Surface glass transition temperatures of monodisperse polystyrene films by scanning force microscopy

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Abstract

Surface molecular motion of monodisperse polystyrene (PS) films was examined by scanning viscoelasticity microscopy (SVM) in conjunction with lateral force microscopy (LFM). The dynamic storage modulus, \( E' \), and loss tangent, \( \tan \delta \), at a PS film surface with a smaller number-average molecular weight, \( M_n \), than 40k were found to be smaller and larger than those for the bulk sample even at room temperature, meaning that the PS surface is in a glass–rubber transition state or a fully rubbery one at this temperature if the \( M_n \) is small. In order to elucidate quantitatively how vigorous the molecular motion at the PS surface is, SVM and LFM measurements were made at various temperatures. The glass transition temperature, \( T_g \), at the surface was discerned to be markedly lower than its bulk \( T_g \), and the discrepancy of \( T_g \) between surface and bulk becomes larger with the decreasing \( M_n \). Such an intensive activation of thermal molecular motion at the PS surfaces can be explained in terms of an excess free volume in the vicinity of the film surface induced by the preferential segregation of chain end groups.

Keywords: Surface glass transition; Monodisperse polystyrene films; Scanning force microscopy

1. Introduction

The physical properties at surfaces and interfaces of polymeric materials have received great attention recently, and are of pivotal importance in many technological applications such as lubrication, adhesion and biomaterials [1]. Hence, the systematical understanding of these properties, which cannot be deduced by extrapolating the bulk ones, is crucial so that the performance of the polymeric materials could be promisingly improved.

In the last decade, dynamics in thin films and at interfaces of amorphous polymers, mainly polystyrene (PS) and poly(methyl methacrylate) (PMMA), have been extensively studied owing to the manifestation of modern spectroscopic methods and microscopy. Restricting ourselves within the reports to the discussion of PS alone for brevity, the consistent conclusion obtained so far is that the glass transition temperature, \( T_g \), in thin films differs markedly from that for the bulk [2–7]. A depression of the \( T_g \) in thin films seems to be accounted for by the peculiar mobility of polymer chains existing in the vicinity of the outermost surface rather than the geometrical confinement effect of polymer chains.

Authors have embarked on the surface molecular motion of PS films by a family of scanning force microscopy, e.g. scanning viscoelasticity [8–11] and lateral force microscopy [12–14] (SVM and LFM). The principle of SVM is briefly stated here. Under the condition that the sample surface is deformed by the indentation of a tip, the tip is sinusoidally modulated. This leads to the sinusoidal modulation of the force acting between the sample surface and the cantilever tip if the modulation signal, stimulation strain, is imposed within the linear viscoelasticity region. Measuring the amplitude of the modulated deformation for the sample (response stress) and the phase lag between the stimulation strain and the response stress, the dynamic viscoelastic functions at the sample surface can be evaluated. LFM has been used as a powerful tool to investigate the surface properties of various polymers [15,16]. In the case of polymeric materials, lateral force between the sample surface and a probe tip is postulated to come from the energy dissipation of molecular movement. Hence, it becomes possible to examine the surface molecular motion based on the scanning rate dependence of the lateral force, which corresponds well to the relation...
2. Experimental

The purpose of this study is to rationalize the thermal molecular motion at the surface of the monodisperse PS films, which are typical amorphous polymers, by SVM in conjunction with LFM measurements. Especially, our intention in this review article is to show how polymer films, which are typical amorphous polymers, by SVM in molecular motion at the film surface is far from clear for the moment. It is to be noted that the thermal molecular motion at the film surface was highly enhanced in comparison with its bulk state [19]. In contrast, these conclusions are not in agreement with a recent report on surface relaxation of PS films with the number-average molecular weight, $M_n$, of 96k based on the spectroscopy of near-edge X-ray absorption fine structure by Russell et al [20]. They have not observed any evidence of vigorous molecular motion on the PS film surface at temperatures below its bulk $T_g$. Hence, it seems that a consistent understanding about the thermal molecular motion at the film surface is far from clear for the moment.

The molecular motion at the PS surfaces was examined using SVM and LFM (SPA 300 HV, Seiko Instruments Industry Co., Ltd) with an SPI 3800 controller. Both measurements were carried out at various temperatures in vacuo to avoid the surface oxidation and a capillary force effect induced by the surface adsorbed water. A piezo-scanner was thermally insulated from the heating stage. A cantilever with the bending spring constant of 0.09 N m$^{-1}$, of which both sides were coated by gold, was used. It was confirmed that the sample surface was not damaged at all by scanning the tip under the current experimental condition.

