Dynamics of Mixing between Partially Miscible Polymers

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We have measured the time dependence of interface formation between two polymers, below their critical temperature for phase separation, using the $^2H(^3He,^4He)^1H$ nuclear reaction as a direct profiling technique. We find that the width of the interface initially increases with time as t^a, where the exponent $a = 0.34 \pm 0.06$ is significantly lower than its value of 0.5 for free diffusion.

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While mutual diffusion between miscible species is well understood,[1] little is known about the kinetics of diffusional mixing between immiscible or partly miscible materials. This is of particular relevance, and has both basic and practical implications, for the case of macro-molecules, since most binary polymer pairs exhibit little compatibility at accessible temperatures.[2] This incom-patibility stems from a very low combinational entropy of mixing (which scales inversely with the degree of po-lymerization N) together with interactions between the different monomers which are generally unfavorable.[3] Interpenetration across an interface between two poly-mers which are not fully miscible is limited to a region of finite width $w_i(\infty)$ at long times;[4,5] this is in contrast to the classical diffusion-controlled extent of interpenetra-tion,[6]

$$w(t) = \text{const} \times (Dt)^{1/2},\qquad(1)$$

where the width of the interface $w(t)$ between miscible species is controlled by their mutual diffusion coefficient D and increases indefinitely with time t. We report here the experimental determination of mixing kinetics at the interface between two bulk polymers at temperatures below the critical point for phase separation, i.e., in a re-gion of the phase diagram where the polymers are only partly miscible. We find that the initial broadening of the interface follows a power law quite different from the classical $\sqrt{t}$ relation, while at long times the interface is characterized by a mixing zone of finite extent as expect-ed, in accord with earlier observations.[7]

The polymers studied were deuterated polystyrene (dPS) of molecular weight $M = 1.03 \times 10^6$, and its pro-tonated analog hPS, with $M = 2.89 \times 10^6$. This binary mixture is known to have an upper critical solution tem-perature T_c, resulting from weak repulsive interactions between the deuterated and protonated monomers.[8] For the molecular weights in this investigation T_c is evalu-ated as 198 °C, based on neutron-scattering studies of dPS/hPS mixtures.[8] The composition of the polymer samples on the two sides of the interface was adjusted to correspond to that of the coexisting[9] phases for this binary mixture at the respective temperatures of the ex-periments. This was done in order to minimize bulk

transport across the interface during the interfacial-broadening process. A sharp interface was created by spin casting an hPS/dPS[9] film from toluene onto a high-ly polished silicon wafer. A dPS film[10] was similarly cast onto a glass slide, floated onto a water surface, and laid on top of the hPS layer; the bilayers were then an-nealed for different times t in a vacuum oven. Experi-ments were carried out at four different temperatures $T < T_c$ in the range 140–170 °C (well above the glass transition temperature of 100 °C for polystyrene).

The broadening of the interface was monitored by nuclear-reaction analysis. The details of this technique are described in detail elsewhere.[7,11] In essence, the nu-clear reaction $^2H(^3He,^4He)^1H$ is employed in a direct profiling technique; a ^3He beam, produced by a Van de Graaff accelerator, undergoes a nuclear reaction with the ^2H nuclei of the deuterated species. The outcoming ^4He particles are measured at a forward angle of 30° to the incoming beam, and their energy spectrum contains in-formation on the depth at which they were emitted by the nuclear reaction. From this spectrum a concen-tration (ϕ) versus depth (z) profile of the deuterated species is constructed. This technique has a high intrin-sic spatial resolution which enables a clear determination
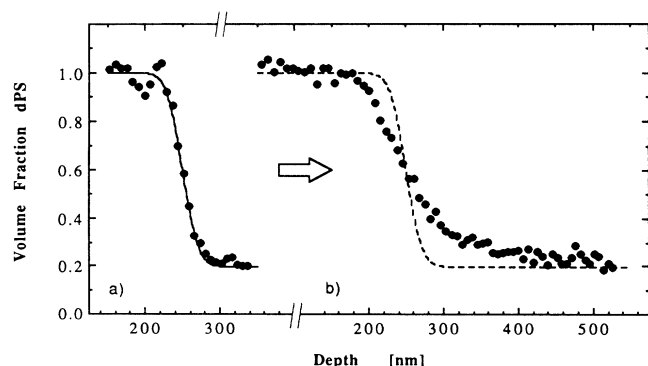

