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Annealing effects on thickness of polystyrene thin films as studied by neutron reflectivity

T. Kanaya[a,*], T. Miyazaki[a,b], H. Watanabe[a], K. Nishida[a], H. Yamano[a], S. Tasaki[c], D.B. Bucknall[d]

[a]*Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan*
[b]*Nitto Denko Corporation, 1-1-2 Shimohozumi, Ibaraki, Osaka-fu 567-8680, Japan*
[c]*Research Reactor Institute, Kyoto University, Kumatori, Osaka-fu 590-0494, Japan*
[d]*Department of Materials, Oxford University, Parks Road, Oxford, OXON OX1 3PH, UK*

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Abstract

We performed neutron reflectivity measurements on deuterated polystyrene thin films supported on silicon substrate as a function of temperature. In order to see effects of annealing on the thickness, the films were annealed at 80 °C for 12 h and 135 °C for 12 h, termed *weakly* and *strongly annealed* films, respectively. One of the main purpose of this study is to see if the negative expansivity reported for very thin films [Phys. Rev. Lett. 71 (1993) 867] is caused by unrelaxed structure due to lack of annealing. It was found that the *weakly annealed* films show negative expansivity in the glassy state and it disappears for the *strongly annealed* films with thickness above about 90 Å. This suggests that the negative expansivity is due to the unrelaxed structure. In addition to this relaxation process, the thickness difference between the heating process and the cooling process suggests that there is another very slow relaxation process in thin films detectable at around 135 °C or about 32 °C above the glass transition temperature T_g. As a candidate for this slow process a sliding motion proposed by de Gennes is discussed.

Keywords: Polymer thin film; Glass transition; Negative expansivity

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1. Introduction

Properties of polymer thin films and/or polymer surfaces are very different from those of the bulk and related to many phenomena such as adhesion, wetting, surface friction, and hence are important from viewpoints of not only science but also industrial applications [1–3]. Glass transition of thin films and/or surfaces is also one of the most interesting phenomena because many properties such as mechanical and thermal ones drastically change at the glass transition temperature T_g. Aiming to elucidate the special nature of glass transition of thin films and/or surfaces, many studies have been performed using many techniques such as ellipsometry [4,5], X-ray and neutron reflectometry [6–9], positron annihilation [10], dielectric relaxation [11–13], Brillouin light scattering [14–16] and atomic force microscopy [17–19]. In a pioneering work by Keddie et al. [4], they measured the thickness of polystyrene thin films supported on a silicon substrate as a function of temperature using an ellipsometer, and determined the glass transition temperature from the change of thermal expansivity. It was found that the glass transition temperature T_g decreases with decreasing film thickness in a range lower than ~400 Å. This observation on polystyrene films was confirmed by other experiments [20]. However, it is now recognized that such reduction in T_g is observed only for systems with weak interactions between polymer and substrate such as polystyrene and silicon while for systems with strong interactions such as poly(methyl methacrylate) (PMMA) and silicon, the glass transition temperature T_g increases with decreasing film thickness [5], suggesting that the interfacial interactions affect T_g of thin films. In fact, the glass transition temperature T_g of freely standing polystyrene films, which have two free surfaces, shows much larger T_g reduction than supported films [16,21].

Thus, we are gradually getting common understandings on the glass transition of polymer thin films, but there are still many controversial problems. In an early work, Orts

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[*] Corresponding author. Tel.: +81-774-38-3141; fax: +81-774-38-3146.
E-mail address: kanaya@scl.kyoto-u.ac.jp (T. Kanaya).

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et al. [6] reported that negative thermal expansivity was observed by X-ray reflectometry for polystyrene films thinner than ~250 Å, which were annealed at 90 °C for 1 h before the measurements. Now it is considered that the negative expansivity is due to unrelaxed structure of the thin films [2]. It is expected that as-deposited films are very much stressed by strain brought about during the spin-coating, producing unrelaxed structure. Usually neutron reflectivity (NR) and X-ray reflectivity (XR) measurements take so long that the structure of films gradually relaxes on heating during the measurements to decrease the film thickness. If the reduction in the thickness overcomes the thermal expansion, apparent negative expansivity should be observed. As far as we know, however, there are no direct experiments to clarify the annealing effects on film thickness, thermal expansivity and glass transition temperature. In this work, therefore, we have investigated annealing effects on film thickness, thermal expansivity and glass transition temperature of deuterated polystyrene thin films. For this purpose, we employed neutron reflectometry because we can evaluate film thickness very precisely in this method compared with other ones such as ellipsometry.

