# Segmental Motion in Polystyrene Thin and Ultrathin Films Based on Dynamic Viscoelastic Measurement

Kei-ichi AKABORI<sup>\*1</sup>, Keiji TANAKA<sup>\*1</sup>, Toshihiko NAGAMURA<sup>\*1</sup>, Atsushi TAKAHARA<sup>\*2</sup> and Tisato KAJIYAMA<sup>\*3</sup> <sup>\*1</sup>Graduate school of Engineering, Kyushu University, <sup>\*2</sup>Institute for Materials Chemistry and Engineering, Kyushu University, \*<sup>3</sup>Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, JAPAN Tel: 81-92-642-3560, Fax: 81-92-651-5606, e-mail: akabori@cstf.kyushu-u.ac.jp

Segmental motion in polystyrene (PS) thin and ultrathin films supported on substrates was studied by dynamic viscoelasticitic measurement. Here, a polymer film, which has the thickness comparable to or less than the twice of radius of gyration of an unperturbed chain  $(2R_g)$ , is defined as an ultrathin film. In the case of PS,  $\alpha_a$ -relaxation process corresponding to the segmental motion is generally observed at approximately 380K. Even for both the PS thin and ultrathin films, the  $\alpha_a$ -absorption peak was clearly observed. A rheological analysis revealed that the  $\alpha_a$ -relaxation behavior for the thin films with the thickness of about 200 nm was the same as that of the bulk sample. On the contrary, in the case of the PS ultrathin films, the  $\alpha_a$ -absorption peak on temperature-loss modulus  $(E^{n})$  curve was broadened toward both lower and higher temperature sides. This can be interpreted by taking into account that the segmental motion in the vicinities of surface and interface is detectable for such the ultrathin films, which should be faster and slower than that in the bulk, respectively. And, it was found that the apparent activation energy ( $\Delta H$ ) for the  $\alpha_{a}$ -relaxation in the ultrathin films became smaller than the bulk value due probably to the surface effect. Finally, an interfacial effect on the  $\Delta H$  was studied by using different substrates. When the interaction between PS and substrate became stronger, the  $\Delta H$  value for the  $\alpha_a$ -relaxation in the ultrathin films increased. These results imply that the segmental motion in the polymer ultrathin films is strongly influenced by surface and interfacial effects.

Key words: dynamic viscoelasticitic measurement, segmental motion, polymer ultrathin film, polystyrene, surface, interface

## 1. INTRODUCTION

In recent nanotechnology, polymer ultrathin films, of which the thickness is comparable to, or less than, the molecular dimension, <sup>1)</sup> become more important than before. Such can be easily seen in the fields of coating, adhesion, lubrication, biomaterials and multi-layer devices. In order to design and construct highly functionalized materials, which can be promisingly used in the above applications, it is necessary to understand precisely thermal molecular motion in the practical geometry, that is, polymer ultrathin films supported on substrates.

So far, glass transition behavior in polymer ultrathin films on substrates has been studied by a variety of experimental techniques such as X-ray and neutron reflectivity, ellipsometry and so on. Consequently, a conclusion obtained is consistently that glass arrived transition temperature  $(T_g)$  in the ultrathin states is quite different from the bulk value because of surface and interfacial effects and/or chain confinement effect.2,3) However, little information on molecular dynamics in the ultrathin films has Fukao et al. have made a great been known. success to examine molecular dynamics in polymer ultrathin films by dielectric relaxation spectroscopy.<sup>4)</sup> For this electrical method, unfortunately, it is necessary to sandwich a polymer film with electrodes, resulting in difficulty to study a free surface effect on molecular dynamics in polymer ultrathin films. Dynamic viscoelastic measurement enables us to gain direct access to viscoelastic properties by mechanically modulating a sample, and has been extensively used for bulk polymers. In this method, the sample surface is covered with nothing. Hence, dvnamic viscoelastic measurement might be a possible method to study molecular dynamics in polymer ultrathin films. However, a question should be addressed is whether this bulk technique is sensitive enough to examine molecular dynamics in such thin and ultrathin polymer films. In this study, the answer to this question is first presented using PS thin and ultrathin films. Then, further

 Table 1 Characterizations of monodisperse polystyrenes

 used in this study.

M <sub>n</sub>	$M_{\rm w}$ / $M_{\rm n}$	$R_{\rm g}$ /nm <sup>2)</sup>	$T_{\rm g}^{\rm b}$ / K
1.46M <sup>1)</sup>	1.04	33	378
53.4k	1.03	6.3	376

2) by  $R_g^2 = Nb^2/6$ 

N : degree of polymerization, b : Kuhn s segment length of PS (0.68 am)

discussion about segmental motion in the ultrathin films spun-coated on substrates is made if possible.

