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Short-Time Interdiffusion at Polymer Interfaces

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Understanding the dynamics of entangled polymer chains in the melt is of great fundamental interest as well as practical importance. In the last 20 years, the focus has been on the "reptation" model which was proposed by de Gennes[1] and later developed by Doi and Edwards.[2] The reptation model postulates that individual chains, constrained by their neighbors, move primarily along their own contours in a snakelike fashion which requires the chain ends to lead the chain centers. Even though the literature is replete[3] with experiments designed to verify this phenomenologically simple theory, its validity remains a puzzle. To mention a few examples, the zero-shear melt viscosity of linear polymers (η) scales with the molecular weight (M) as $\eta \sim M^{3.4}$,[4] instead of $\eta \sim M^3$ as predicted by the reptation model. In contrast, the reptation model's prediction for the diffusion coefficient D, of a probe chain in a matrix of molecular weight P, as $D \sim M^{-2}P^0$ has been fairly well established.[3,5,6] Reptation cannot account for a similar dependence of viscosity on the molecular weight of polymer rings as for linear chains,[7] but it can correctly explain the slower relaxation of star polymers as compared to the linear chains.[8] Though this subject has also been investigated through computer simulations,[9-11] a definitive statement regarding the validity of the model has been missing as the current status of computers prohibits the accurate simulation of a dense melt of sufficiently high molecular weight to accurately probe the reptation dynamics.

Previous studies[6,12,13] using secondary ion mass spectroscopy (SIMS) and neutron reflection have shown that only for times in excess of the reptation time τ_d can classical Fickian profiles be used to describe the interdiffusion of polymers across an interface. These studies also show that the average monomer diffusion depth $X(t)$ behaves as $X(t) \sim t^{1/4}$ at $t < \tau_d$ and $X(t) \sim t^{1/2}$ at $t > \tau_d$. Among the few experiments done on the microscopic state of the system, Richter et al.[14] using neutron spin echo found a marked decrease in the intermediate dynamic structure factor at approximately the crossover time τ_e from unrestricted Rouse behavior to restricted behavior. This, of course, is supportive of the existence of entanglements or a "tube" that impedes the later motion of the chain. However, it has not yet been possible to measure the time-dependent correlation function beyond τ_e. Using fluorescently labeled DNA molecules (ca. 100 μm long) with a 1-μm latex bead attached to one end, Perkins et al.[15] were able to visually observe the retraction of a single stretched (draw ratio up to about 4) DNA molecule in an entangled solution of other DNA molecules. They observed that the molecule relaxed along a path defined by its own contour. Such studies provide additional support for the existence of topological constraints and the Rouse-like retraction dynamics of a chain along its own length but do not confirm reptation dynamics. In this paper, we present the results of neutron reflectivity experiments designed to examine the motion of polymer chains at $t < \tau_d$ and at penetration depths $X < R_g$ (radius of gyration).

We report the results of interdiffusion between thin film layers of polystyrene triblocks. These polymers are symmetric triblocks composed of segments of polystyrene-d_8 (dPS) and (normal) polystyrene-h_8 (PS). In one material (DHD), the composition is 25/50/25 by weight dPS/PS/dPS. In the HDH polymer, the complementary structure is 25/50/25 by weight PS/dPS/PS. The molecular weight and the amount of deuteration were designed to be equal in both the layers such that initially there was no variation of concentration across the HDH–DHD interface. Thus, with the HDH/DHD matching pairs, if the chain ends and the chain centers diffuse at the same rate, no variation in the concentration of the H or D segments across the interface will be found. However, if anisotropic motion of the chain occurs as in reptation, then the chain ends will diffuse across the interface first, thus enriching the HDH layer by dPS and the DHD layer by PS.

Interdiffusion of HDH/DHD matching pairs with reptation dynamics creates a ripple in the concentration profile as shown in Figure 1. The amplitude of this ripple increases and reaches a maximum at times on the order of $\tau_d/4$ and then decreases. These profiles were obtained by simulating interdiffusion between random-walk chains at the HDH–DHD interface. The simulated chains were initially constrained by the interface and interdiffused by reptating on a two-dimensional lattice. The diffusion process was studied up to times greater than the reptation time τ_d. Complete details of this procedure are being published separately.[16] The growth and the decay of the concentration ripple will yield unambiguous information about the chain dynamics at the polymer interface. The ripple in the concentration profile was recently observed by SIMS.[17] The enhanced resolution of neutron reflectivity, 0.5–1 nm as compared to 5–10 nm for SIMS, makes it possible to better quantify the detailed profile and compare with computer simulations.