2. Experimental

The sample used in this experiment was deuterated polystyrene (PS-d$_8$) with molecular weight $M_\mathrm{w} = 300,000$ and molecular weight distribution $M_\mathrm{w}/M_\mathrm{n} = 1.06$, where M_w and M_n are weight-average and number-average molecular weights, respectively. The bulk glass transition temperature T_g of this PS-d$_8$ was determined to be 103 °C from DSC measurements. PS-d$_8$ solutions in toluene were spin-coated on Si (111) at 2000 rpm after filtering through 0.22 Milipore filter. Before spin-coating, silicon wafers were rinsed in toluene, in acetone, in methanol and then in distilled water. Native oxide layer on the surface was not removed in this experiment. Thickness of films was controlled with varying polymer concentration. As-deposited PS-d$_8$ films were annealed in vacuum under two conditions: one was annealed at 80 °C for 12 h and the other at 135 °C for 12 h. The former and latter annealing temperatures are 23 °C below T_g and 32 °C above T_g, respectively. Hereafter, the former and the latter films are termed *weakly annealed* films and *strongly annealed* films, respectively. After annealing, the films were kept at room temperature (25 °C) for about one week before measurements.

NR measurements were performed on two spectrometers. One is MINE spectrometer [22] installed at a cold neutron guide in JRR-3M reactor, Tokai, and the other is CRISP spectrometer [23] at a pulsed neutron source in ISIS, Didcot. The NR measurements were performed at several temperatures in a heating process from 25 to 135 °C while the measurements in a cooling process were also performed for some samples after the heating process. The measurements were performed in vacuum for MINE and in

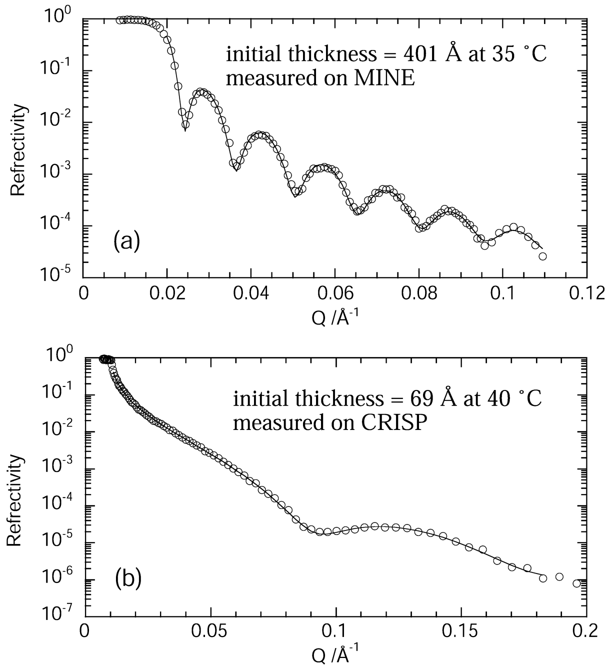

Fig. 1. Neutron reflectivity profiles from deuterated polystyrene thin films. Solid curves are the results of fits using a single layer model: (a) measured at 35 °C on MINE, (b) measured at 40 °C on CRISP.

