

Relaxation dynamics of polymer thin films under solvent annealing process

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1. Introduction

Polymer thin films have been widely used in various fields in our daily life. A spin coating method has been often used to fabricate a polymer thin film with a thickness less than micrometers. In a spin coating process, a polymer solution flows on a spinning substrate and the solvent evaporates rapidly. Therefore, an as-spun thin film is in an un-equilibrium state. To reach an equilibrium state of a polymer thin film, an annealing method in vapor of a good solvent has been often used. Many research groups have extensively studied the relaxation dynamics of polymer materials at the surface and interface under a thermal annealing condition; however, little is known about the relaxation process in the solvent annealing. Therefore, in the current study, the polymer dynamics in a thin film under solvent annealing conditions will be examined by neutron reflectometry.

2. Experiment

The layered polymer thin film sample as shown in Figure 1 was prepared by hydrogenated and deuterated poly(methyl methacrylate) (hPMMA and dPMMA, respectively). A toluene solution of hPMMA was spin-coated on a glass plate to form a 20-nm-thick PMMA film and it was floated on a water surface. The hPMMA on water is scooped by a Si wafer covered with a 20-nm-thick film of dPMMA. By repeating the deposition of dPMMA

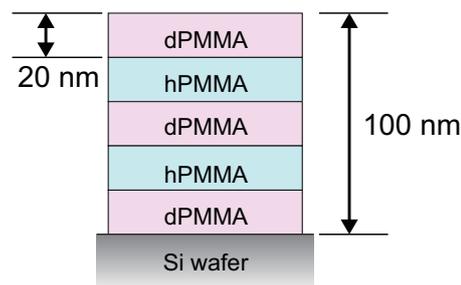


Figure 1: Structure of the 5-layer stacked film of dPMMA and hPMMA.

and hPMMA films, 5-layered stacked films of dPMMA and hPMMA with a total thickness of 100 nm were obtained. A 100-nm-thick film of dPMMA was also prepared.

The NR measurement was carried out at BL16 in MLF, J-PARC. The *in situ* measurement in an annealing process was conducted using a neutron beam with a wavelength of 0.24 – 17.6 nm (double-frame mode) and at an incident angle of 1.2°. The data acquisition was started immediately after the sample film and chloroform (0.5 mL) was sealed in an aluminum chamber with a volume of ~ 100 cm².

3. Results

Figure 2 shows the time evolution of the NR spectrum for a 100-nm-thick dPMMA film in the solvent annealing process in chloroform vapor. It can be seen that the reflectivity and the fringe gap decreased with the increase of time. The scattering length densities (SLDs) for

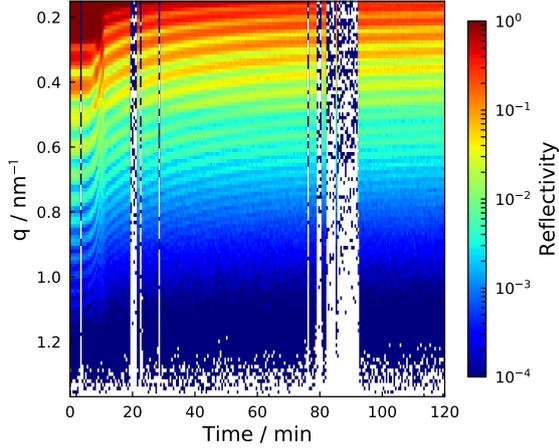


Figure 2: Time evolution of NR spectrum for a 100-nm-thick dPMMA film in chloroform vapor.

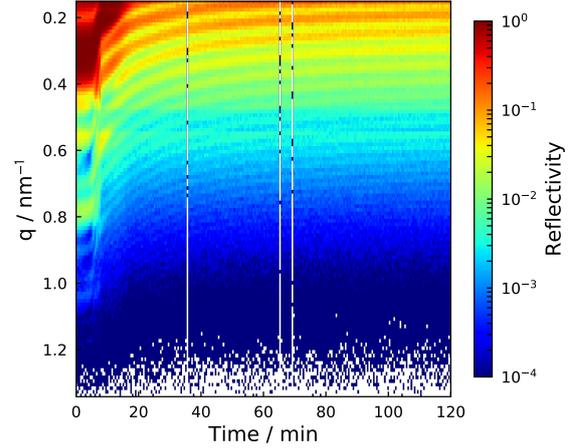


Figure 3: Time evolution of NR spectrum for a 5-layered stacked film of dPMMA and hPMMA in chloroform vapor.

dPMMA and chloroform are 6.88×10^{-4} and $2.38 \times 10^{-4} \text{ nm}^{-2}$, respectively. The absorption of chloroform molecules from vapor lowers the neutron refractive index contrast between the air and the dPMMA film, resulting in the decrease of the reflectivity. The decrease of the fringe gap indicates the increase of the film thickness. Thus, it was found that the PMMA film absorbs the chloroform molecules from the vapor phase and that the thickness increased by swelling of PMMA with chloroform.

The time evolution of the NR spectrum for the 5-layered dPMMA/hPMMA film is shown in Figure 3. At the initial state, the peaks at 0.55 and 0.80 nm^{-1} are found in the NR spectrum, which are assigned to the correlation of the thickness of the 20-nm-thick layers of dPMMA and hPMMA. Moreover, a narrow fringe pattern attributed to the total thickness is also observed. After the annealing time of 18 min, the peaks for the dPMMA/hPMMA layer disappeared and only the correlation signal from the total thickness is seen in the NR spectrum. This indicates that the layered structure of dPMMA and hPMMA collapsed by the inter-diffusion of the PMMA chains.

4. Conclusion

The *in situ* NR measurement revealed that the structure relaxation of a PMMA thin films in an solvent annealing process in chloroform vapor completed in 20 min by the inter-diffusion of the polymer chain. The quantitative relaxation dynamics will be discussed from the time evolution of the SLD distribution for each component by the detailed analysis of the NR spectra.