HDH and DHD triblocks were anionically synthesized using *sec*-butyllithium initiator and dichlorodimethylsilane as the coupling agent. Their (near-monodisperse) molecular weights were 245 000 and 225 000, respectively. The percent deuteration of the two polymers was measured from neutron reflectivity measurements on thin films of the HDH and DHD polymers and found to be about 51% (HDH) and 42% (DHD). For the HDH/DHD bilayer interdiffusion experiments, a thin film (~1500 Å) of DHD was first spin-coated onto a silicon wafer and annealed under vacuum at 170 °C for 24 h. It should be noted that these experiments indicated no chain end, or deuterated block segregation to the surface. Therefore, the sample composition was uniform at the beginning of these experiments. The top layer of HDH (~750 Å) was spun onto a precleaned glass slide and floated onto water before being deposited on the bottom DHD layer. The thickness of each layer was measured by ellipsometry. The HDH/DHD bilayers were then annealed in vacuum at ~70 °C to remove the water entrapped at the interface. The interdiffusion was studied at an annealing temperature of 118 °C for times ranging from 10 to 2340 min. The reptation time was determined from published diffusion

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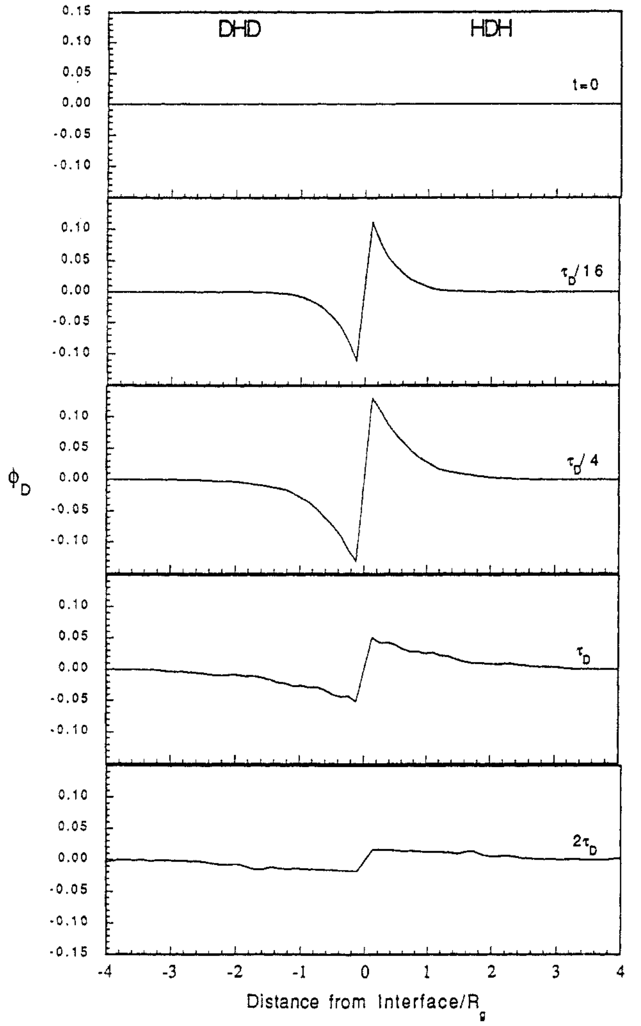

Figure 1. Excess concentration profiles obtained from computer simulation of interdiffusion between HDH and DHD layers of equal deuteration.[15]

data[5,6] as the time required by the chain to diffuse a distance equal to its radius of gyration R_g, as $\tau_d = 2R_g^2/\pi^2 D$,[1] where the self-diffusion coefficient $D = 2.93 \times 10^{-18}$ cm^2/s[5] and $R_g = 127$ Å. Using the latter relation for τ_d and the formulas given by Doi and Edwards[2] for the Rouse relaxation time, $\tau_{RO} \sim M^2$, the characteristic relaxation times were estimated to be $\tau_d \sim 1860$ min and $\tau_{RO} \sim 21$ min. The neutron reflection measurements were made at room temperature, following the constant temperature anneal at 118 °C. The experimental geometry used on the POSY-II reflectometer at the Intense Pulse Neutron Source at the Argonne National Laboratory has been described elsewhere.[18] Published methods of fitting the reflectivity data with model profiles were used.[19]

