

## **X-ray reflectivity of a polystyrene surface peeled from a Si(100) mold: Morphology and surface glass transition**

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### **Introduction**

X-ray diffraction is known to be a powerful tool for non-destructive studies of surface structures. Especially, with the usage of intense synchrotron radiation sources, X-ray reflectivity (XR) has been dedicated to investigate surface structures and morphology of non-crystalline materials under various conditions [1, 2].

Surface and interface of polymers is attracting a great interest due to its potential ability for electronic devices in near future, and of course, due to scientific interest in statistical physics of two-dimensional complex systems. However, lots of the polymer surfaces studied so far have been prepared by the so-called spin-cast method in which unexpected, nuisance effects of the solvent and those from the highly confined geometry of the thin polymer layers, being sometimes comparable with the polymers' gyration radius are inevitable. We would like to observe a solvent-free surface of a polymer sample with macroscopic thickness, which is prepared by a novel method, so as to study the surface glass transitions more naturally. In the present study, we tried to measure the XR from a flat polymer surface with elevating temperatures so as to study glass transitions at polymer surfaces.

### **Experimental**

A flat polystyrene (PS) surface was obtained as follows: (1) a lump of melted PS ( $M_w=310000$ , bulk glass transition temperature  $T_g(\text{bulk})=370\text{K}$ ) was dropped onto a polished silicon wafer; (2) annealed up to 450K for six hours and quenched down to the room temperature; (3) the PS of which dimension was 20mm\*20mm\*2mm was peeled from the flat silicon wafer at room temperature. The measurements were performed by using high resolution four-circle diffractometers installed at BL4C and at BL17A; the wavelengths were chosen to be 1.54 Angstrom and 1.3Angstrom, respectively. Dimension of the incident X-ray was about 0.1mm\*1.0mm at the sample position. The PS sample was mounted on a home made oven of which temperature was controlled by a PID unit within 0.5K ranging from the room temperature to 400K.

### **Results and Discussion**

The observed XR revealed the density profile along the surface normal direction; it indicated a fairly flat surface with the root mean square roughness of 1nm. X-ray diffuse Reflectivity showed the non-fractal height-height surface correlation at room temperature; it appeared that the interface between the PS and the Si was formed after condensation of capillary wave fluctuations.

The XR changed drastically with the heating process indicating the considerable variation in electron density at the surface, although the X-ray diffraction from the bulk PS showed no variation. Consequently, the surface glass transition temperature  $T_g(\text{surface})$  of the sample was estimated to be 50K lower than that of  $T_g(\text{bulk})$ . On the other hand, a surface of PS which was fully placed at room temperature for a long time (more than 14 days) did not show such complex variation observed in this study. Present results should be discussed on a standpoint of conformation of polymers. Furthermore, such a large difference between  $T_g(\text{surface})$  and  $T_g(\text{bulk})$  can be compared with that between the surface melting temperature and bulk melting temperature for ordinary crystals.

### **References**

- [1] M. Tolan, *X-ray Scattering from Soft-Matter Thin Films*, Springer, Berlin Heidelberg, 1999.
- [2] R. J. Roe, p236 in *Methods of X-ray and Neutron Scattering in Polymer Science*, Oxford Univ. Press, Oxford, 2000.

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