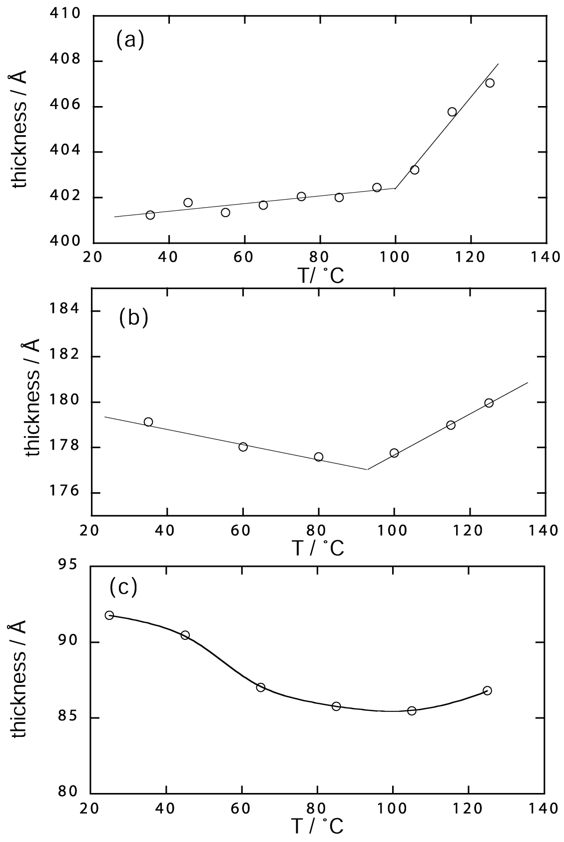

Fig. 2. Temperature dependence of thickness of weakly annealed deuterated polystyrene thin films with various values of initial thickness. Measurements were done in heating process.

dry nitrogen gas for CRISP. It was confirmed that the data were hardly affected by nitrogen gas, especially the temperature dependence of the thickness. Data acquisition times at a given temperature were 8 h for MINE and 2 h for CRISP, respectively. We have to pay our attention on these data acquisition times when we discuss the annealing effects on the film thickness because they are comparable to the annealing time.

The observed reflectivity was analyzed by a home-made program, which is based on a recursion formula derived by Parratt [24] to calculate reflectivity from successive interfaces and modified to include effects of interfacial roughness [25]. In fitting to the data, we employed a single layer model with surface and interfacial roughness in addition to an oxide layer on Si surface.

3. Results and discussion

Fig. 1(a) and (b) show typical reflectivity profiles for a weakly annealed PS-d_8 film measured by MINE at 35 °C and that for a strongly annealed sample measured by CRISP at 40 °C, respectively. The solid lines in the figures are the results of fits using a single layer model. The agreements are very good, showing that the single layer model is appropriate to describe the reflectivity from PS-d_8 films. The evaluated film thickness is shown in Fig. 2(a)–(c) for weakly annealed PS-d_8 films with initial thickness at 25 °C $d_0 = 401$, 179 and 91 Å, respectively. For the film with $d_0 = 401$ Å in Fig. 2(a), the film thickness increases with temperature up to 101 °C with thermal expansivity of 0.31×10^{-4}/°C and begins to increase more steeply above 101 °C with expansivity of 4.5×10^{-4}/°C. It is obvious that the temperature 101 °C is the glass transition temperature of this thin film. The value of expansivitiy in the glassy state below T_g is much smaller than the expected value (1.1×10^{-4}/°C) from the bulk expansivity assuming that thin films are constrained along the substrate [7], but that in the melt above T_g is rather close to that expected from the bulk (5.1×10^{-4}/°C). The thinner weakly annealed film with $d_0 = 179$ Å (Fig. 1(b)) shows a negative expansivity below about 93 °C, which must be a glass transition temperature T_g, while the expansivity in the melt ($= 5.1 \times 10^{-4}$/°C) above 93 °C is the same as the value expected from the bulk. The negative thermal expansivity is much clearly observed for the thinner films with $d_0 = 91$ Å (Fig. 2(c)). For this film, we cannot estimate T_g because no clear reflection point is observed. The present observations show that the weakly annealed thin films have the small or negative expansivity in glassy state compared with that expected from the bulk, and this tendency is enhanced as the film thickness decreases. These results agree with those reported by Orts et al. [6]. In order to confirm whether this small or negative expansivity is due to lack of annealing or unrelaxed structure NR measurements were performed on the strongly annealed thin films to evaluate the thickness as a function of temperature.