Reflectivity profiles at several annealing times are shown in Figure 2. Reflectivity, R, is plotted as a function of the neutron momentum normal to the surface, $k_{z,0} = 2\pi \sin(\theta/\lambda)$, where θ is the grazing angle of incidence and λ is the wavelength. It is instructive to analyze the raw profiles. Two types of oscillations are apparent: those with the higher frequency relate to the interference of the neutrons reflected from the air surface and the silicon substrate (e.g., at 10 min), while those with the low frequency (e.g., at 450 min) represent the interference between the surface and the HDH–DHD interface. The amplitudes of the latter oscillations, particularly for $0.01\ \text{Å}^{-1} < k_{z,0} < 0.02\ \text{Å}^{-1}$, increase until 450 min and then decrease with further annealing. This amplitude depends on the contrast at the polymer–polymer interface, i.e., the difference in scattering length density of the two layers at the interface. Therefore, it is evident that the HDH layer becomes enriched with D and DHD layer with H.

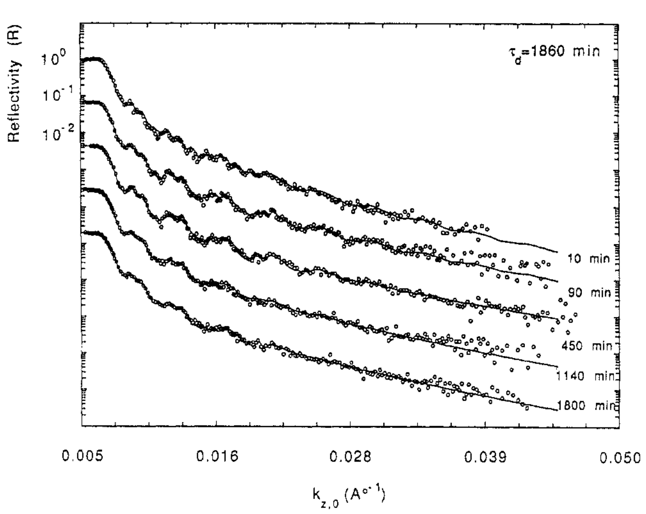

Figure 2. Reflectivity data (offset on the vertical axis) for the 230K HDH/DHD layers at annealing times between 10 and 1800 min. The solid lines are fits to the concentration profiles described in the text and shown in Figure 3.

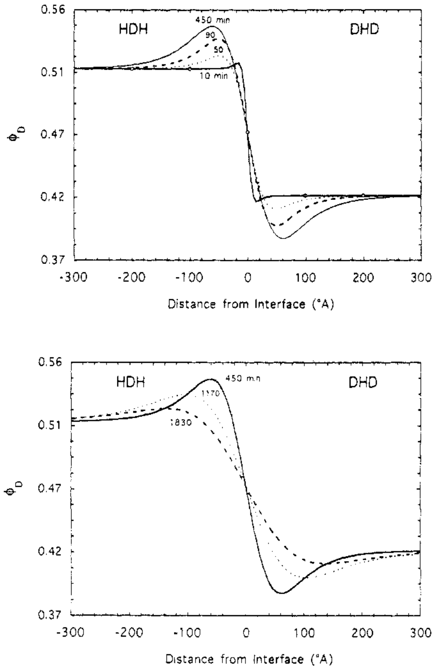

Figure 3. Concentration profiles obtained from the neutron reflection experiment (Figure 2) are shown at several annealing times. Top: profiles from 10 to 450 min. Bottom: profiles from 450 to 1830 min. $\tau_{RO} \approx 21$ min the $\tau_d \approx 1860$ min.

