

## Dynamics of Interdiffusion at Interface between Partially Miscible Polymers

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We have studied the behavior of interdiffusion between partially miscible polymer pair from a theoretical viewpoint by applying the reptation model for collective interdiffusion and spinodal decomposition in polymer mixtures with different molecular weights. We find that our predictions agree well with the experiments of Klein and co-workers, where the exponent  $\alpha$  of the initial increase of interfacial width with time in  $t^\alpha$  is significantly lower than 0.5 for free diffusion.

### Introduction

Binary liquid mixtures of deuterated and protonated polymers are characterized by the upper critical solution temperature.<sup>1,2</sup> At temperatures lower than the critical point for miscibility, polymer mixtures will demix through the spinodal decomposition. Likewise, two isotopically different polymers in contact do not in general interdiffuse freely into each other. When the system is not far from the critical point, phase separation into two coexisting phases cannot be perfect and partial mixing via interdiffusion will occur between deuterated polymer and protonated polymer. The diffusion between the two different polymers in contact is not free in the sense of Fickian transport, and an interfacial zone of finite width  $W$  separates them at equilibrium. de Gennes<sup>3</sup> was the first to point out that because the combinatorial entropy of mixing of polymers is so small, scaling as  $N^{-1}$  where  $N$  is the degree of polymerization, the mutual diffusion of chemically dissimilar polymers will be dominated by the excess enthalpy and entropy of segment-segment mixing. Since  $N$  is large and interaction ( $N$  independent) between the different monomers are generally unfavorable, the driving force for mixing is very weak. Therefore, a relatively small positive Flory  $\chi$  parameter is sufficient to make the mixtures phase-separate. For a miscible polymer pair the interfacial width  $W$  increases with time  $t$  as  $W \sim (Dt)^{1/2}$ , where  $D$  is the mutual diffusion coefficient. Klein and co-workers have obtained the first *direct* measurement of time-dependent composition profiles at the interface between two *partially* miscible polymers  $A$  and  $B$  (deuterated and protonated polystyrenes).<sup>4,5</sup> They found that the initial broadening of the interface at the temperatures below the critical point for phase separation follows a power law quite different from the Fickian  $\sqrt{t}$  relation, while at long times the interface is characterized by a mixing zone of finite extent as expected, and the exponent  $\alpha = 0.34 \pm 0.06$  in  $t^\alpha$ , falling between 0.25 (the Cahn-Hilliard<sup>12</sup> term dominant) and 0.5 (Fickian characteristic), is significantly lower than its value of 0.5 for free diffusion.

We have studied the interdiffusion between partially miscible polymers with different molecular weights from a theoretical viewpoint.<sup>6</sup> By comparing our reptation model<sup>6</sup> with experiments of Klein and co-workers, we obtain good agree-

ment. Our model provides a *quantitative* analysis of Klein's experiments, which is different from the previous *semi-quantitative* analysis of polymer mixtures with *same* molecular weights.<sup>7</sup>

### Theory

We consider the interdiffusion between *pure* polymer  $A$  and *pure* polymer  $B$  with isotopically different segments. The dynamical diffusion equation<sup>6</sup> in terms of the rescaled variables is given by

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{2}{1+R+(R-1)\psi} \left( \left\langle 1 + \frac{1}{R} - \chi + \left( \frac{1}{R} - 1 \right) \psi + \chi \psi^2 \right\rangle \frac{\partial \psi}{\partial x} - \frac{\partial^3 \psi}{\partial x^3} \right) \right\} \quad (1)$$

where  $R (= N_B/N_A)$  represents the molecular weight ratio and  $N_A, N_B$  are the degrees of polymerization of polymers  $A$  and  $B$ , respectively. The length was scaled by the natural length  $K^{1/2}$  and the time was scaled with unit  $\tau = 2K/D_A$  which is on the order of the reptation time of a single chain in melt. The  $K (= N_A a^2)$  has the magnitude of square of the radius of gyration and  $a$  is the segment length of polymers  $A$  and  $B$ .  $D_A$  is of the magnitude of the self-diffusion coefficient<sup>6</sup> in entangled polymer melt. The composition variable was redefined as  $\psi = 2(\phi_A - 1/2)$  so that the order parameter  $\psi$  takes values between +1 (pure  $A$ ) and -1 (pure  $B$ ) as composition profile  $\phi_A$  drops from 1 to zero, and we also made a change of notation:  $N_A \chi \rightarrow \chi$  where  $\chi$  is the Flory parameter. After we have made a change of notation,  $\chi_c$  in the Flory-Huggins mean field model of polymer mixing is given by

$$\chi_c = \frac{(1 + \sqrt{R})^2}{2R} \quad (2)$$

In Eq. (2),  $\chi_c = 2$  for the symmetric case ( $R = 1$ ) and  $\chi_c = 1.24$  for  $R = 3.02$ .