FIG. 1. Concentration-depth profiles of dPS-hPS bilayers in the interfacial region. (a) Unannealed; the solid line is a step function convoluted with a Gaussian of 21 nm HWHM. (b) Annealed for 4.92×10^4 s at $T = 150$ °C; the broken line corre-sponds to the unannealed profile in (a).
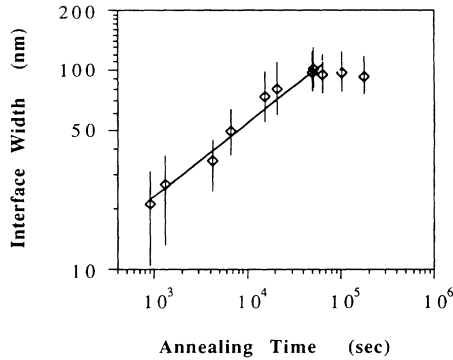
FIG. 2. Log-log plot of the variation with time of the interfacial width between coexisting hPS-dPS bilayers at an annealing temperature of 160 °C. The error bars reflect the uncertainty in determining the maximal slope of the composition profile at the interface. The solid line shows the interfacial width increasing as $w_i \propto t^a$, with $a = 0.36$.
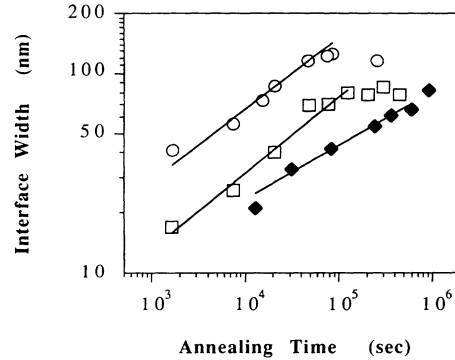

FIG. 3. Log-log plot of the variation with time of the interfacial width in coexisting hPS-dPS bilayers. The symbols are for annealing temperatures 140 °C ($\blacklozenge$), 150 °C ($\square$), and 170 °C ($\bigcirc$). The solid lines show the interfacial width increasing as $w_i \propto t^a$, with the values of a given in Table I.

of interfacial broadening within the spatial regimes of interest. Figure 1(a) shows the depth-concentration profile of the hPS/dPS interface prior to annealing, while Fig. 1(b) is a typical broadened profile, following annealing for a time $t = 4.92 \times 10^4$ s at $T = 150$ °C.

A quantitative measure for the interfacial broadening is the interfacial width w' defined as the inverse of the slope at the point of the interface where the composition profile $\phi(z)$ varies most rapidly:

$$w' = \tfrac{1}{2} (d\phi/dz)_{max}^{-1}. \qquad (2)$$

In our experiments, the maximum slope is determined by linear regression and the interfacial width is then corrected for the (small) instrumental broadening by quadratic subtraction to yield $w_i(t) = [w'(t)^2 - w'(0)^2]^{1/2}$.

Figure 2 shows the development with time of $w_i(t)$ at $T = 160$ °C, on a double-logarithmic plot. w_i increases at short times, and eventually levels off to a constant value (within error) at $t \geq 5 \times 10^4$ s. The initial variation of the interfacial width with time for $t < 5 \times 10^4$ s is well represented by the power-law relation (solid line, Fig. 2)

$$w_i(t) = \text{const} \times t^a, \qquad (3)$$

where $a = 0.36 \pm 0.06$. The scatter arises mainly from the uncertainty in determining the maximum slope[12] $(d\phi/dz)_{max}$. This power variation is significantly different from the free-diffusion $\sqrt{t}$ relation of Eq. (1). Earlier data[7] taken for interdiffusion in a similar dPS/hPS bilayer *above* the critical temperature (i.e., in conditions of unrestricted interpenetration) do show a clear $\sqrt{t}$ dependence of the interfacial width.

