Distribution of Glass Transition Temperature Tg in a Polymer Thin Film by Neutron Reflectivity

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Recent extensive studies on polymer thin films have revealed very interesting but unusual properties of polymer thin films. It was reported that the glass transition temperature Tg of polystyrene thin films supported on silicon substrate decreases with decreasing thickness below 40 nm. Similar results were reported by many researchers on Tg of polystyrene thin films supported on silicon substrate. These results were explained in terms of multi-layer structure consisting of surface mobile layer, middle bulk-like layer and interfacial immobile layer near the substrate. It is now believed that revealing the multi-layer structure is essential to understand the unusual properties. This has been already pointed out by de Gennes [2000, Eur. Phys. J. E 2 201], and he mentioned that further experiments should not aim at the determination of a single Tg, but at a distribution of Tg 's. In this report we have studied the distribution of glass transition temperature Tg in a three-layer polystyrene thin film by neutron reflectivity, aiming to elucidate the multi-layer structure of polymer thin films. For neutron reflectivity (NR) measurements we used deuterated polystyrene (d-PS) and hydrogenated polystyrene (h-PS) with molecular weight Mw = 7.31 x 10^5 and Mw = 7.69 x 10^5, and molecular weight distributions were Mw/Mn = 1.18 and 1.08, respectively. The bulk glass transition temperatures Tg of h-PS and d-PS are 100 C and 103 C, respectively. NR measurements were performed using MINE spectrometer at JRR-3 reactor in Tokai.

Figure 1 shows neutron reflectivity profiles from the three-layer thin film at 30, 60, 85 and 110 C. It is very clear that the reflectivity profiles gradually shifts to lower q with increasing the temperature, showing thermal expansion of the film. The temperature dependence of the total film thickness is shown for the total film thickness, the top (surface), the middle and the bottom layers are shown in Figures 2(a), (b), (c) and (d), respectively. The surface layer increases in thickness with the thermal expansivity of ~1.3 x 10^-4 K^-1, which is close to the expected value (= 1.1 x 10^-4 K^-1), while it begins to increase above ~85 K more steeply, showing that the glass transition temperature of the surface layer is ~18 K lower than the bulk Tg. The middle layer shows a very similar thermal expnsivity in the glassy state with the top layer, but the glass transition temperature is ~105 K which is very close to or little bit higher than the bulk Tg. The middle layer behaves as the bulk layer. On the other hand, the bottom layer shows very different temperature dependence of the thickness from other layers. The film thickness is almost independent of temperature below ~130 C, suggesting that the glass transition temperature of the bottom layer must be higher than 130 C. The present results clearly show that the thin film has a distribution of Tg.

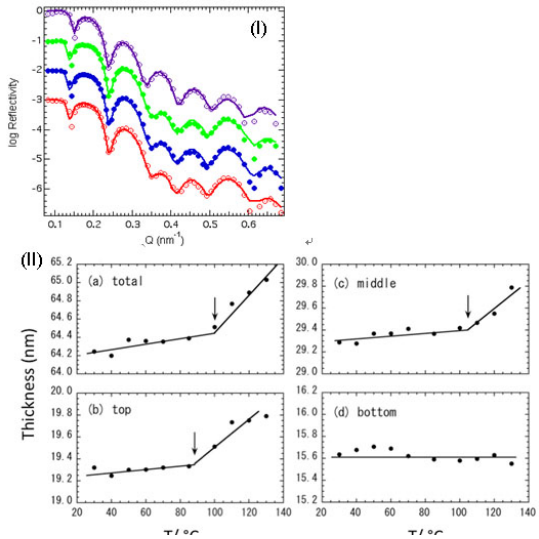

Fig. 1. (I) Neutron reflectivity profiles of three-layer polystyrene thin film. (II) Temperature dependence of film thickness. (a) total, (b) top layer, (c) middle layer, (d) bottom layer.