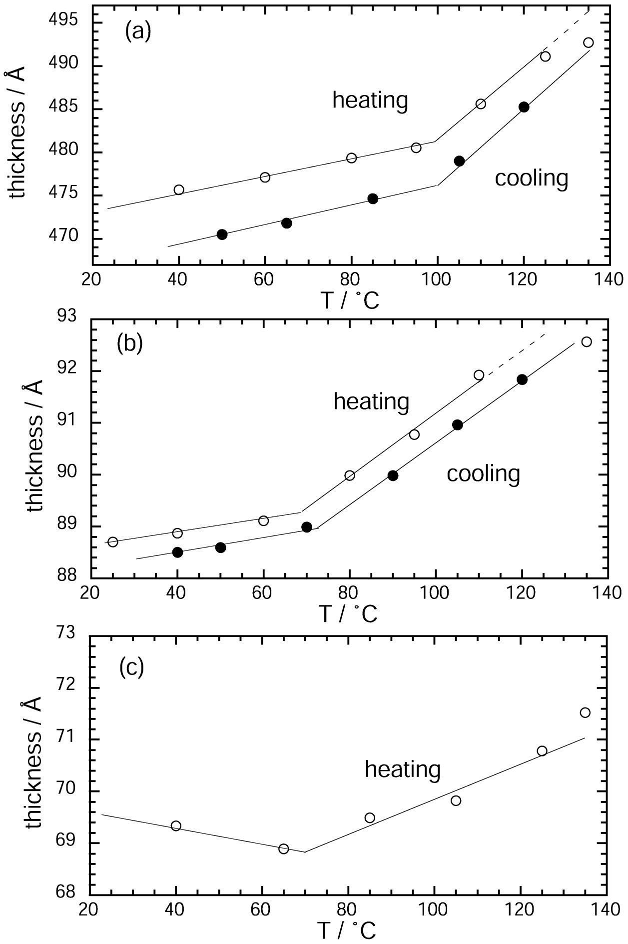

Fig. 3. Temperature dependence of thickness of strongly annealed deuterated polystyrene thin films with various values of initial thickness. Measurements were done in heating (m) and cooling (l) processes.

Fig. 3(a)–(c) show the temperature dependence of thickness for strongly annealed PS-d_8 films with initial thickness at 25 °C $d_0 = 474$, 89 and 69 Å, respectively. NR measurements were also done in a cooling process after a heating process for the films with $d_0 = 474$ and 89 Å. The values of expansivity of the films in the glassy state are about 1.8×10^{-4} and 1.1×10^{-4}/°C, respectively, which are slightly larger than and very close to that expected from the bulk. Comparing these values with those of the weakly annealed films having almost the same thickness (for example, see Figs. 2(c) and 3(b)), it is obvious that the structural relaxation occurs during the pre-annealing at 135 °C and the small or negative expansivity in the weakly annealed thin films recovers to the value expected from the bulk. The values of expansivity in the melt are 6.7×10^{-4}, 6.6×10^{-4} and 7.6×10^{-4}/°C for the films with $d_0 = 69$, 89 and 474 Å, respectively. These values are slightly larger than or rather close to that expected from the bulk and those of the weakly annealed films, suggesting that the annealing effects on the melt expansivity are not large.

However, it is surprising that the strongly annealed film with $d_0 = 69$ Å in Fig. 3(c) still shows a negative or almost zero expansivity below T_g nevertheless it was annealed at 135 °C, being 30 °C above T_g, for 12 h. This implies two possibilities. One is that there is a very slow relaxation process in very thin films below about 80 Å so that the annealing at 135 °C for 12 h is not enough for structural relaxation. The other is that the expansivity of such a very thin film is inherently very small or negative. A clue to this problem can be found in the thickness difference between the heating and cooling processes in Fig. 3.

As clearly seen in Fig. 3(a) and (b), the film thickness measured in the cooling process is smaller than that in the heating process. As mentioned above, thickness evaluated by NR measurements is rather reliable compared with other methods, and the difference of thickness between the heating and cooling processes is out of errors in the measurements and the data analysis. It is interesting to point out that the thermal expansivities are almost identical in the heating and cooling processes in both the glassy state and the melt. The difference in both the processes is only the thickness at a given temperature. Carefully seeing the data in the heating and cooling processes, we can find that the value of thickness at 135 °C, which is the highest temperature in the measurements and the same as the pre-annealing temperature, is lower than the value extrapolated from the lower temperatures in the melt (see dashed lines in Fig. 3(a) and (b)). This means that reduction in thickness during the measurements is negligibly small at temperatures below about 125 °C so that the expansivity is the same between the heating and cooling processes. On the other hand, the rate of structural relaxation is rather fast at around 135 °C so that the reduction in thickness is observed at 135 °C. This makes thickness difference between the heating and cooling processes. Taking into account that these samples were already annealed at 135 °C for 12 h before the measurements, it is expected that the rate of structure relaxation at 135 °C is not fast enough to complete the structural relaxation for 12 h. If it is true we have to consider another slow relaxation process even above the glass transition temperature in thin films in addition to a relatively fast relaxation process dominating the negative expansivity in the glassy state. There is a possibility that the slow relaxation is caused by unexpected interactions between polystyrene and silicon substrate. However, the reduction in T_g with decreasing thickness [5] suggests that the interactions are weak between polystyrene and silicon substrate. Hence, we did not consider about this possibility in this paper. One possible explanation of this very slow process is a 'sliding motion' in a thin film proposed by de Gennes [26], which has been proposed to explain the molecular weight dependence of glass transition temperature in thin freely standing films reported by Forrest et al. [14–16,21]. In this model, a chain advances along its own path (probably via a few mobile 'kinks'). The free volume required for the sliding motion involves only the side chains and is much less than bulk cooperative motion. Sliding is blocked in the bulk because chain ends would have to invade new territory, and this requires a large free volume. Near a free surface, the situation could be different: the monomers in direct contact with the air are nearly fluid and sliding motion easily occurs near a free surface. Such sliding motion is possible in thin films in which surface fraction is large and should depend on molecular weight.