The best fits to the reflectivity profiles (shown as the solid lines in Figure 2) were obtained using the scattering length density profiles shown in Figure 3. The only independent parameters required to fit the reflectivity profiles were the amplitude and width of the ripple. A Gaussian convolution function was used to account for the mismatch in the deuteration level of the two polymers. In Figure 3 (top), the amplitude or the height of the ripple which characterizes the enrichment at the interface increases to a maximum value at 450 min (which is close to $\tau_d/4$) and then decays [Figure 3 (bottom)]. A quantitative comparison of the experimental height of the ripple contribution with that predicted from the reptation model (from Figure 1) is given in Figure 4 as a function of annealing time. The time dependence of the ripple peak

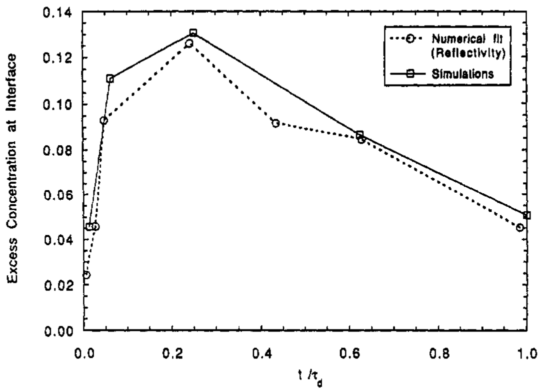

Figure 4. Comparison of the excess concentration peak $C(0,t)$ found from reptation simulations (Figure 1) and neutron reflection analyses of HDH–DHD interfaces.

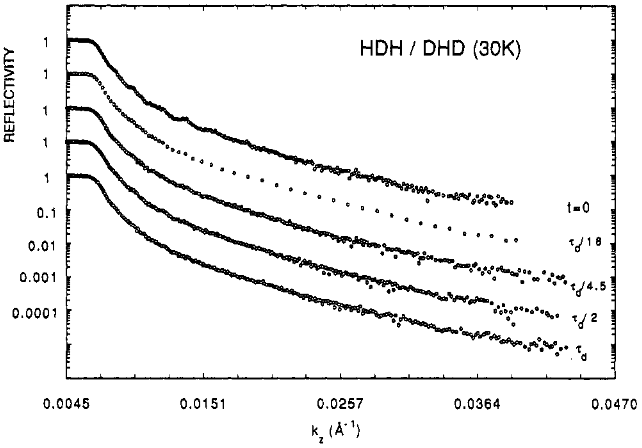

Figure 5. Reflectivity data (offset on vertical axis) for the 30K HDH/DHD layers at annealing times 0–τ_d, at 107 °C. The initial deuteration levels were 49/51% which accounts for the small oscillations at $t = 0$ which die out with annealing.

$C(0,t)$ is predicted to behave approximately as $C(0,t) \approx {}^1/_4(t/\tau_d)^{1/2}$, for $t \leq \tau_d/4$.[20] Its maximum value is independent of molecular weight and occurs at $\tau_d/4$ such that $C(0,\tau_d/4) \approx 0.125$, as observed in Figure 4.

It is important to note that similar experiments performed on HDH/DHD with molecular weights of 30 000 (Figure 5) and 50 000 do not exhibit any ripples (of H or D). In Figure 5, the top 30K HDH layer thickness was 800 Å. However, at all annealing times, the interface remained invisible to neutrons and we failed to see the characteristic oscillations corresponding to the ripple in the concentration profile (as noted in Figure 2 for the 230K sample). For these polymers which have molecular weights close to the critical entanglement molecular weight of polystyrene (30 000), the dominant mode of diffusion is via Rouse type motions. Consequently, the absence of the ripple implies that Rouse motion cannot be used to explain our experimental observations. This result is further supported by computer simulations of HDH/DHD chains with Rouse dynamics where only very weak ripples are found.[16] These Rouse ripples, if they exist, may not appear above the noise level in our low molecular weight experiments. Also, the simulated Rouse concentration profiles were not observed in our experiments.

Given the correspondence of the growth and persistence of the ripple at the interface with the times calculated from the reptation model, these results favor reptation as the governing mechanism of polymer–polymer interdiffusion. Alternate explanations based on other dynamic models are being further investigated. The molecular weight dependence of the ripple evolution contains much additional information and is currently being analyzed.[21,22]

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