Inelastic and Quasielastic Neutron Scattering Studies on Polymer Thin Films

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Polymer thin films show very interesting but unusual properties, which are related to many significant phenomena such as dewetting, adhesion and surface friction. Therefore extensive investigations have been performed on thin films from both scientific and industrial points of view. One of the most interesting findings so far reported is the reduction of glass transition temperature T_g in polystyrene (PS) thin films. Another interesting finding is apparent negative thermal expansivity. In the previous papers [1,2], we showed that the apparent negative expansivity was caused by unrelaxed structure due to lack of annealing. However, after enough annealing we also found the reduction in thermal expansivity in the glassy state below about 20 nm. It is evident that studies on the dynamics of thin films are essential to reveal the molecular origins of the above-mentioned interesting but unusual phenomena. In this work we therefore performed inelastic and quasielastic scattering measurements on PS thin films 20, 40 and 100 nm thick in a temperature range from 10 to 423 K covering the glass transition temperature.

We used polystyrene (PS) with molecular weight M_w=2.9 × 10^5 and molecular weight distribution M_w/M_n=1.06, where M_w and M_n are the weight average and the number average of the molecular weight, respectively. The bulk glass transition temperature T_g is 423 K. PS thin films were prepared by spin-coating toluene solutions on flat glass plates. The film was removed from the glass surface onto water surface and collected on thin Al foil, and then annealed at 413 K for 12 h after drying in vacuum at room temperature for 2 days. For the measurements, 299 sheets were used to get higher scattering intensity. The inelastic neutron scattering measurements were performed with LAM-40 spectrometer in KEK, Tsukuba, and MARI and OSIRIS spectrometers in ISIS, Didcot. The energy resolutions of LAM-40, MARI and OSIRIS are 0.2 meV, 0.35 meV and 15 μeV, respectively. In the measurements on LAM-40 [3] and MARI we mainly observed the Boson peak as well as the picosecond fast process characteristic to disordered materials in meV region while we found another quasielastic component in μeV region in the OSIIRIS measurements.

We first analyze the Q dependence of incoherent elastic scattering intensity $I_{el}(Q)$ observed with LAM-40 to evaluate the mean square displacement $\langle u^2 \rangle$. The evaluated $\langle u^2 \rangle$ decreases with film thickness, suggesting that potential hardening occurs in the thin films. The evaluated harnomic force constants f were 5.8, 6.5 and 8.7 N/m for the bulk and the 100 and 40 nm thin films, respectively. We have evaluated the density of phonon states $G(\omega)$ from the inelastic scattering and shown in Figure 1 in a form of $G(\omega)/\omega^2$ vs ω. The Boson peak is observed at around 1.5 meV and decreases in intensity with film thickness, showing the potential hardening as the film thickness decreases. This agrees with the results on the mean square displacement. Why do the polymers have higher force constant in the thin films than in the bulk? There are two possible explanations: one is that the hardening is caused by the chain deformation due to the confinement. The other is due to the immobile dead layer at the interface between the thin film and the Si substrate. In the conference this will be discussed in details.

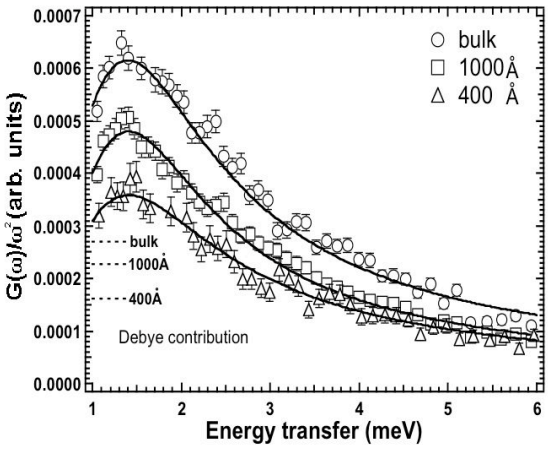

Fig. 1. Density of phonon states $G(\omega)$ divided by ω^2 for PS bulk, thin films 40 and 100 nm thick.

In addition to the LAM-40 results [3], we will discuss the anisotropy and heterogeneity of glassy dynamics in the thin films in meV region revealed in the MARI measurements, and the relaxation process in μeV region observed by the OSIRIS spectrometer in the conference.

References

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