Activated Physical Properties at Air-Polymer Interface

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Introduction

Since polymer surface contacts with other environments, its energy state is different from that in the bulk region. Such an energy difference makes surface structure and physical properties different from the corresponding bulk ones. The surface structure and physical properties play key roles in many functional applications such as selective permeability, wetting property, biocompatibility, etc. So far, surface aggregation structure has been extensively explored with the advent of modern spectroscopic and microscopic methods. On the other hand, studies for surface molecular motion have been emerged at last. In my talk, it will be reviewed how thermal molecular motion at the surface can be experimentally studied, and also, how active surface molecular motion is in comparison with the bulk one.

Scanning viscoelasticity microscopy

Local viscoelastic measurement at polymer surfaces can be realized by using a family of scanning force microscopy. As the sample surface is deformed by a tip indentation, the modulation of the tip leads to the displacement modulation of the sample surface. If such a displacement to the sample surface is sinusoidally applied, the dynamic viscoelastic properties at the sample surface can be evaluated by measuring the amplitude of the response force signal and the phase lag between modulated displacement and response force signals. A forced modulation atomic force microscope (AFM), so-called "scanning viscoelasticity microscope (SVM)", was designed by remodeling a commercially available AFM [1].

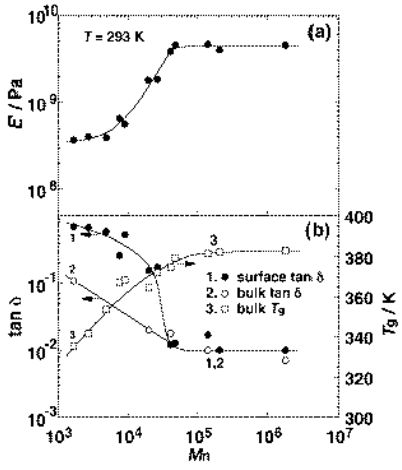

Figure 1 M_n dependences of surface E' and surface tan δ for PS-H films at 293 K. For a comparison, bulk tan δ and T_g^b are also shown.

Molecular weight dependence of surface dynamic viscoelastic functions

Monodisperse proton-terminated polystyrene (PS-H) was prepared by a living anionic polymerization using *sec*-butyllithium as an initiator and methanol as a terminator. Hence, both chain ends were composed of *sec*-butyl group and a proton-terminated repeating unit. The PS-H films of 200 nm-thick were coated onto silicon wafers with native oxide layer by a spin-coating method. SVM measurement was carried out at 293 K in air. The modulation frequency and amplitude at the supporting part of the cantilever were 4 kHz and 1.0 nm, respectively. Figure 1 shows the molecular weight dependence of surface storage modulus, E' and surface tan δ for the monodisperse PS-H film at 293 K [2]. Also, bulk tan δ and bulk glass transition temperature, T_g^b were plotted in it. In the case of M_n larger than 40k, surface E' and surface tan δ were constant and their magnitudes were ca. 4.5 GPa and 0.01, respectively. In contrast, when M_n became smaller than 40k, surface E' and surface tan δ decreased and increased with decreasing M_n, respectively, at 293 K, as shown in Figure 1. This result implies that the PS-H surface with M_n smaller than 40k is in a glass-rubber transition or rubbery state even at 293 K. Thus, it is conceivable that thermal molecular motion at the film surface is more active than that in the bulk region, especially in the case of M_n smaller than 40k.