Eq. (1) is a non-linear equation for  $\phi_A$ , and solving it generally requires numerical computation obtained by discretizing Eq. (1) with finite differences. The evolution of the bilayer system starting from the initial profile of a step function is described by application of the standard Crank-Nicholson method to update at every time step the profile

described by Eq. (1). We discretize  $\partial\psi(x, t)/\partial t$  as  $(\psi_i^{n+1} - \psi_i^n)/\Delta t$ ,  $\partial\psi(x, t)/\partial x$  as  $(\psi_i^n - \psi_{i-1}^n)/2\Delta x$ , and similarly for its higher spatial derivatives with  $\Delta t = 0.01$  and  $\Delta x = 0.5$ . The total grid points are 700, so that the total thickness is  $350 K^{1/2}$ . We take the initial interface of the bilayer system as  $300 \Delta x$  ( $\sim 150 K^{1/2}$ ). The boundary conditions to solve the above diffusion equation are  $\partial\psi(x, t)/\partial x = 0$  and  $\partial^3\psi(x, t)/\partial x^3 = 0$  at the outer two ends of the bilayer. Then, the system is allowed to evolve  $10^5$  time steps ( $\sim 10^3 \tau$ ) with an initial interfacial width of a reasonable magnitude as long as the boundary condition will remain valid.

The interfacial width  $W(t)$  defined as the inverse of the slope at the point of the interface where the composition profile  $\psi(x)$  varies most rapidly:

$$W(t) = \left[ \left( \frac{\partial\psi(x, t)}{\partial x} \right)_{\max}^2 - \left( \frac{\partial\psi(x-300\Delta x, t=0)}{\partial x} \right)^2 \right]^{1/2} \quad (3)$$

where  $W(t)$  is given in units of  $K^{1/2}$ .

Klein and co-workers<sup>4,5</sup> have determined the composition profiles at the interface between deuterated polystyrene, dPS (sample A,  $N_A = 9,196$ ) and protonated polystyrene, pPS (sample B,  $N_B = 27,788$ ), and then between deuterated polystyrene, dPS (sample A,  $N_A = 9,196$ ) and protonated polystyrene, pPS (sample C,  $N_C = 8,654$ ). In particular, interfacial broadening with elapse time was studied in detail. The studies by Bates and co-workers<sup>1,8</sup> have demonstrated that mixtures of deuterated and of protonated analogs of the same polymer are characterized by a small positive value of the interaction parameter  $\chi$ , resulting from slight difference between isotopically different segments. For mixtures of dPS and pPS this interaction varies with temperature as<sup>1,8</sup>

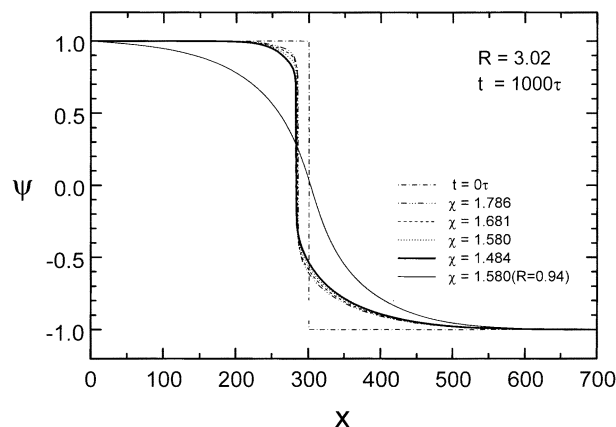
$$\chi = \{(0.20 \pm 0.01)/T - (2.9 \pm 0.4) \times 10^{-4}\} \times N_A \quad (4)$$

so that for the values  $N_A$  and  $N_B$  of Klein's polystyrene samples the critical temperature  $T_c$  for phase separation is predicted to be around  $200^\circ\text{C}$ . Klein and co-workers studied the interface at temperature *below* this critical point though still considerably above the glass transition temperature ( $T_g \cong 100^\circ\text{C}$ ) of the polymer,<sup>9</sup> that is, in conditions where the two polymers would demix spinodally.<sup>10</sup> Here, we compare our theoretical predictions with Klein's data in the same conditions as Klein's experiments.