## 2. EXPERIMENTAL

Monodisperse PS with number-average molecular weight  $(M_n)$  of 1.46M and 53.4k were purchased from Polymer Laboratories Ltd. and synthesized by an anionic polymerization, respectively. Table 1 shows  $M_n$ , polydispersity index  $(M_w/M_n)$ , where  $M_w$  is weight-average molecular weight, the radius of gyration of an unperturbed chain  $(R_g)$  and bulk glass transition temperature  $(T_g^{b})$  for these samples.  $T_g^{b}$  was measured by differential scanning calorimetry (DSC) under dry nitrogen purge at the heating PS films with various rate of 10 K•min<sup>-1</sup>. thicknesses were spin-coated from toluene solutions onto substrates. Film thickness was controlled by changing the solution concentration. The substrates used in this study were commercial polyimide (PI: KAPTON) film with the thickness of 7.5 µm and the Si-deposited PI (Si). In order to remove residual solvent and to eliminate stress imposed by the spin-coating procedure, the PS films were dried at room temperature for more than 24 h and then annealed at a temperature above  $T_g^{b}$  for 24 h in a vacuum oven. After annealing, the films were cooled down to room temperature at the rate of about 0.5 K•min<sup>-1</sup>.

Thermal molecular motion in PS thin and ultrathin films was examined by dynamic viscoelasticitic measurement (Rheovibron, DDV-01FP, A&D Co., LTD). Static and dynamic strains were set to be less than 0.05 and 0.2 %, respectively. The measurement of temperature dependence of dynamic loss modulus  $(E^{"})$  was carried out at the heating rate of 1 K•min<sup>-1</sup> under nitrogen atmosphere. The evaluation of frequency dependence of E" was also conducted in the frequency range of  $10^{-2}$  - $10^1$  Hz with a given temperature.

#### 3. RESULTS AND DISCUSSION

Fig.1 shows the typical temperature dependence of  $E^n$  for a PS thin film with  $M_n$  of 1.46M. The thickness of the film was about 200



**Fig.1** Typical temperature dependence of  $E^{"}$  for a PS thin film with  $M_{\rm p}$  of 1.46M.



**Fig.2** (a) Temperature and (b) frequency dependences of  $E^{n}$  for a PS 1.46M thin film.

nm being much larger than the molecular size of  $2R_g$ . This means that an effect of chain confinement on thermal molecular motion can be ignored. On the E<sup>m</sup>-temperature curve, a distinct  $\alpha_a$ -relaxation peak corresponding to the segmental motion was observed at approximately 380 K for the PS thin film supported on PI, whereas in the case of the control PI film, this was not the case. Hence, it is clear that the observed relaxation process comes up with molecular motion in the PS thin film.

Fig.2 shows (a) temperature and (b) frequency dependences of E" for a PS 1.46M thin film. The peak position shifted to the higher temperature side with increasing frequency. The relation between frequency and peak temperature ( $T_{\rm max}$ ) can be simply converted to the temperature dependence of the relaxation time. Hence, based on Vogel-Fulcher equation,  $T_{\rm g}$  of the thin film was calculated, and the value so obtained was 381 K. This value was in good accordance with the  $T_{\rm g}^{\rm b}$  by DSC. Also,



**Fig.3** Semilogarithmic plots of (1) frequency and (2) shift factor versus reciprocal absolute temperature for the PS 1.46M thin film.

E"-frequency relation successively varied with temperature. At lower and higher temperatures,  $E^{*}$  decreased and increased with increasing frequency, respectively. Also, at a middle temperature, a clear peak was observed, meaning that the film was in a glass-rubber transition state. Accordingly, time-temperature superposition principle was applied to these results. Fig.3 shows semilogarithmic plots of (1) frequency (f) and (2) shift factor  $(a_{\rm T})$  versus reciprocal absolute temperature for the thin film. Here,  $a_{\rm T}$ is an amount of horizontal shift, when the master curve of  $\alpha_a$ -relaxation was made from the E"-frequency relations. Invoking that the relations in Fig.3 are linear, the apparent activation energy ( $\Delta H$ ) for the  $\alpha_a$ -relaxation process was obtained to be about 650 kJ mol<sup>-1</sup> and was good agreement with the bulk value.<sup>5)</sup> From these experimental results, it should be here emphasized that the dynamic viscoelastic measurement, which used to be regarded as only for bulk experiments, is quite useful even for thin films as well. And, it seems most likely that the  $\alpha_{s}$ -relaxation behavior in the PS thin films with the thickness of approximately 200 nm or thicker is essentially the same as the bulk one.

Fig.4 shows the temperature dependence of  $E^{n}$  as a function of thickness for PS 1.46M films supported on (a) PI and (b) Si substrates. The  $\alpha_a$ -absorption peak could be also observed even for the case of films being thinner than  $2R_g$ , as displayed below the dot lines in the parts (a) and (b). However, once the thickness became thinner than the chain dimension, the peaks started to broaden toward both lower and higher temperature sides. This would be explained in terms of surface and interfacial effects, because the ratio of surface and interfacial areas to volume becomes extremely larger for such the



Fig.4 Temperature dependence of E" as a function of thickness for PS 1.46M films supported on (a) PI and (b) Si substrates.



Fig.5 Temperature dependence of E" for PS 53.4k thin films on PI substrates.

ultrathin state. In addition, in the ultrathin films, polymer chains are constrained in the narrow space. This might be a reason why the breadth of the  $\alpha_a$ -relaxation process became larger.