Direct determination of surface glass transition temperature

In order to determine directly surface glass transition temperature, T_g^s, the temperature dependence of surface phase lag between imposed displacement and detected force signals, δ^s was examined. Figure 2 shows the temperature dependence of δ^s for the monodisperse PS-H film with M_n of 140k [3]. A distinct α_a-relaxation loss peak corresponding to micro-Brownian motion at the surface was observed at a temperature lower than its T_g^b of 376 K. An onset temperature, that is, a temperature at which δ^s starts to increase, can be empirically defined as T_g^s. Hence, based on Figure 2, T_g^s for the PS-H film with M_n of 140k can be determined to be 328 K. Similarly, T_g^s for the PS-H film could be examined on the basis of lateral force microscopy. Figure 3 shows the molecular weight dependences of T_g^s and T_g^b for the monodisperse PS-H films. T_g^s was strongly dependent on M_n compared with T_g^b, and was remarkably lower than the corresponding T_g^b. Since T_g^s for the PS-H film with M_n lower than ca. 40k was below 293 K, it is envisaged that the PS-H film surface with M_n lower than ca. 40k is in a glass-rubber transition state or a rubbery state even at room temperature. This is in excellent accordance with the results shown in Figure 1. Also, the T_g^s - M_n relation was well supported by Morita et al. using coarse-grained molecular dynamics simulation [4].

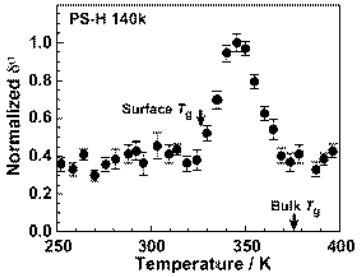

Figure 2 Temperature dependence of surface phase lag for the PS-H film with M_n of 140k.

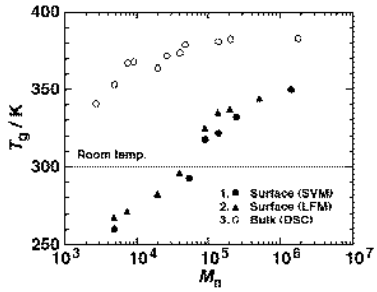

Figure 3 M_n dependence of T_g^b and T_g^s for the PS-H films.

As shown in Figure 3, the M_n effect on T_g^s is much stronger than that on T_g^b. Thus, it seems reasonable to consider that in the case of the monodisperse PS-H, the number density of chain end groups at the surface is larger than that in the interior bulk region due to their more hydrophobic character than the main chain part. Actually, surface localization of chain ends for the PS-H was experimentally confirmed by dynamic secondary ion mass spectroscopic measurement [2]. Since chain ends induce an excess free volume on account of their

larger freedom in comparison with the main chain part, T_g^s is lowered from the corresponding bulk value.

So far, we have explained on the basis of chain end effect why T_g^s is lower than the corresponding T_g^b. If this notion is universal, the T_g^s value should be strongly dependent on chain end structure. Hence, T_g^s of monodisperse α,ω-diamino-terminated and α,ω-dicarboxy-terminated polystyrenes (α,ω-PS$(NH_2)_2$ and α,ω-PS$(COOH)_2$) were examined. As a general trend, T_g^s was again lower than the corresponding T_g^b. This result makes it clear that thermal molecular motion at the surface is more active than that in the bulk, independent of chain end chemistry. However, the magnitude of T_g^s was strongly dependent on the chain end species at a given M_n [5]. Hence, it is clear that the chain end effect is one of the responsible determining factors on the magnitude of T_g^s. T_g^s asymptotically increased with increasing M_n and was remained to be still lower than the bulk one even for high M_n of ca. 1M, where chain end effect should be ignored due to its extremely low concentration, as shown in Figure 3. Thus, it seems that the surface molecular motion is activated by not only the surface segregation of chain end groups but also other factors, presumably an existence of the free space on the polymer phase.

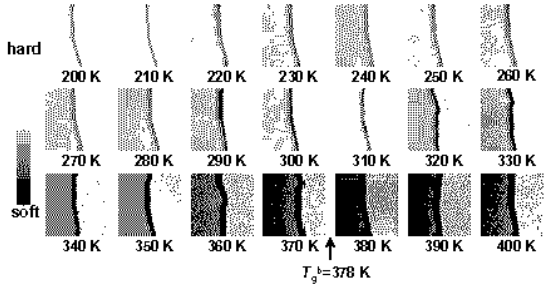

Figure 4 SVM images of the PS film at various temperatures. The left- and right-hand side regions correspond to PS and Si surfaces, respectively.

