than the corresponding bulk value. The results were compared with T_g^s for *sec*-Bu-PS-H. While T_g^s value was strongly dependent on chain end structure in a middle molecular weight region, such was not the case for a lower molecular mass regime. These were explained in terms of chain end concentration at the surface.

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