3. Results and discussion

3.1. Surface viscoelastic functions at room temperature

Parts (a) and (b) of Fig. 1 show the molecular weight dependence of dynamic storage modulus, $E'$, and loss tangent, $\tan \delta$, at the monodisperse PS film surface on molecular weight, $M_n$. Bulk $\tan \delta$ and glass transition temperature, $T_g$, are present in part (b) as well.

![Figure 1](image-url)

**Fig. 1.** Dependence of (a) storage modulus, $E'$, and loss tangent, $\tan \delta$, at the monodisperse PS surface on molecular weight, $M_n$. Bulk $\tan \delta$ and glass transition temperature, $T_g$, are present in part (b) as well.

between the measuring frequency and the mechanical loss modulus.

Jean et al., and De Maggio and co-workers, using positron-annihilation lifetime measurement, independently observed that the $T_g$ in the thin surface layer of PS films was suppressed [17,18]. Lap-shear strength measurement clearly indicated that the strength at the PS/PS interface can be developed due to interdiffusion of PS chains at a temperature below the bulk $T_g$, and concluded that the mobility at the free surface was highly enhanced in comparison with its bulk state [19]. In contrast, these conclusions are not in agreement with a recent report on surface relaxation of PS films with the number-average molecular weight, $M_n$, of 96k based on the spectroscopy of near-edge X-ray absorption fine structure by Russell et al [20]. They have not observed any evidence of vigorous molecular motion on the PS film surface at temperatures below its bulk $T_g$. Hence, it seems that a consistent understanding about the thermal molecular motion at the film surface is far from clear for the moment.

The purpose of this study is to rationalize the thermal molecular motion at the surface of the monodisperse PS films, which are typical amorphous polymers, by SVM in conjunction with LFM measurements. Especially, our intention in this review article is to show how polymer chains at the film surface are thermally activated in comparison with those in the internal bulk phase.

2. Experimental

Monodisperse PS films with various $M_n$s were synthesized by a living anionic polymerization using sec-butylithium and methanol as an initiator and a terminator, respectively. Hence, the chemical structures at both ends of a chain are composed of a sec-butyl group and a repeating unit terminated by a proton. The PS film was coated from a toluene solution onto a cleaned silicon wafer by a spin-coating method. The film was dried at 296 K for more than 72 h and then annealed at 423 K for 24 h under vacuum. The film thickness evaluated by the ellipsometric measurement was approximately 200 nm, which did not show any ultra-thinning effects on the surface molecular motion.

The molecular motion at the PS surfaces was examined using SVM and LFM (SPA 300 HV, Seiko Instruments Industry Co., Ltd) with an SPI 3800 controller. Both measurements were carried out at various temperatures in vacuo to avoid the surface oxidation and a capillary force effect induced by the surface adsorbed water. A piezo-scanner was thermally insulated from the heating stage. A cantilever with the bending spring constant of 0.09 N m$^{-1}$, of which both sides were coated by gold, was used. It was confirmed that the sample surface was not damaged at all by scanning the tip under the current experimental condition.

3. Results and discussion

3.1. Surface viscoelastic functions at room temperature

Parts (a) and (b) of Fig. 1 show the molecular weight dependence of dynamic storage modulus, $E'$, and loss tangent, $\tan \delta$, at the monodisperse PS film surfaces at a controlled ambient temperature. The modulation frequency and amplitude at the supporting part of the cantilever for SVM measurement were 4 kHz and 1.0 nm, respectively. The bulk $\tan \delta$ and $T_g$ values, which were measured by Rheovibron and differential scanning calorimetry (DSC), respectively, are plotted in it to make a comparison with the surface ones. Before starting to discuss the surface molecular motion, it is to be noted that the bulk $T_g$'s of all PSs used are far above room temperature, that is, the internal bulk states of the PS films are glassy at room temperature, independent of $M_n$. In the case of a PS with $M_n$ larger than 40k, the surface $E'$ and surface $\tan \delta$ were constant with regard to $M_n$, and their magnitudes were approximately 4.5 GPa and 0.01. Since these magnitudes of the surface $E'$ and surface $\tan \delta$ are typical values for glassy PS, it is clear that the surface is in a glassy state at 293 K for a PS film with $M_n$ larger than 40k. On the contrary, the surface $E'$ and surface $\tan \delta$ vary in magnitude with $M_n$ once $M_n$ falls short of 30k. That is, the surface $E'$ and the surface $\tan \delta$ decrease and increase with the decreasing $M_n$, respectively, as shown in Fig. 1(a). Hence, it is plausible that while the internal phase of the PS film is in a glassy state, the surface of a PS film with $M_n$ smaller than 30k is in a glass–rubber transition state or rubbery one even at 293 K. The $\tan \delta$ of the bulk PS sample was measured by the technique of dynamic spring analysis to
compare with the surface one. At an $M_n$ smaller than 30k, the surface $\tan \delta$ is much larger than the bulk $\tan \delta$. This implies once again that thermal molecular motion at the PS surface is activated in comparison with that for the bulk sample in this $M_n$ range. It is worthwhile to note that the above-mentioned SVM results do not deny the possibility of peculiar molecular motion at the surface for a larger $M_n$ PS.