## Results and Discussion

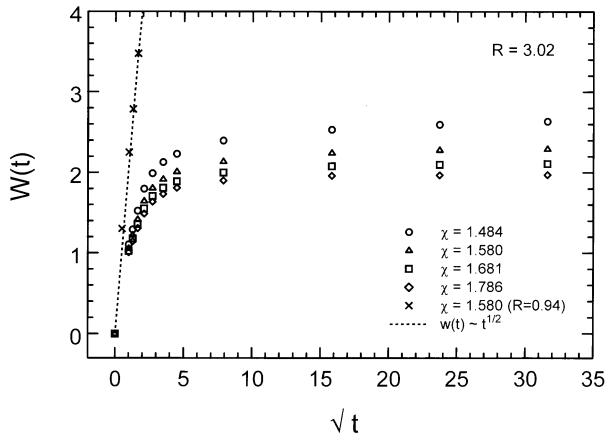
To quantify our analysis and to compare with experimental data,<sup>4,5</sup> we have considered two values of molecular weight ratio  $R = 3.02$  ( $-N_B/N_A$ ) and  $0.94$  ( $-N_C/N_A$ ), corresponding to the following two pairs of polystyrene samples:  $N_A = 9,196$  and  $N_B = 27,788$ ;  $N_A = 9,196$  and  $N_C = 8,654$ . For  $R = 3.02$  ( $\chi_c = 1.24$ ), four values of  $\chi = 1.786$  (at  $140^\circ\text{C}$ ),  $\chi = 1.681$  (at  $150^\circ\text{C}$ ),  $1.580$  (at  $160^\circ\text{C}$ ), and  $1.484$  (at  $170^\circ\text{C}$ ) are obtained by using Eq. (4), then  $\chi = 1.580$  (at  $160^\circ\text{C}$ ) for  $R = 0.94$  ( $\chi_c = 2.06$ ).

Figure 1 shows the composition profiles of polymer A for A/B diffusion couples ( $R = 3.02$ ) which were diffused at  $\chi =$

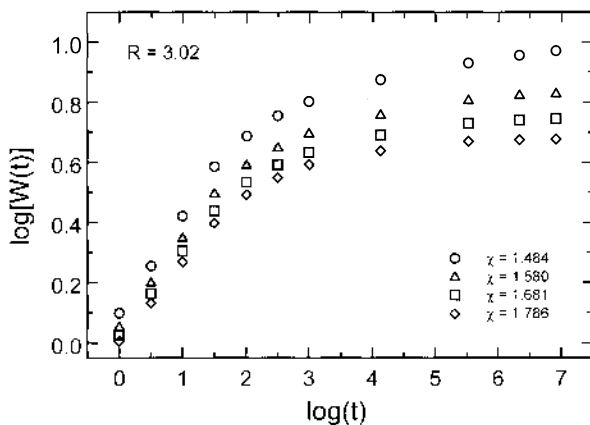


**Figure 1.** The composition profiles of  $\chi = 1.786$ ,  $\chi = 1.681$ ,  $\chi = 1.580$  and  $\chi = 1.484$  for  $R = 3.02$ , and  $\chi = 1.580$  for  $R = 0.94$  at  $t = 1000\tau$ . The time is expressed in units of  $\tau$  ( $= 2K/D_A$ ) and length in units of  $0.5K^{1/2}$ .

