

## Distribution of glass transition temperature in poly(methyl methacrylate) thin film as revealed by neutron reflectivity

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It is well known that physical properties of polymer thin films are very different from those of bulk. The thickness dependence of  $T_g$  is extensively studied because  $T_g$  is related to the thermal stability of thin film. It was reported that  $T_g$  decreased as the film thickness decreases with little apparent dependence of substrate for polystyrene (PS) thin film. As for poly (methyl methacrylate) (PMMA) thin films, the situation is complicated compared to that for PS thin films. For example, PMMA thin films supported to Si substrate with native oxide,  $T_g$  increased with decreasing thickness, on the other hand  $T_g$  decreased with thickness for PMMA supported on gold-coated Si substrate, suggesting that difference of interfacial properties was responsible for observed  $T_g$  anomalies. It is considered that mobile surface layer is responsible for the decrease of  $T_g$  and the interfacial layer contributed the increase of  $T_g$ . That is to say, the resulting physical properties of polymer thin films are the competition between surface effect and interfacial effect. In order to observe the competition between free surface and interfacial effect it directly, is straightforward to study the distribution of  $T_g$  in thin film. In this report, we studied the distribution of  $T_g$  in PMMA thin films with 3-layered thin film consisting of h-PMMA layer and d-PMMA layer by neutron reflectivity (NR).

The NR profiles from d-PMMA/h-PMMA/d-PMMA 3-layered thin film measured at several temperatures are shown in Figure 1 (a) and 3-layered model could describe our prepared 3-layered PMMA thin film fairly well, supporting the preserve of layered structure. We evaluated the temperature dependence of the thickness of each layer, which were

termed the first, second and third layer from the bottom to the top as shown in Figure 1 (b). Except for the third layer, which was directly deposited to the substrate we could observe the clear change of thermal expansivity between glassy state and molten state. The evaluated  $T_g$ 's for 1st layer and 2nd layer are 393K and 405K, respectively. The  $T_g$  of 1st layer was almost the same as bulk  $T_g$  (393K), which was evaluated from DSC measurements, on the other hand  $T_g$  of 2nd layer was about 10K higher than that of bulk. As for the bottom or 3rd layer we again observed thermal zero thermal expansivity and it is considered that interfacial  $T_g$  shifted out of the experimental temperature range ( $T > 413K$ ). We could not observe the reduction of  $T_g$  compared to bulk  $T_g$  even for the free surface, implying that the interfacial effect dominated the surface effect for PMMA thin film.

Utilizing the multi-layered thin film we succeeded to evaluate the distribution of  $T_g$  in PMMA thin film. Further analysis including the molecular mobility at different position is on progress.

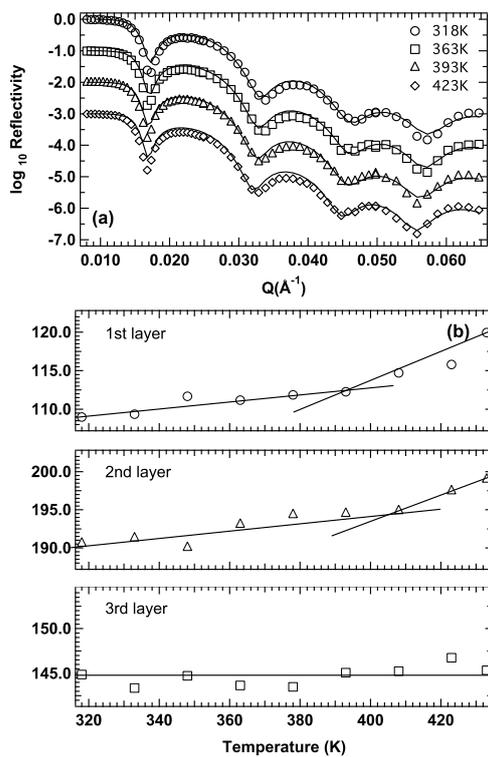


Fig. 1. (a) Neutron reflectivity profiles from d-PMMA/h-PMMA/d-PMMA 3-layered thin films measured at various temperatures. (b) Temperature dependence of 1st layer, 2nd layer and 3rd layer.