Here, the above-mentioned discussion is visually shown. Figure 4 shows the SVM images for the PS film with M_n of ca. 1M, which was partially cut by a blade, collected at various temperatures from 200 K to 400 K [6]. Thus, PS and Si surfaces could be observed. Since the surface modulus of the silicon substrate should be invariant with respect to temperature in the employed range, the contrast enhancement between the PS and Si surfaces with temperature reflects that the modulus of the PS surface starts to decrease. In the case of a lower temperature, the image contrast was trivial, as shown in the top line of Figure 4. On the other hand, as the temperature went beyond 330 K or 340 K, the contrast between the PS and Si surfaces became remarkable with increasing temperature, meaning that the PS surface reached glass-rubber transition state at around these temperatures. Here, it should be recalled that the T_g^b of the PS by DSC was 378 K. Hence, we *visually* present in Figure 4 that surface mobility in the PS film was enhanced in comparison with the bulk one.

Rheological analysis of surface molecular motion

In order to evaluate an apparent activation energy of the surface α_a-relaxation process, the temperature dependence of δ^s was measured as a function of frequency, f. Figure 5 shows such a plot for the PS-H with M_n of 140k [7]. In all measuring frequencies, clear absorption peaks corresponding to the surface α_a-relaxation were observed on δ^s–temperature curves, and its peak position shifted to higher temperature region with increasing frequency. Also, again, it is apparent from Figure 5 that all peak temperatures are lower than its T_g^b of 376 K. Assuming that the reciprocal of a temperature, at which δ^s exhibits the maximum value, $1/T_{max}$ is proportional to the natural logarithm of the measuring frequency in glass-rubber transition region, the apparent activation energy, ΔH^* of the surface α_a-relaxation process can be obtained by $\Delta H^* = -R\ \mathrm{d}(\ln f) / \mathrm{d}(1/T_{max})$, where R is the gas constant. Figure 6 shows ln f vs. $1/T_{max}$. According to (1), ΔH^* of the surface α_a-relaxation process can be obtained from the linear slope shown in Figure 6, and its value was 200±20 kJ•mol^{-1}, which was definitely lower than the reported bulk values of ΔH^* ranging from 360 to 880 kJ•mol^{-1}. This means that the cooperativity for the surface α_a-relaxation was reduced in comparison with that in the bulk. Such a reduction of the cooperativity at the surface might be arisen from the existence of the free space on the polymer surface. Hence, it seems reasonable to conclude that the activation of thermal molecular motion at the surface can be attained by the reduced cooperativity in addition to the chain end effect. Also, an effect of the chain entanglement, which might be depressed at the surface, on the surface molecular motion should be considered in detail.

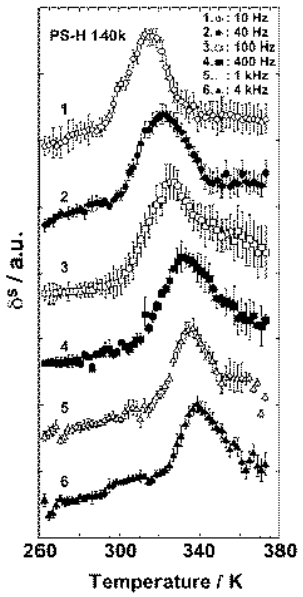

Figure 5 Temperature dependence of δ^s for the PS-H film with Mn of 140k at various frequencies.

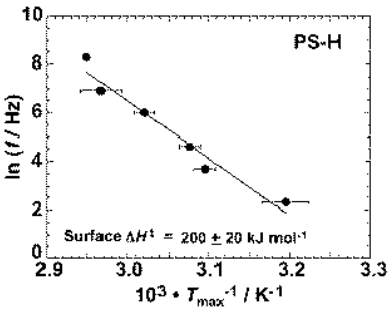

Figure 6 Semilogarithmic plot of measuring frequency against reciprocal absolute temperature for the PS film with M_n of 140k.

References

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