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Comparison of Interdiffusion Behavior between Cyclic and Linear Polystyrenes with High Molecular Weights

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Much attention has been paid to physical properties of cyclic polymers, including chain dimension in solution[1−5] and in bulk,[5−8] glass transition temperatures,[9−12] viscoelasticity,[12−14] and phase-separated structures of cyclic diblock copolymers.[15] In particular, diffusion of cyclic polymers having no chain ends is one of the most attractive subjects of polymer dynamics since chain ends play an important role for diffusion of linear polymers. It is well accepted that diffusion of linear polymers with a relatively high molecular weight can be described within a framework of the reptation theories proposed by de Gennes[16] and Doi and Edwards.[17] On the basis of these theories, a polymer chain starts moving from chain ends. Hence, cyclic polymers can never move in the original sense of the reptation theory. How cyclic chain can move in the melt is the original motivation of this work.

Since it is difficult to prepare cyclic polymers being sufficient for diffusion experiments, there exist few experimental reports on diffusion of cyclic polymers. Kramer et al. studied the tracer diffusion of cyclic polystyrene, c-hPS, into deuterated linear polystyrene, l-dPS, by forward recoil spectorometry.[18] They found not only the reptation and the constraint release processes but also the two additional diffusion processes for c-hPS: (1) restricted reptation for some fraction of c-hPS molecules, which is unthreaded by constraints of l-dPS matrix; (2) constrained c-hPS diffusion, in which some fraction of c-hPS threaded once through linear chain matrix diffuses along this linear media. By these two additional diffusion processes for cyclic polymers, the motion of cyclic chains were slower than that of linear chains. However, these studies have merely revealed how cyclic polymers move in the entangled media. Besides, von Meerwall et al. reported that cyclic alkanes at carbon numbers of 6−16 diffuse slower than the corresponding linear ones based on pulsed gradient spin-echo nuclear magnetic resonance and simulation.[19,20] This result can be explained in terms of higher densities of cyclic alkanes than linear ones induced by absence of chain ends with their free volume contribution. The effect of the difference in the densities on diffusion is expected to become negligible with the molecular weight increase, and then, the other factors determining diffusion are remarkable. Hence, it is important to clarify the interdiffusion of cyclic polymers at high molecular weight, especially at the entanglement regime. In this paper, we first demonstrate that interdiffusion of c-PS is faster than that of l-PS at much higher molecular weight than the critical entanglement molecular weight, M_c, for l-PS based on dynamic secondary ion mass spectroscopy (DSIMS) in conjunction with neutron reflectivity (NR) measurements.

Polymers used in this study are monodisperse cyclic and linear PSs (c-hPS, l-hPS) and those deuterated counterparts (c-dPS, l-dPS). Purity of c-PSs is higher than 95% based on liquid chromatography at the critical condition.[21,22] Weight-averaged molecular weights, M_ws, for c-hPS, c-dPS, l-hPS, and l-dPS were evaluated by multiangle laser light scattering, and their values are 109K, 117K, 115K, and 127K, respectively, which are much larger than the M_c of ca. 30K for l-PS. (l-hPS/l-dPS) and (c-hPS/c-dPS) bilayer and (l-hPS/c-hPS/c-dPS) trilayer films were prepared by the floating technique, which has been described in detail elsewhere.[23,24] Time evolution of interfacial thickness with annealing was evaluated by NR and DSIMS. The details of experimental procedures are described in the Supporting Information.

Figure 1 shows NR profiles for (a) (l-hPS/c-hPS/c-dPS) trilayer and (b) (l-hPS/l-dPS) bilayer films as a function of the reduced annealing time, *t*, at 120 °C. Experimental data sets are represented by symbols, while solid curves denote the best-fit calculated reflectivities to the experimental data based on the model scattering length density (b/V) profiles. Parts c and d of Figure 1 show the best-fit (b/V) profiles for the (c-hPS/c-dPS) and (l-hPS/l-dPS) interfaces, respectively. The calculated (b/V) values for dPS and hPS are 6.46×10^{-4} and 1.41×10^{-4} nm^{-2}, respectively, using the scattering lengths per monomeric units and bulk densities of these polymers. Since the calculated curves are in good agreement 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 interface. It should be noted that broadening of the (c-hPS/c-dPS) interface takes place much more rapidly than that of corresponding linear ones, meaning that c-PS diffuses much faster than l-PS.