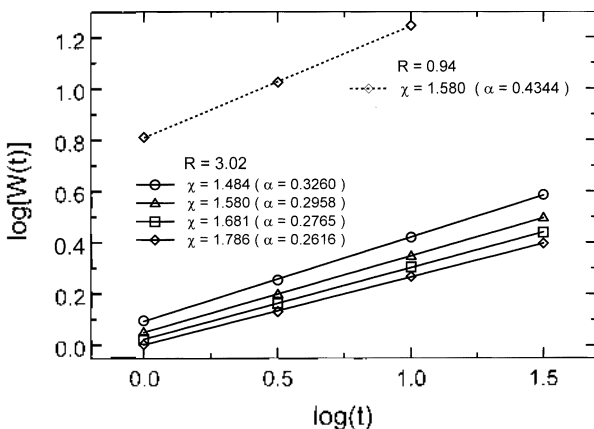
$1.786$ ,  $1.681$ ,  $1.580$ , and  $1.484$  for diffusion time  $\tau$  of  $1000t$ . The thin solid curve in Figure 1 represents the composition profile of polymer A for A/C system ( $R = 0.94$ ) for the same diffusion time. The time is expressed in units of  $\tau$  ( $= 2K/D_A$ ) and length in units of  $x$  ( $= 0.5 K^{1/2}$ ). The diffusion behavior for  $R = 3.02$  is asymmetric as we anticipated while almost symmetric for the case of  $R = 0.94$ . As we see in Figure 1, the lower molecular weight polymer A diffuses more deeply into the high molecular weight side of polymer B because of the entanglement effect. For  $R = 3.02$ , the lower  $\chi$  ( $=$  the higher temperature) from the critical point of  $\chi_c = 1.24$ , the faster polymer A diffuses. This is because mixtures of deuterated and protonated analogs of the same polymer are characterized by the upper critical solution temperature. The development of interface width  $W(t)$  with the square root of time  $t^{1/2}$  at different  $\chi$  values ( $=$  temperatures) higher than  $\chi_c$  is shown in Figure 2. The width initially increases with time but then levels off at a constant value. For  $R = 0.94$ , we see obviously the monotonic increase in the interface width expected for unrestricted diffusion, with no indication of leveling off at long times. The dotted line is plotted against  $W(t) \propto t^{1/2}$  scaling relation expected for the Fickian-type diffusion. Our theoretical predictions strongly resemble the Klein's data of Figure 2 in ref 4. Figure 3 shows natural log-log plots of the variation with time of the interface width in A/B system. The further away the critical point given by  $\chi_c = 1.24$ , *i.e.*, the larger  $\chi$ , the slower  $W(t)$  increases, which agrees well with Figure 2 and Figure 3 in ref 5. Since the curves are not straight lines throughout the time interval in Figure 3, power law such as  $W(t) \propto t^\alpha$  holds only for a certain initial period during the interdiffusion. The certain initial period of interdiffusion in Figure 3 where the power law is valid, is shown in detail in Figure 4. The solid lines in Figure 4 are the linear fits for  $R = 3.02$  and the dotted line is the linear fit for  $R = 0.94$ , whose slopes yield the scaling exponents  $\alpha$ . In the case of  $R = 3.02$ , the values of  $\alpha$  are  $0.3260$  ( $\chi = 1.484$ ),  $0.2958$  ( $\chi = 1.580$ ),  $0.2765$  ( $\chi = 1.681$ ), and  $0.2616$  ( $\chi = 1.786$ ). For  $R = 0.94$ , the value of  $\alpha$  is  $0.4344$  ( $\chi = 1.580$ ). The values of  $\alpha$  in all four cases of  $R = 3.02$  are



**Figure 2.** Interface width  $W(t)$  against the square root of time  $t^{1/2}$  for  $R = 3.02$  and  $R = 0.94$ . The units are the same as in Figure 1.



**Figure 3.** Natural log-log plot of variation with time of the interfacial width for  $R = 3.02$ .



**Figure 4.** Linear fits of the natural log-log plots of the interfacial width with time for  $R = 3.02$  (solid lines) and  $R = 0.94$  (dotted line) in the certain initial period of interdiffusion of Figure 3 where the power law is valid. Exponents  $\alpha$  are obtained from the slope

smaller than the 0.5 for the Fickian-type diffusion. We can see that the deeper in the two-phase region (*i.e.* the larger  $\chi$ ), the exponent  $\alpha$  is smaller than 0.5, but larger than 0.25. A mean-field approach<sup>11</sup> suggests that, closer to the critical temperature, the exponent may be between 1/4 and 1/2.