Even though the $T_g$ at the surface, $T_g^s$, is somewhat reduced from its bulk value, such a depression of the $T_g$ cannot be detected by the SVM measurement at room temperature if the declined $T_g^s$ is higher than the measuring temperature, namely, room temperature. This issue will be discussed later in a quantitative way. Deferring why the $T_g$ must be reduced at the PS surface, the parallel experiment is carried out by another technique, LFM, to make an assurance.

### 3.2. Surface relaxation behaviors at room temperature

Since the frictional behavior of polymeric solids is closely related to their viscoelastic properties [21], it is possible to examine the surface molecular motion of the polymeric solids by dragging a tip on surface with various speeds. Postulating that the lateral force arises from the energy dissipation of the molecular movement, the variation of lateral force with the measurement temperature and the scanning rate can be regarded as the temperature and frequency dependencies of the dynamic loss modulus [10,15]. In either case that the surface is completely in a glassy or rubbery state, the magnitude of the lateral force might be independent of the measurement temperature at a given scanning rate or the scanning rate at a given temperature. On the contrary, the lateral force varies with the temperature (or scanning rate) and a peak is observable on the lateral force–temperature (scanning rate) curve when the surface is in a glass–rubber transition state. Thus, it can be judged that the surface is in a glass–rubber transition state, if the magnitude of the lateral force increases or decreases with the temperature (scanning rate). A more detailed interpretation of the lateral force for polymeric materials has been published elsewhere [10].

Fig. 2 collects the plots of the lateral force against the scanning rate as a function of $M_n$ at room temperature. In the case of $M_n$ of 140k, the lateral force is independent of the scanning speed, meaning that the surface of this PS film is glassy at room temperature, whereas the lateral force for a PS film with $M_n$ smaller than 40k alters with the scanning rate. Note that this trend is in good agreement with our parallel experiment using SVM shown in Fig. 1. Although in the case of $M_n$ of 40k, the lateral force is apparently constant against the sliding speed of the tip at the higher side, it is increased with a decrease in the scanning rate at the lower side. This result makes it clear that the state of molecular motion is strongly dependent on the sample deformation rate even at the film surface, as extensively observed in the molecular motion of bulk polymer samples, and the PS surface with this $M_n$ is in a transition state and a glassy one at the lower and higher scanning rate regions, respectively. In contrast, the lateral force for the PS films with $M_n$ of 27k and 20k monotonically decreases with the increasing scanning rate in all the ranges employed here. As the $M_n$ becomes further smaller, e.g. 9k and 5k, the peak appeared on the lateral force–scanning rate curve, indicating that these surfaces are in a fully rubbery state. Fig. 3 shows the master curve drawn by horizontal and vertical arbitrary shifts of each curve in Fig. 2. Since this master curve is very similar to the lateral force–temperature curve, which will be shortly shown, it can be considered that the pattern of the lateral force against the scanning rate and the $M_n$ reflects the successive change of the surface molecular motion from a glassy to a rubbery state via the glass–rubber transition even at room temperature. By taking into account the facts that the internal phase of the PS film is in a glassy...
state, it seems reasonable to conclude that thermal molecular motion is intensively activated at the PS film surface compared with its bulk state.

