

Aggregation Structure and Dynamics of Polymers at the Interface with Water I: Analysis of Aggregation Structure by Neutron Reflectivity

Hironori Atarashi(1), Toshihiko Nagamura(1), Masahiro Hino(2), Keiji Tanaka(1)

1. *Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan,* 2.

Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-0494, Japan

Recently, a microwave treatment has been widely adopted for polymer synthesis because the treatment accelerates the movement of reactants in the system. The advantage of the treatment is not only shortening of the reaction time but also easy controlling of the yield and tacticity. However, it seems to us that the effectiveness of the microwave treatment on time evolution of aggregation states in polymer solids has not been discussed yet. In this study, we examined the microwave effect on interfacial evolution of polystyrene (dPS) bilayers with the aid of neutron reflectivity (NR) so that acceleration of chain diffusion by microwave can be discussed.

Monodisperse PS and deuterated PS (dPS) were used as samples. Molecular weights of PS and dPS were 87k and 80k, respectively. A dPS film was prepared on a silicon (Si) substrate with a native oxide layer by a spin-coating method. And, a PS film, which was independently spin-coated on a glass substrate, was mounted onto the dPS film by a floating method. Each film thickness was approximately 50 nm. The PS/dPS films so-prepared were dried under vacuum for 24 h at room temperature, and microwave with the power of 150 W was irradiated on them under the ambient atmosphere for 1.5 min and 3 min. Then, the specimens were applied to NR measurements using MINE2 spectrometer.

Figure 1 (a) shows the NR profiles for the PS/dPS bilayer films before and after the microwave treatment. The open symbols denote experimental data and solid lines show best-fitting curves calculated on the basis of the model scattering length density (b/V) profiles shown in the panel (b) of Figure 1. The interface between PS and dPS layers before the treatment was sharp.

The width is basically arisen from the surface roughness of the original PS and/or dPS film/s. On the other hand, once the bilayer was treated by microwave, the interface disappeared and the (b/V) value in the internal region became $3.72 \times 10^{-4} \text{ nm}^{-2}$, which was almost the middle of the (b/V) values for PS and dPS. This means that PS and dPS chains interdiffused each other, resulting in the formation of homogenous phase in the film. The (b/V) profiles treated for 1.5 min and 3 min were almost the same. Thus, chain interdiffusion in the bilayer reached a quasi-equilibrium state even by the 1.5 min.-treatment. Interestingly, the (b/V) value was higher near the substrate interface than in the interior region. This makes it clear that the dPS component was enriched at the substrate interface in the film being in a quasi-equilibrium state. The detail mechanism of how the treatment affects on chain diffusion, especially, a thermal effect induced by surrounding substance, will be reported in the near future.

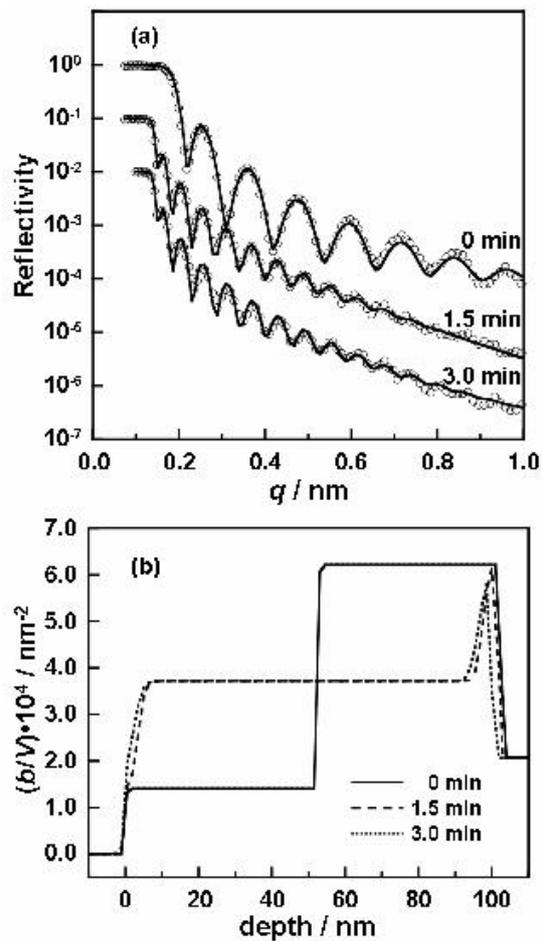


Fig. 1. Figure 1 (a) Neutron reflectivity for a PS/dPS film treated by microwave for 0, 1.5, and 3 min. The scattering length density profiles is shown in (b). For clarity, each data is off-set by a decade.