

# Surface/interface Effect on Glass Transition in Polymer Thin Films

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## 1. Introduction

Polymer thin films have been widely used in various fields in our daily life. The physical and thermal properties of polymer materials have great influence on the stability and durability of the films. It has been regarded that the properties of polymer materials in thin-film states were the same as those of the bulk material. However, recent studies on polymer thin films shown that the thermal and physical properties of thin films are modified from the bulk state. Especially, the glass transition temperature ( $T_g$ ) of the polymer thin films has been extensively studied by many research groups. It has been reported that  $T_g$  of polymer thin films is dependent on the thickness. The previous studies showed that  $T_g$  is dependent on the depth from the surface:  $T_g$  near the surface is lower the bulk  $T_g$ ; on the other hand,  $T_g$  near the interface is higher than the bulk  $T_g$ . Moreover, it has been shown that the glass transition is modified by the interaction between the polymer and the interface. The glass transition phenomenon is related to the segmental motion of a polymer chain. The decrease of  $T_g$  at the surface is considered as the enrichment of the chain end segment with the higher mobility compared to the main chain segment. On the other hand, at the interface, the mobility of the polymer chain segment would be restricted by the solid wall of the substrate and chemical interaction between the polymer and the interface, resulting in the increase of  $T_g$ . However, the details on the effect of the surface/interface are still unclear. Whereas the interaction of the polymer chain and the interface/surface must be localized at the molecular scale, the previous works implies that the surface/interface effect would propagate at the length scale of 10 nm. In the current experiment, the effect of the surface and interface on the glass transition is quantitatively discussed from the experiment of the  $T_g$  evaluation dependent on the depth from the surface and interface.

## 2. Experiment

Poly(methyl methacrylate) (PMMA) with a molecular weight of  $1.2 \times 10^6$  were used as a sample.  $T_g$  is evaluated as the inflection point of the thickness-temperature curve. In order to probe  $T_g$  at the surface, a 15-nm-thick layer of deuterated PMMA (PMMA-d) was put onto the surface of a buffer layer of hydrogenated PMMA (PMMA-h) with various thickness as shown in Figure 1a. The sample code of the PMMA-d layer deposited on a PMMA-h film with a thickness of  $t$  is denoted by D15/Ht/Si. On the other hand, the samples having a 15-nm-thick PMMA-d layer between a PMMA-h layer and a Si wafer to examine  $T_g$  at the substrate interface (Figure 1b), which are denoted as Ht/D15/Si.

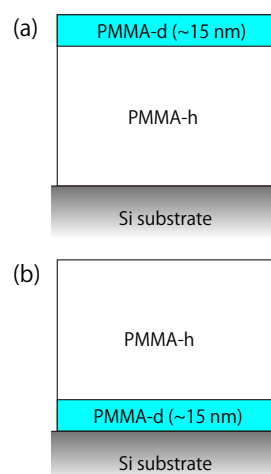


Figure 1: Layer structure of the sample to examine  $T_g$  at surface (a) and interface (b).

The NR measurements were conducted at BL16 SOFIA in MLF J-PARC. Neutron reflectivity was measured at incidence angles of 0.3, 0.7, and 1.6° at a neutron wavelength range of 0.24–0.88 nm. The measurements were carried out in a vacuum heat stage at a temperature range of 70 – 150°C. The NR profile was fitted to a theoretical reflection curve to obtain the depth profile of the scattering length density (SLD) in the sample film. The temperature dependence of the thickness of the PMMA-d layer was obtained.

### 3. Results

Figure 2 shows the NR profiles for the sample film D15/D90/Si at a temperature range from 70 to 150°C. Each NR spectrum shows two kinds of interference fringes patterns with narrow and wide gaps, which corresponds to the correlation between the interfaces of the PMMA-h and PMMA-d layers, respectively. The interference fringe gap decreased with the increase of the temperature, indicating the thermal expansion of the sample film. By fitting the experimental data to a theoretical reflection profile using MOTOFIT, the thickness of the PMMA-d layer was evaluated. Figure 3 shows the temperature dependence of the 15-nm-thick film of dPMMA directly deposited on a Si wafer and the dPMMA layer of D15/H90/Si. The 15-nm PMMA film on a Si wafer showed  $T_g$  of 125°C, which is higher than the bulk  $T_g$  (120°C). On the other hand,  $T_g$  of the PMMA-d layer on the 90-nm-thick PMMA-h film was 110°C.

### 4. Conclusion

The effect of the surface and interface on the glass transition temperature of PMMA films was successfully confirmed by the NR measurements of stacked films of deuterated and hydrogenated polymers. The analysis of the other samples would provide further insight into the effect of the surface and interface on the glass transition of polymer thin films.

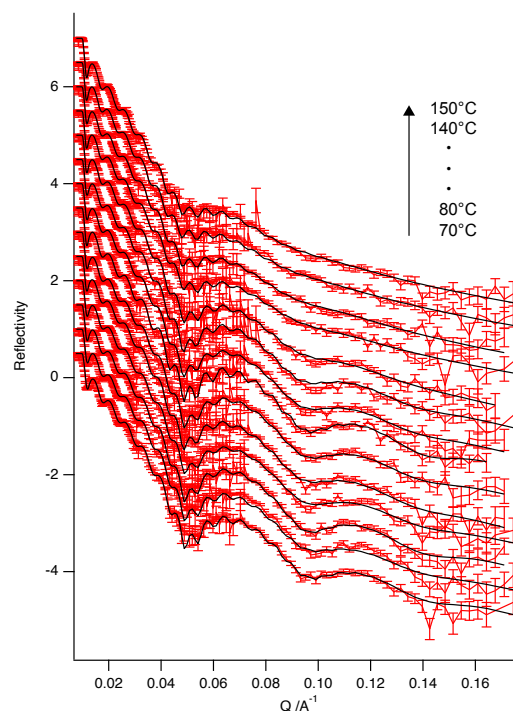


Figure 2: NR spectra for D15/H90/Si at a temperature range from 70 to 150°C. Red points with error bars and black solid curves indicate the experimental and theoretical NR profiles, respectively.

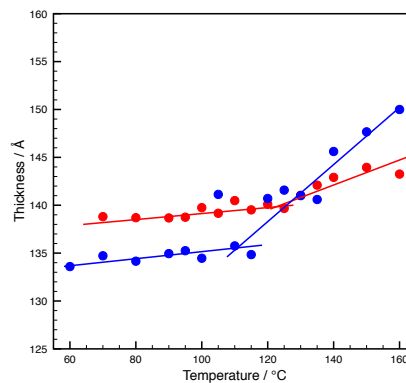


Figure 3: Temperature dependence of the PMMA-d layer in the sample film D15/H90/Si (blue) and a 15-nm-thick film of PMMA-d on a Si wafer (red).