X-ray Reflectivity Study on the Miscibility of the Block Copolymers in Thin Film

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Introduction

Block copolymers have been extensively studied theoretically as well as experimentally during last two decades. Upon microphase separation, diblock copolymers may show several characteristic domain structures such as sphere, cylinder, ordered bicontinuous double diamond and lamella depending on the relative volume fraction of one block to the total chain.

For symmetric diblock copolymers, lamella morphology is obtained upon microphase separation. The lamella thickness L is scaled as N^{α} where constant α is close to 1/2 and 2/3 for the weak and strong segregation regime, respectively.

It has been clearly demonstrated that thin films of symmetric diblock copolymers on the substrate forms lamella morphology of which lamella plane is parallel to the substrate due to the preferential interaction between the blocks and substrate/air. For the PS-PMMA diblock copolymers, for example, PMMA chains interact favorably with silicone oxide layer used as substrate and PS blocks reside at the air interface. Since the thickness of microphase separated lamella structure has to be either nL or (n+1/2)L depending the preferential interaction between blocks and interfaces, the block copolymer forms island or holes to release the thickness constraint. For the cases of forming holes on the air surface, the hole height should be close to L.

In the present study, two block copolymers A-B having different overall chain length were mixed to form thin layers on the substrate. The initial film thickness were adjusted to form hole structure on the surface. The lamella thickness at different compositions was measured from the hole height with x-ray reflectivity and atomic force microscopy to obtain the scaling constant α. Miscibility behavior of A-B with A-C block copolymers in the thin films has also been studied on the silicon substrate coated with the polystyrene brush.

Results and Discussion

Shown in Figure 1 is X-ray reflectivity profile of [P(S-b-nBMA)(99K). Reflectivity is plotted as a function of momentum transfer $Q=(4\pi/\lambda)\sin\theta$ perpendicular to the film surface, where θ is the angle of incidence with the surface.

Reflectivity was also calculated using the density profile along the thickness direction of the film shown in the inset according to the method published earlier and shown in Figure 1 in solid line. Air interface resides at z=0 and the substrate(Silicon oxide layer) at z ≅ 750.

As can be seen from the Figure 1, calculated reflectivity is close to unity below the critical angle due to the total reflection and decreases as kz,o increases. The agreement between the two reflectivity profiles is reasonably good. It is clear that there are two oscillation frequencies, higher one corresponding to the total film thickness and lower one corresponding to the total thickness less the step height. This type of analysis can be used to analyze the miscibility of the block copolymers in the thin film. Furthermore, X-ray reflectivity study on the LB film will be discussed to demonstrate the usefulness of the X-ray reflectivity method on the thin film study.