Figure 2 represents double-logarithmic plots of time evolution of interfacial thicknesses at the (c-hPS/c-dPS) and (l-hPS/l-dPS) interfaces. Both thicknesses of (c-hPS/c-dPS) and (l-hPS/l-dPS) interfaces increase with increasing *t* at 120 °C, and that of (c-hPS/c-dPS) bilayer films is much higher than that of (l-hPS/l-dPS) ones at any given *t*. This means again that diffusion of c-PS is much faster than that of l-PS. For (l-hPS/l-dPS) bilayer films, interfacial thickness is proportional to $t^{0.22}$ at shorter time, while it is proportional to $t^{0.52}$ at longer time. The crossover appears at around $t \sim 6 \times 10^3$ s, which agrees well with the reptation time, τ_d, calculated to be 4.0×10^3 s for l-PS with M_w of 115K at 120 °C.[17,26] Previous studies on interdiffusion revealed that interfacial thickness evolves with $t^{1/4}$ at $t < \tau_d$, whereas it increases with $t^{1/2}$ at $t > \tau_d$.[25,26] Our result is in good agreement with previous results, and it can be understood by taking into account of two time regimes of diffusion, that is, segmental diffusion at $t < \tau_d$ and conventional Fickian diffusion of whole chain at $t > \tau_d$, respectively. On the other hand, for the (c-hPS/c-dPS) interface, an increase of interfacial thickness is initially proportional to $t^{0.19}$, while it is proportional to $t^{0.48}$

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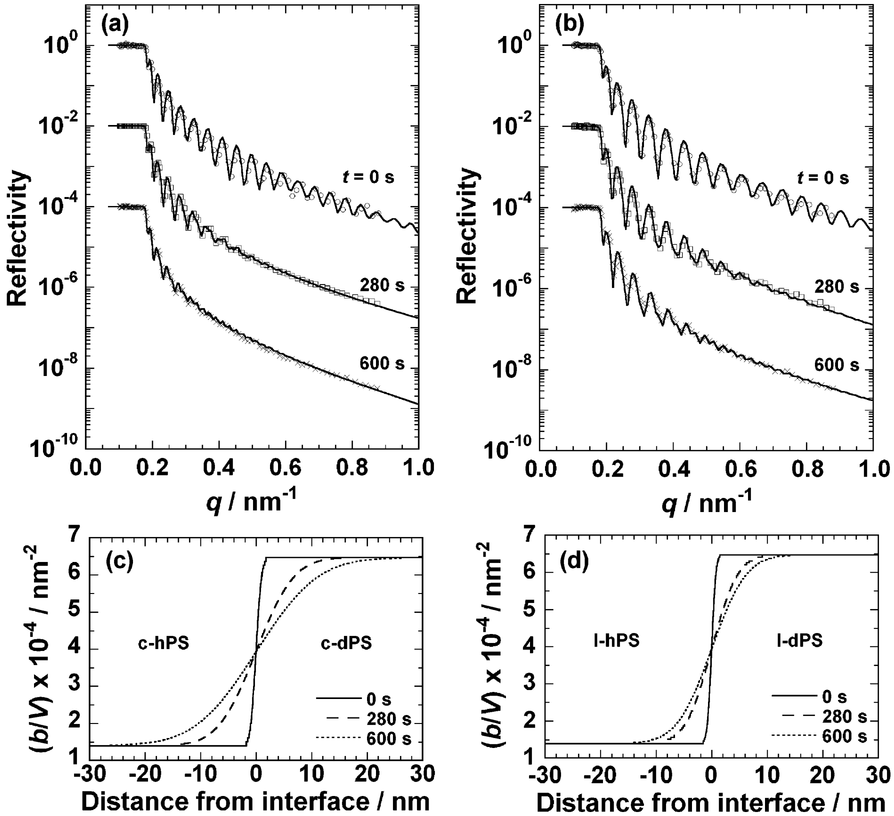

