Diffusion of Cyclic / Linear Polystyrenes Studied by *in-situ* Neutron Reflectivity Measurements

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Much attention has been paid to physical properties of cyclic polymers including chain dimension in solution and in bulk, glass transition temperatures, viscoelasticity, etc. In particular, diffusion of cyclic polymers is one of the most attractive subjects of polymer dynamics since chain ends play an important role for diffusion of linear polymers. We have previously demonstrated that interdiffusion of cyclic polystyrene(c-hPS)/cyclic deuterated polystyrene(c-dPS) is faster than that of linear polystyrene(l-hPS)/linear deuterated polystyrene(l-dPS) at a same molecular weight based on dynamic secondary ion mass spectroscopy (DSIMS) in conjunction with neutron reflectivity (NR) measurements. In this paper, interdiffusion of l-hPS/c-dPS was examined by time-resolved neutron reflectivity measurements.

Cyclic deuterated polystyrene, C, with M_w of 117k and High-molecular-weight linear polystyrene, L_h, with M_w of 427k were used. The L_h/C bilayer films were prepared by a floating technique onto silicon wafers. Neutron reflectivity, NR, measurements were conducted using SPEAR reflectometer with high temperature cell for interdiffusion experiments. The temperature of the cell was fixed at 395 K, which is above the glass transition temperatures of the polymers. All reflectivity datasets were fitted using the Motofit program.

Figure 1(a) shows the scattering vector, q, dependence of NR of L_h/C bilayer film annealed at 395 K as a function of annealing time. Experimental datasets were represented by open circles, while the solid lines denote best-fit calculated reflectivities to the experimental data based on the model scattering length density, (b/V), profiles as shown in Figure 1(b). Since the calculated curves are in good accordance with the experimental data, it can be conceived that the model (b/V) profiles well represent the composition profiles in the film along normal to the surface. The L_h/C interface shifted toward L_h side with increasing time. This means that fluxes of L_h across the interface is much larger than that of C. These results clearly indicate that cyclic polymers are hard to diffuse into the entanglement media formed by linear polymers.

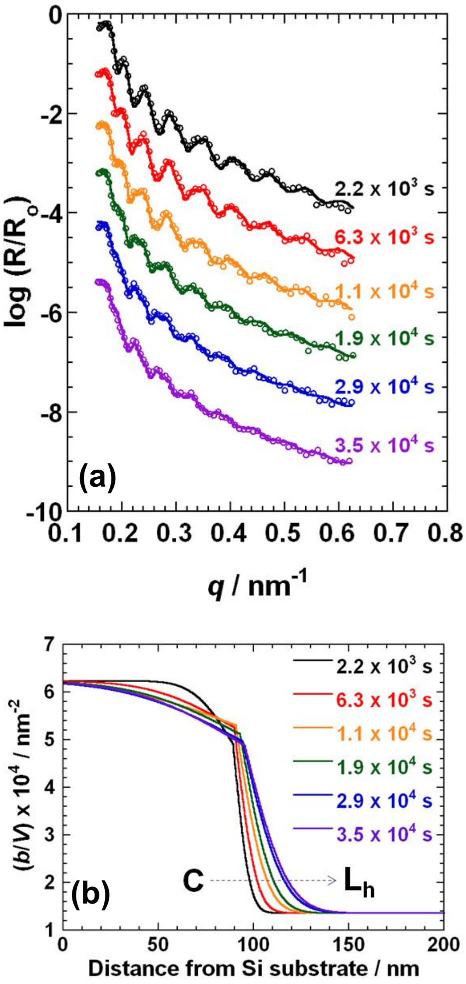

Figure 1. (a) NR curves of L_h/C bilayer film annealed at 395 K as a function of annealing time. (b) Model scattering length density profiles of the bilayer film.