

Morphology of Polystyrene Surface near Glass transition Temperature; X-ray Reflectivity Study

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Introduction

Polymer surfaces play an important role in our daily life. For lubrication, biomaterials, coatings and adhesion, behavior of polymer molecules in surface region is known to be crucial. To apply polymeric materials more intelligently, it is necessary to understand the physical properties of polymer molecules near the surfaces. Therefore, there have been many theoretical works and experiments on polymer surfaces. However, most of them have been focused on thin polymer films. Thus, they seem to be affected by the substrates and film thickness comparable to radius of gyration R_g which may be referred to as "Confined Geometry". In order to avoid the effects of the confined geometry and elucidate the nature of polymer molecules in surface region, we prepare atomically flat polystyrene (PS) surfaces with macroscopic thickness and perform X-ray reflectivity (XR) measurements around the glass transition temperature T_g .

Sample preparation

PS surfaces were prepared by the following procedure: (1) a lump of melted atactic PS ($M_w=310 \times 10^3$, $R_g=170 \text{ \AA}$, $T_g=373 \text{ K}$) without any solvent was dropped onto a polished silicon wafer, the surface of which has a native oxide layer of 18 \AA thickness and root mean square (rms) surface roughness of 6.4 \AA ; (2) annealed up to 460 K for 6 hours and cooled down to room temperature within 2 hours in low vacuum (60 torr); (3) the PS of which dimension was $20 \times 20 \times 2 \text{ mm}^3$ was removed from the silicon matrix. We measured the PS surface which had stuck to the silicon wafer.

X-ray Reflectivity Results

The value of roughness indicating the surface width in the inset of Figure 1 is $5\text{-}6 \text{ \AA}$, which is almost the same as that of the silicon wafer. Thus, we can conclude that our procedure can yield the atomically flat PS surfaces, which afford the quantitative study on the PS surfaces at various temperatures. The fitted (z) curve at 300 K clearly indicates a low density (about 85% of bulk density) region about 100 \AA thick at the surface. It claims that some PS molecules remain on the silicon wafer, after the removal of the PS sample from the silicon wafer (procedure (3)). If so, there should be some free volume randomly distributed on the surface where the PS molecules were pulled out by the silicon wafer. Since

many particles comparable to R_g on the PS removed silicon wafer are confirmed by AFM measurements, such a speculation seems to be quite plausible for us.

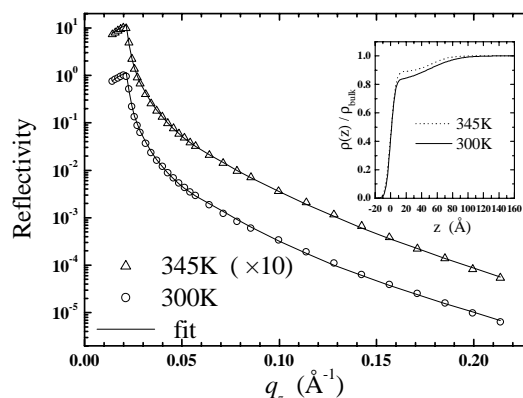


Figure 1. Specular X-ray reflectivity $R(q_z)$ at 300K (circles), and at 345K (triangles). For clarity $R(q_z)$ at 345K is shifted vertically. The solid curves are calculated by using the fitted parameters. The inset displays the best-fitted density (z) profiles at the surface. Both of them are normalized by the electron density in bulk.

In the heating from 300 K to 345 K , $R_{\text{OBS}}(q_z)$ showed slight variation as indicated in the Fig.1, although profile of XR in the transverse scans showed a complex variation in this temperature range, which will be published elsewhere. The fitted (z) at 345 K shows interesting features: (i) Density of the surface region becomes higher; (ii) The range of the surface region becomes smaller; (iii) however the rms surface mobility in the surface region is greatly enhanced at 345 K . If we recall this temperature is about 30 K lower than T_g , we have to recognize that such a variation on the PS surface with macroscopic thickness is quite unusual. Consequently, we succeeded to make the unexpectedly active, but atomically flat polymer surface free from the constraint of confined geometry. It surely gives us a key to understand the nature of polymer surface near the glass transition temperature. Measurements of specular XR at higher temperatures close to T_g , and measurements of off-specular XR below and above T_g are now in progress, which would give us fruitful information on surface morphology in lateral directions.

References

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