3.3. Direct evaluation of surface glass transition temperatures

So far it has been qualitatively stated that the $T_{g}$ is lower than the bulk $T_{g}$. Therefore, the time is ripe to quantitatively show how peculiar the surface molecular motion is. Here the $T_{g}$ is directly evaluated by SVM in conjunction with LFM at various temperatures. Fig. 4 shows the temperature dependence of the surface phase lag, $\delta_{s}$, between strain and stress, and the lateral force for the PS films with $M_{n}$ of 140k. The shape factor related to how a cantilever tip contacts with the surface must be precisely determined so that the experimental $\delta_{s}$ is converted into the surface tan $\delta$. At present, however, it is difficult to obtain this factor when the ambient temperature is kept changing such as a temperature-dependent measurement. Hence, the $\delta_{s}$ itself is used here as an index of the molecular motion instead of the surface tan $\delta$. Besides the lateral force variation with temperature is collected at a given scanning speed of $10^{3}$ nm s$^{-1}$. The ordinates in Fig. 4 are normalized by the maximum value of the $\delta_{s}$ and lateral force to show how these values vary with temperature around a transition region. The peaks on both curves are assigned to the $\alpha$-absorption corresponding to the micro-Brownian motion of polymeric chains at the PS surface [22]. While the bulk $T_{g}$ of this PS is 376 K, the $\delta_{s}$ lateral force start to increase at a much lower temperature, as shown in Fig. 4. Thus, it seems most likely that the glass–rubber transition at the surface for the PS film with $M_{n}$ of 140k is present below its bulk $T_{g}$ of 376 K.

An onset temperature on the $\delta_{s}$ or lateral force–temperature curve, i.e. the temperature at which the magnitude of the lateral force starts to increase, can be empirically defined as $T_{g}^{s}$ [23]. Fig. 5 shows such temperatures as a function of $M_{n}$. The bulk $T_{g}$ are again plotted in it to make a comparison with the $T_{g}^{s}$. The arrow beside the ordinate denotes room temperature, which is abbreviated as “R.T.” in Fig. 5. The results in Fig. 5 make it clear that the $T_{g}^{s}$ has stronger $M_{n}$ dependence than the bulk $T_{g}$, that is, a decrement of the $T_{g}^{s}$ with a decrease in $M_{n}$ is more remarkable in comparison with the bulk $T_{g}$. Even at an ultra-high molecular weight, $M_{n}$ of 1450k, the $T_{g}^{s}$ is definitely lower than the bulk $T_{g}$ and also in the case of a lower $M_{n}$ lesser than approximately 30k, the $T_{g}^{s}$ is below room temperature. These results strongly advocate our previous conclusion, which is guided by measurements at room temperature, that the PS film surface is in a glass–rubber transition or fully rubbery state even at room temperature if the $M_{n}$ is lesser than 40k.

3.4. Surface localization of chain end groups

The physical meaning of the variation of $M_{n}$ related to glass transition temperature is now discussed. According to the Fox–Flory equation [24], the dependence of bulk $T_{g}$ on $M_{n}$ is given by

$$T_{g} = T_{g,\infty} - K/M_{n}$$

where $T_{g,\infty}$ and $K$ are the bulk $T_{g}$ for the infinite longer PS and a material constant, respectively. Eq. (1) means that the bulk $T_{g}$ declines with a decrease in the $M_{n}$ and this $T_{g}$ variation has been interpreted based on the increasing number density of chain end groups. It is clearly discerned that the
effect of $M_n$ on $T_g$ at the film surface is stronger than the bulk sample, as shown in Fig. 5. Thus, it seems reasonable to infer that the number density of chain end groups at the surface is larger compared with its internal phase.

In order to confirm whether such a situation, preferential surface segregation of chain end groups, becomes true, the dynamic secondary ion mass spectroscopic (DSIMS) measurement is made using deuterated PS (dPS), whose chain end groups were labeled by protonated groups, as a sample. Fig. 6 shows the typical SIMS depth profile of the end-labeled dPS film. The dashed vertical line depicts the air–polymer interface. The depth before reaching the film surface means the etching of the platinum layer to avoid charging up the specimen during the measurement. Since the intensity of carbon ion, $C^+$, is almost constant through the polymer film, it can be judged that the steady-state etching proceeds. Although the secondary ion efficiency of hydrogen atom is generally higher than that of the heavy hydrogen atom, the stronger intensity of deuterium ion, $D^+$, is maintained through the polymer film. This is due to the larger fraction of heavy hydrogen atom in the end-labeled dPS film. At the air–polymer interface, an apparent increase in the $H^+$ intensity and a decrease in the $D^+$ count are observed. All styrene units were deuterated, and protons were present only in both chain end portions. Thus, the SIMS depth profile indicates a remarkable enrichment of chain end groups at the film surface. Fig. 7 displays a cartoon of the most plausible conformation of a PS chain at the film surface drawn on the basis of the DSIMS result. Since the localized chain ends at the surface might induce an excess free volume induced by the enriched chain end groups at the surface.

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