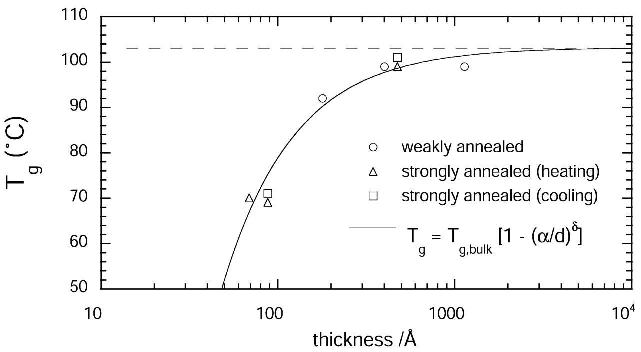

Fig. 4. Glass transition temperature T_g of deuterated polystyrene thin films as a function of initial thickness. Solid curve is a result of fit using Eq. (1).

The present results suggest that there are two relaxation processes in thin films: one is a relatively fast relaxation process which is the cause of the negative expansivity and the other is a very slow relaxation process detectable above about 135 °C. Taking into account these results as well as the fact that the *strong annealed* film with initial thickness $d_0 = 69$ Å has still a negative or almost zero expansivity (Fig. 3(c)), it is expected that the expansivity of very thin film probably below about 80 Å must be inherently very small or negative. This problem will be discussed in a forthcoming paper [27].

Finally we would like to discuss the thickness dependence of the glass transition temperature T_g. The glass transition temperature T_g evaluated from the discontinuous change of thermal expansivity is plotted against the initial film thickness in Fig. 4, including the weakly annealed samples and the strongly annealed samples in the heating and cooling processes. It was clearly found that the glass transition temperature T_g decreases with film thickness as reported in many papers.[1] Keddie et al. [4] showed that the thickness dependence of T_g can be described by the empirical relation

$$T_g(d) = T_g^{\mathrm{bulk}}\left[1 - \left(\frac{\alpha}{d}\right)^{\delta}\right] \tag{1}$$

where α and δ are constants. We fit this equation to our data in Fig. 4 and the result is given by a solid line, showing that our data is also described by this equation. The values of α and δ in Eq. (1) were 26.1 Å and 1.07, respectively. The values are slightly different from the reported ones ($\alpha = 32$ Å and $\delta = 1.8$ [20]). Glass transition temperature T_g of polystyrene thin films evaluated by various methods

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[1] See Fig. 2 on p. 262 in Ref. [20].

are rather scattered [20] and the present T_gs are within the experimental error, showing that the difference in α and δ is also within the experimental error. One of the most interesting results is that the values of T_g are almost independent of its thermal history whether it is weakly annealed or strongly annealed before the measurements and whether it is in a heating process or cooling process although the thickness itself strongly depends on the thermal history (Fig. 3(a) and (b)). As expected from the thickness difference in the heating and cooling process, this fact also suggests that the structure relaxation process is very slow compared with the data acquisition time, at least below 125 °C, and hence T_g is independent of the thermal history.

4. Conclusion

In this work we have investigated annealing effects on thickness of deuterated polystyrene thin films supported on silicon substrate using neutron reflectometry. It was found that the negative expansivity of thin films in the glassy state is caused by unrelaxed structure due to lack of annealing. In addition to the relaxation process, we found another very slow relaxation process detectable above about 135 °C, which reduces the thickness but does not affect the expansivity in the glassy state because it is frozen in or extremely slow below about 125 °C. One of the candidates to this slow process is a sliding motion proposed by de Gennes.

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