Concentration fluctuation for polymer blend thin film close to critical

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Many interesting phenomena are reported on thin films of polymer blends. We also found in optical microscope and light scattering measurements that spinodal decomposition type dewetting preferentially occurs in the PS and PVME blend thin films for the in-plane structure in a thickness region less than 100 nm in the two phase region. In this study we investigated the density profile perpendicular to the film surface, using neutron reflectivity (NR) before dewetting. We found from the NR results that concentration fluctuations occur normal to the surface before dewetting, which may induce the dewetting. NR measurement was carried out using the MINE neutron reflectometer installed at the cold neutron guide C3-1-2-2 in JRR-3M reactor. We used deutareted PS (dPS, Mw=288,000) and hydrogenated PVME (Mw=90,000) in this study. The fraction of PS dps in the blend was 0.3, which corresponds to the critical composition in the bulk. The polymer blends were prepared by spin-coating onto a silicon wafer. Thicknesses of the polymer blend films were 98nm. All the films were pre-annealed at 90 °C in the one phase region for 30 min and then temperature-jumped into the two phase region for phase separation, and annealed for a given duration. The films were rapidly quenched to room temperature for the measurements. Figures 1 show the time evolution of neutron reflectivity profiles (a) and density profiles (b). A typical example of time evolution of NR profiles at 0, 1, 3, 120, 360 min after T-jump from one phase region to two phase region are shown in Figure 1(a). Time evolution of the composition fluctuations along z-axis evaluated from NR profiles is shown in Figure 1(b). In one phase region (t = 0 min) the NR profile is well described by three layer model (PVME/(PVME/PS)/PVME), and we found that the interface roughness between surface PVME and PS/PVME (or surface roughness) increases with annealing time. The fringed pattern in the profile disappeared once due to dewetting. However, further annealing of 360 minutes show that fringes appear again. It suggests that PVME thin layer segregate on the Si substrate.

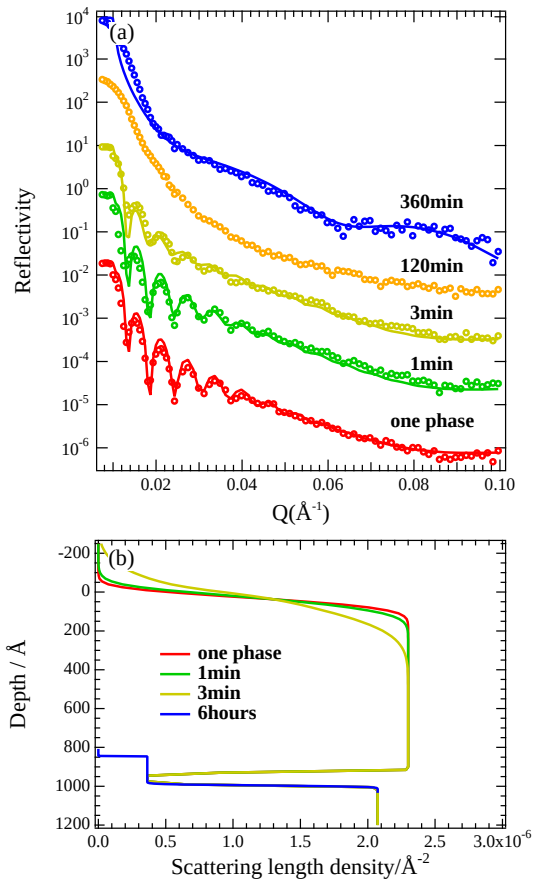

Fig. 1. Time evolution of neutron reflectivity in two phase region (a)and Time evolution of composition fluctuations in depth direction in two phase region(b).