In order to confirm to what extent a chain confinement effect affects on the peak broadening, PS 53.4k thin films with the thickness of 37 and 103 nm on PI substrates were also examined as well. Fig.5 shows the result. The  $2R_{a}$  of a PS 53.4k chain is calculated to be 12.6 nm, meaning that the chain confinement effect should be trivial, if any. Nevertheless, the  $\alpha_a$ -absorption peak for the 37 nm-thick film was much broader than that for the 103 nm-thick This makes it clear that the surface and film interfacial effects is dominant for the broadening of  $\alpha_a$ -absorption peak. Similar inclination related to the breadth broadening of glass transition has been observed in the PS ultrathin on Si substrates by ellipsometric films measurements.<sup>6)</sup> ellipsometric Since measurement just traces thermal expansion of a



**Fig.6** Typical relation between  $\ln f$  and  $1/T_{\text{max}}$  for the PS 1.46M thin and ultrathin films.

film, however, they did not discuss about details of molecular motion in a glass transition region. In contrast, dynamic viscoelastic measurement can proceed more as follows.

We finally come to rheological analysis for the  $\alpha_a$ -relaxation process in the PS ultrathin films. Fig.6 shows the typical relation between  $\ln f$  and  $1/T_{\text{max}}$  for the PS 1.46M thin and ultrathin films. In the thin films, the relation was invariant with respect to the chemical nature of the substrate. On the other hand, the linear slope for the ultrathin films seems to be dependent on what the substrate is. And, it should be noted that the linear slopes for the ultrathin films differ from those for the thin films. Table 2 shows  $\Delta H$ values in the PS films with various thicknesses, and quantitatively explains the dynamics in the ultrathin films appeared in Fig.6. In the case of PS films thicker than about 60 nm,  $\Delta H$  was almost constant regardless of the thickness and the substrate. And, it should be recalled that the value is essentially the same as the bulk value. In contrast, the  $\Delta H$  value in the 37 nm thick-ultrathin films was dependent on the chemical nature of the substrate. Based on static contact angle measurement, it was revealed that the interfacial free energy for the PS and PI pair was much smaller than that for PS and Si. In other words, the chemical interaction between PS and PI is stronger than that for the pair of PS and Si, meaning that interfacial molecular motion of PS on PI is supposed to be more restricted than the case of PS on Si. This leads to increase in the  $\Delta H$  value, and can account for the  $\Delta H$ discrepancy for the ultrathin films on between PI and Si. However, those values were much lower than the corresponding bulk value. Taking into account that thermal molecular motion at the surface is enhanced in comparison with the interior bulk region,<sup>7)</sup> it can be claimed that the segmental motion in the PS ultrathin films was

Table 2 Apparent activation energies for  $\alpha_a$ -relaxation process in PS thin and ultrathin films with various thicknesses.

PS 1.46M on PI		PS 1.46M on Si	
<i>t  </i> nm	∆ <i>H /</i> kJ · mol <sup>-1</sup>	<i>t /</i> nm	∆ <i>H</i> / kJ∙mol <sup>-1</sup>
201	580±30	196	$550 \pm 30$
64	$510\pm70$	66	$520\pm60$
50	$500\pm50$	56	440±70
37	$240\pm20$	37	200±10

more strongly influenced by surface than interface with the substrate.

## 4. CONCLUSIONS

Thermal molecular motion of PS thin and ultrathin films supported on substrates was first studied by dynamic viscoelasticitic measurement. The  $\alpha_a$ -relaxation process corresponding to the segmental motion was clearly observed at around 380 K even for the thin and ultrathin films. Α rheological analysis revealed that the  $\alpha_{a}$ -relaxation behavior in the thin films essentially agreed with that of the bulk sample. On the contrary, the  $\alpha_a$  relaxation in the ultrathin films was broadened in temperature, being toward both lower and higher temperature sides. Also, it was revealed that  $\Delta H$  values for the ultrathin films were much lower than that in the thin films due probably to surface effect. Moreover, the  $\Delta H$  for the ultrathin films on PI substrates showed a higher value than that on Si substrate. These results imply that segmental motion in polymer ultrathin films is strongly influenced by surface and interfacial effects.

### References

[1] K. Shuto, Y. Oishi, T. Kajiyama and C. C. Han, *Polymer J.*, **25**, 291-300 (1993).

[2] J. L. Keddie, R. A. L. Jones and R. A. Cory, *Europhys. Lett.*, 23, 59-64 (1994).

- [3] J. L. Keddie, R. A. L. Jones and R. A. Cory, *Faraday Discuss.*, **98**, 219-230 (1994).
- [4] K. Fukao and Y. Miyamoto, *Europhys. Lett.*, 46, 649-654 (1999).
- [5] N. G. McCrum and B. E. Read, "Anelastic and Dielectric Effects in Polymeric Solid" Dover: New York, 1967.
- [6] S. Kawana and R. A. L. Jones, Phys. Rev. E, 63, 021501 (2001).

[7] K. Tanaka, A. Takahara and T. Kajiyama *Macromolecules*, **33**, 7588-7593 (2000).

(Received October 29, 2003; Accepted November 25, 2003)