**Table 1.** Klein's and our values of the exponents in the relation  $W(t) = \text{const} \times t^\alpha$  at four different temperatures  $T$

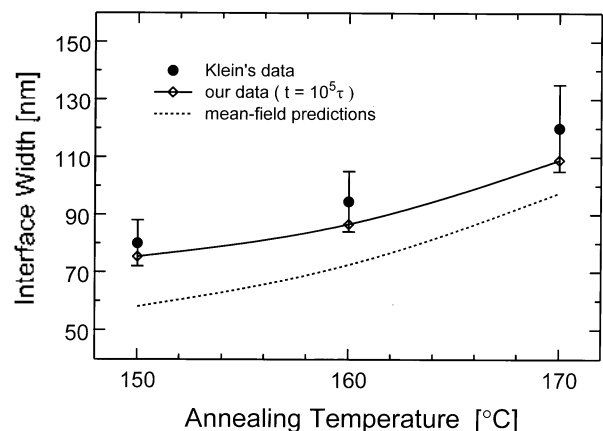
$T$ ( $^{\circ}\text{C}$ )	$\alpha$ (Klein's data)	$\alpha$ (Our data)
140	$0.27 \pm 0.08$	0.2616
150	$0.38 \pm 0.06$	0.2765
160	$0.36 \pm 0.06$	0.2958
170	$0.36 \pm 0.04$	0.3260

Comparison with Klein's data<sup>5</sup> is given in Table 1. Both Klein's experimental data and our calculation data are considerably smaller than the Fickian exponent 1/2, falling between 0.25 and 0.5. Within the error range, our predictions of interfacial width are quantitatively agree well with the Klein's data. In case of  $R = 0.94$  ( $\chi = 1.580$ ), the value of  $\alpha = 0.4344$  is closer to 1/2 for the Fickian-type free diffusion. Because the value of  $\chi = 1.580$  ( $\sim 160$   $^{\circ}\text{C}$ ) in  $R = 0.94$  is lower than the predicted critical  $\chi_c$  of 2.06 for the  $N_c/N_A$  system (*i.e.*, higher than the predicted critical temperature of  $\sim 115$   $^{\circ}\text{C}$ ), we can expect for free interdiffusion with  $\alpha = 1/2$ . As we see in Figure 2 and Figure 4, our data do show a clear  $\sqrt{t}$  dependence of the interfacial width and agree well with Klein's experimental data.<sup>4</sup>

The long-time limit of the interfacial width  $W(t)$  for different temperatures (*i.e.*, at different  $\chi$  ( $T$ ) values) as we approach  $T_c$  from below is shown in Figure 5. The solid line is our calculation result at a diffusion time,  $t = 10^5 \tau$  with segment size  $a = 6.6$   $\text{\AA}$ , same as the value of ref 4. The filled circles are Klein's experimental data with the broken curves corresponding to the uncertainty limit. The dotted line is the mean-field prediction, which is evaluated from Eq. (2) in ref 4. Within the spread implicit, our data are in good quantitative agreement with the Klein's.

## Conclusions

We have compared our reptation model with Klein's data<sup>4,5</sup> and good agreement is found. Particularly, our model



**Figure 5.** The long-time limit of the interfacial width  $W(t)$  for  $T = 150$   $^{\circ}\text{C}$ ,  $160$   $^{\circ}\text{C}$  and  $170$   $^{\circ}\text{C}$ . The solid line is our calculation data at  $t = 10^5 \tau$  and the filled circles are Klein's data with the spread implicit. The dotted line is the mean-field prediction by Eq. (2) of Ref 4. The units are the same as in Figure 1.

provides a *quantitative* analysis (not a *semiquantitative*<sup>7</sup>) for the experiments of refs 4 and 5. We find the interfacial width to increase with time  $t$  at short times as  $t^\alpha$ . All the values of  $\alpha$  theoretically determined in the present study, as summarized in Table 1, are between 1/4 and 1/2. These theoretical results agree well with Klein's data<sup>4,5</sup> within the error range and with the mean-field approach.<sup>11</sup> We also note that the interfacial widths for long times (Figure 5) are in accord with Klein's experimental data.<sup>4,5</sup> Finally, we conclude that our reptation model<sup>6</sup> is capable of making various and reasonable predictions for the interdiffusion with different values of the  $N_A/N_B$  couple.

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