Figure 1. Neutron reflectivity profiles for (a) (l-hPS/c-hPS/c-dPS) trilayer and (b) (l-hPS/l-dPS) bilayer films with various annealing times. Symbols are experimental values, and solid lines are calculated ones from scattering length density profiles for (c) (c-hPS/c-dPS) and (d) (l-hPS/l-dPS) interfaces.

after $t \sim 3 \times 10^3$ s. Although Fickian diffusion clearly occurs at $t > 3 \times 10^3$ s, some sort of diffusion over fairly long distance is observed at the shorter time clearly. In general, displacement of center of mass for linear polymer is an order of chain dimension, R_g ($\sim$9 nm), at $t < \tau_d$. In this case, however, interfacial thickness for the (c-hPS/c-dPS) interface evolves with $t^{0.19}$ even though it reaches to $2R_g$. This result might imply that there exist some constraints for c-PS, but its spatial scale must be larger than the entanglement network for corresponding linear chain. Molecular weight dependence of viscoelastic properties for c-PS will give us the answer to this issue. A more conclusive study based on this point of view will be reported shortly.

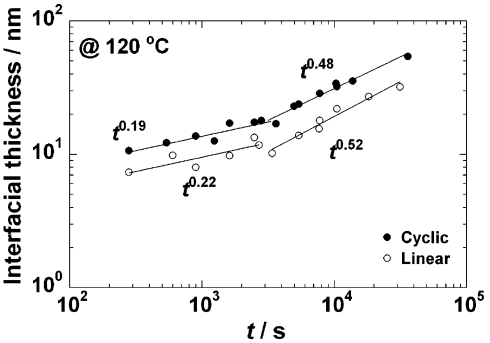

Figure 2. Time evolution of interfacial thicknesses of (c-hPS/c-dPS) and (l-hPS/l-dPS) interfaces.

For more quantitative discussion, diffusion coefficients, Ds, at sufficiently longer time than 4×10^3 s, which is τ_d for l-PS, were deduced for l-PS and c-PS from depth profiles of D$^-$ for DSIMS and (b/V) profiles near the (hPS/dPS) bilayer interfaces. The concentration profile $C(z')$ of D$^-$ along the direction normal to the surface is give by[27]

$$C(z') = 0.5\left[1 - \mathrm{erf}\left(\frac{z'}{\sqrt{4Dt}}\right)\right] \tag{1}$$

where z' is the distance from the center of interface. However, the general DSIMS profiles obtained in experiments are convoluted with the instrument functions. The apparent concentration profile can be expressed as[27]

$$C_{\mathrm{app}}(z') = 0.5\left[1 - \mathrm{erf}\left(\frac{z'}{\sqrt{a^2 + 4Dt}}\right)\right] \tag{2}$$

where a is the apparent broadening factor; our instrument function of 8.8 nm was used for the a.[28] The D value for l-PS, D_l, evaluated using eq 2 is $(4.9 \pm 1.8) \times 10^{-17}$ cm^2/s, and its value is in reasonably good agreement with the estimated value of 6.3×10^{-17} cm^2/s from the previous report based on an empirical equation.[29] On the other hand, the D value for cyclic one, D_c, is $(1.1 \pm 0.1) \times 10^{-16}$ cm^2/s, and hence it has been found to be 2.2 times larger than D_l. More rapid diffusion of c-PS than l-PS at high molecular weight is in contrast to the case of the low molecular weight alkanes.[20] This means that mobility of cyclic molecules is strongly affected by molecular weight, therefore, the D_c/D_l ratio should be dependent on the molecular weight. A more conclusive work will be reported in the near future.

In this Communication, we have compared time evolution of thicknesses for (c-hPS/c-dPS) and (l-hPS/l-dPS) interfaces having nearly the same molecular weights which are much higher than M_c. The thickness of the (c-hPS/c-dPS) interface is larger than that of the (l-hPS/l-dPS) one at any given time, and D_c is approximately twice as large as D_l at time longer than the reptation time for l-PS. These results clearly indicate that diffusion of the cyclic PS is much faster than that of the corresponding linear one.

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Supporting Information Available: Experimental procedure and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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