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X-ray Reflectivity study on polymeric surfaces near glass transition temperature

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Introduction

We have paid great attention to the physical properties at surfaces and interfaces of polymeric materials due to importance for many applications. Recently, there have been many experimental and theoretical works of structure and dynamics at polymer surfaces. Our understanding is getting better through these works. However, these studies have been focused on surfaces and interfaces of thin polymer films; many of the results have seemed to be affected by confined geometries (= effects of substrate and thickness comparable to the radius of gyration). The aim of the present study is the structural analysis of polymer surfaces around the glass transition temperature without confined geometries, by using samples of macroscopic thickness.

Experimental

We have used specular and off-specular X-ray reflectivity (XR) to investigate surface structure of polystyrene (PS) near the glass transition temperature (T_g). A flat PS surface was obtained as follows: (1) a lump of melted PS (M_w=310000, T_g=370 K) was dropped onto a polished silicon wafer; (2) annealed up to 460K for 6 hours and quenched to the room temperature; (3) the PS of which dimension was 20mm×20mm×2mm was removed from the silicon wafer. The X-ray measurements were performed at the beamlines 4C, 17A and 17C of Photon Factory with wavelengths 1.54 Å, 1.30 Å and 1.40 Å respectively. be underlined and centered in the column. Subsection headings are discouraged.

Results and Discussion

The rms roughness of PS surfaces was fairly flat at the room temperature, ranging from 5 to 6 Å. XR showed distinct change far below T_g: In heating, major changes of XR profile which reflected surface morphology were indicated above 340 K. Off-specular XR changed drastically above 350 K. Between 350 K and 360 K, additional peaks (side peaks) appeared and grew as time passed. Growth of them differed with q positions in reciprocal space. It was most appropriate that they were regarded as the Yoneda peaks [1] from the positions. Since the Yoneda peaks were still observed at the same position at the room temperature, a novel phase which had extreme density fluctuation formed at the surface. On the other hand, there was no change in specular XR between 350 K and 360 K. Hence, we concluded that the density fluctuation in the PS surface was incoherent and should be short-range ordered. Side peaks have never been detected except for the first heating. Above 360 K, side peaks disappeared and specular XR varied significantly. Near T_g, a high density layer (200 Å thick) which reached the radius of gyration was formed at the surface. With cooling down from T_g to the room temperature, the surface layer collapsed and the surface recovered uniformity.

Reference

[1] S. K. Sinha, E. B. Sirota, S. Garoff, H. B. Stanley, Phys Rev. B **38**, 2297 (1988).