

## Confinement Effect on Surface Melting in Polymer Thin Films -Grazing-incidence X-ray Scattering Studies-

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### Introduction

The molecular organization in a confined geometry may differ from bulk and lead to significant differences in resulting physical and mechanical properties. In fact, we found that when the thickness of polyethylene (PE) films spun-cast on Si substrates was less than 500Å, the surface softness measured by the shear modulation force microscopy (SMFM) showed a drastic change at the temperature 20-40°C below the bulk melting temperature ( $T_m$ )[1]. The transition in the mechanical property may be an indication of "surface melting". It was found that the large depression in the surface melting temperature ( $T_s$ ) appeared to be a general phenomenon regardless of a choice of polymers. At the same time, as shown in Fig. 1, atomic force microscopy (AFM) images indicated that the morphology of the surface crystalline structures changed with decreasing the film thickness significantly. Further, we found that most lamellae took a nearly perpendicular orientation to the surface in the films more than 300 Å thick, while the lamellae oriented flat-on with respect to the substrate as the thickness decreased below 150 Å. In order to clarify the relationship between the depression in the mechanical property and the in-plane surface structures, we integrated a variety of surface-sensitive scattering techniques, i.e., grazing-incidence x-ray diffraction (GID), grazing-incidence small-angle x-ray scattering (GISAXS), and diffuse scattering.

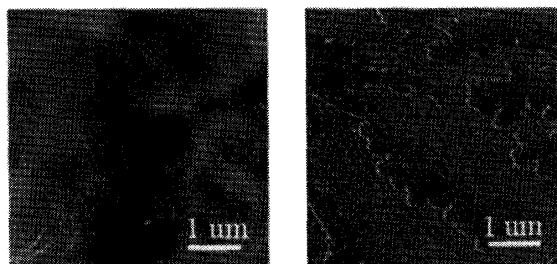


Fig. 1 AFM images of the PE films: (left) 2500Å thick; (right) 150Å thick.

### Experimental

A series of spin-cast PE films varying the film thickness from 180 Å to 1500 Å were prepared on cleaned Si substrates. Details of the sample preparation have been described elsewhere[1]. In-situ GISAXS and GID measurements were performed at Sector 8-ID (APS, Argonne, USA) and Sector 15-IB (APS), respectively. Two different incidence angles of the x-ray beam ( $\alpha_i$ ) were chosen to illuminate "surface" and "bulk" regions individually: (i)  $\alpha_i=0.14^\circ < \theta_0$  (the critical angle of 0.15°), and (ii)  $\alpha_i=0.20^\circ > \theta_0$ . The annealing time before the measurements was set to 45 min for each temperature.

### Results and Discussion

Fig.2 shows the temperature dependence of the GID profiles (with  $\alpha_i=0.14^\circ$ ) for the PE film 500Å thick. The  $T_s$  value was determined to be 100°C by SMFM. From the figure we can see that a broad amorphous peak near the in-plane wave vector ( $q_{xy}$ ) of 1.3 Å<sup>-1</sup> and a sharp (110) peak at  $q_{xy}=1.5$  Å<sup>-1</sup> change as the temperature increases. We found that the (110) reflection disappeared completely at 117°C, i.e.,  $T_m$ . Similar behavior was observed for the bulk measurements with  $\alpha_i=0.2^\circ$ . Hence, the GID data clearly show no difference between  $T_s$  and  $T_m$ . The question is what happens at  $T_s$ ? In the inset of Fig.2, the temperature dependence of the peak intensity of the (110) reflection ( $I_{max}$ ) is shown. We can see that  $I_{max}$ , which is proportional to the crystallinity, shows an abrupt decrease at  $T=100^\circ\text{C}$  where the film got softened. Hence,  $T_s$  may be regarded as the onset of surface "softening" due to the large depression in the crystallinity. Additionally, in situ diffuse scattering, which is sensitive to the surface roughness, indicated that the surface structures underwent the transition at  $T_s$ . In situ GISAXS data will be also discussed to further understand the phenomenon.

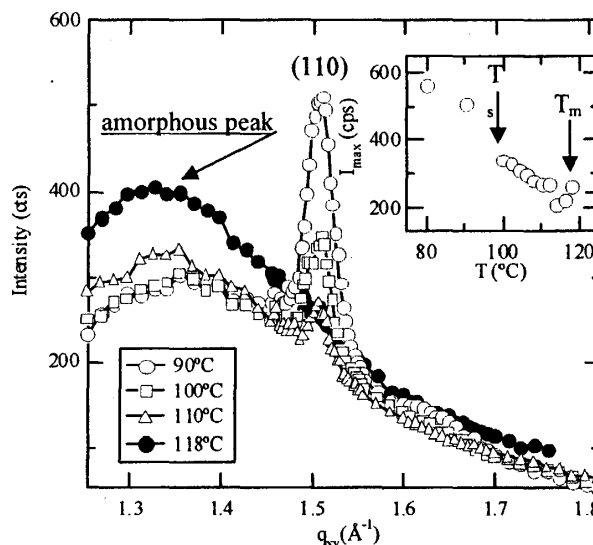


Fig. 2 GID profiles for the PE films 500Å thick expanded near the (110) reflection. In the inset, the peak intensity of the (110) reflection vs. T is shown.

### Acknowledgement

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### Reference

[1] Y. Wang et al., *Macromolecules*, 37, (2004), 3319.