Figure 3 shows $w_i(t)$ for three additional temperatures, 140, 150, and 170 °C (all within ± 0.5 °C). The main features in all cases are similar to Fig. 2: a power-law-like increase at short times, leveling to a constant value of w_i at long times.[13] The solid lines are the linear

fits which yield the exponents a for the time development. Table I summarizes the results for the four temperatures, and we note that a is in all four cases significantly smaller than the exponent 0.5 for free interdiffusion.

While there exists a vast literature concerning kinetics of spinodal decomposition[5,14-16] (i.e., demixing of a homogeneous mixture into coexisting phases), there has to date been little theoretical consideration of the interpenetration dynamics between incompatible species. de Gennes[17] recently considered the mixing of two incompatible polymers with a weak segment-segment interaction $\chi k_B T$ (χ being the monomer-monomer interaction parameter and k_B the Boltzmann constant), which were yet far below their upper critical solution temperature, i.e., in the limit $\chi_c \ll \chi \ll 1$, where χ_c is the value of χ at the critical point for phase separation. In this limit the initial broadening of the interfacial profile was predicted to vary as a power law such as Eq. (3), but with $a = \tfrac{1}{4}$. A very recent mean-field approach[18] suggests that, closer to the critical temperature, the exponent may be between $\tfrac{1}{4}$ and $\tfrac{1}{2}$.

TABLE I. Values of the exponent a in the relation $w_i(t) = \text{const} \times t^a$ [Eq. (3) in text], at different temperatures T. The final column is the long-time limit of the interfacial width $w_i(t)$, as indicated by the plateaus in Figs. 2 and 3. For the annealing temperature $T = 140$ °C, a clearly marked plateau in $w_i'(t)$ was not indicated up to the longest diffusion times studied (Ref. 13).

T (°C)	a	$w_i(t \to \infty)$
140	0.27 ± 0.08	
150	0.38 ± 0.06	80 ± 14
160	0.36 ± 0.06	96 ± 12
170	0.36 ± 0.04	120 ± 14

The values of α experimentally determined in the present study, as summarized in Table I, have a mean value (taken over the four temperatures) $\alpha = 0.34 \pm 0.06$. It is of interest that at the lowest temperature (i.e., the one furthest below T_c) the value of $\alpha = 0.27 \pm 0.08$ is rather close to $\frac{1}{4}$, though within the scatter other exponents are possible. Further experimental work, in particular covering a greater temperature range $T < T_c$, will be necessary to ascertain the appropriate regimes in the phase diagram below the critical temperature and their corresponding exponents.

Finally, we note that the equilibrium values of w for long times (Table I) are in accord with our previous results[7] and with mean-field predictions:[5,7] The interfacial width tends to a constant value at long times,[13] which is an increasing function of the temperature (for $T < T_c$).

In summary, we have followed the broadening with time of an initially sharp interface between two coexisting, partially miscible polymer phases, using a high-resolution profiling method based on nuclear-reaction analysis. We find the interfacial width to increase with time t at short times as t^α, before reaching its equilibrium value at long times. Over the four temperatures studied the exponent α has a mean value of 0.34 ± 0.06, significantly lower than the classical exponent $\frac{1}{2}$ for freely interdiffusing species. Our results are in qualitative agreement with very recent models of the dynamics of mixing between partly compatible chains.

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[9]The coexisting compositions were evaluated from the Flory-Huggins mean-field model (Ref. 3) using the monomer interaction parameter χ for this binary pair determined from neutron scattering (Ref. 8).

[10]For this asymmetric hPS/dPS mixture, the composition of the dPS-rich phase at all temperatures used in our study was within a few percent (Ref. 7) of pure dPS: For this reason we used pure dPS for the top film at the four temperatures studied.

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[12]To do this the entire $\phi(z)$ profile is scanned piecewise and the maximal value of the slope determined. The size of the scanning "window" is varied to ensure an extremal value is obtained.

[13]For the lowest temperature, $140\,^{\circ}\mathrm{C}$, a plateau on the log-log plot of Fig. 3 is not clearly indicated within the annealing times used (up to ca. 10^6 s). The values of w_i at $T = 140\,^{\circ}\mathrm{C}$ for the two longest annealing times are 65 ± 15 and 80 ± 15 nm, comparable within the scatter to the saturation value $w_i(\infty) = 72 \pm 10$ nm indicated for $T = 140\,^{\circ}\mathrm{C}$ from the data of Ref. 7.

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