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Interdiffusion in Binary Polymer Mixtures

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ABSTRACT: The interface between two partially miscible polymer species (A + B) is characterized theoretically under different thermodynamic conditions using the standard model for spinodal decomposition and interdiffusion. Two quantities are introduced to characterize the mass transport process across the interface between the A-rich and B-rich layers. One is the interfacial width W defined as related to the reciprocal of the maximal gradient in composition and is most sensitive to the local structure close to the A/B interface. The other is mass transport M due to diffusion and is most insensitive to detailed profiling of the composition. It is found that the deeper the system is in the two-phase region, the quicker its interfacial width $W(t)$ saturates to a limiting value and the slower its mass transport speeds up. Comparison with recent experiments of Klein and co-workers is made, and good agreement is found.

I. Introduction

Study of interdiffusion in polymeric materials is a vast subject that is directly connected to many fields such as processing of polymer blends, dynamics of phase separation in polymer mixtures, polymer adhesion and welding, kinetics of adhesion, and coating. Understanding of diffusion processes in polymers is key to successful production of polymers and applications of polymer products in industry. Due to relatively slow relaxation processes of polymer chains in comparison to systems of small molecules, polymers also offer the ideal system for fundamental studies of diffusion and kinetics of spinodal decomposition. Therefore interdiffusion between different species of polymers is an extremely important problem that has both great practical relevance and considerable academic significance. However, because of rich equilibrium phase behaviors found in polymeric systems, ranging from miscibility, crystallization, to glass transition, diffusion in polymers is spectacularly complicated.[1-9]

Experiments on self-diffusion and mutual diffusion in polymer melts were originally performed to provide a powerful test of the leading dynamic theory of polymer melts—that of reptation theory developed by de Gennes, Edwards, Doi, and other polymer theorists. Now study of interdiffusion has developed into a unique subject that not only has academic value but also has been recognized as playing an important role in practical applications of polymeric materials. In the past several years a number of new experiments have been reported on interfacial dynamics between compatible and partially miscible polymer blends via interdiffusion processes.[1-7] In such experiments, one takes a thin film of polymer species A and puts it in contact with another polymer (B) film. The evolution of the initially sharp boundary between A and B is monitored as a function of time by various experimental techniques. If polymers A and B are compatible, the initial sharp interface will be smeared out as a result of the ordinary Fickian type diffusion. The situation is somewhat delicate and more interesting when A and B are only partially miscible, i.e., when the ambient temperature is the biphasic region.

Klein and co-workers have recently obtained the first direct measurement of time-dependent composition profiles at an interface between two partially miscible polymers A and B (deuterated and protonated polystyrene).[3,4] In particular, interfacial broadening with elapsing time was studied in detail. Defining the interfacial width W as related to the reciprocal of the maximal composition gradient across the A/B boundary, it was found that the thickness of the interface W increases with time slower than that of a Fickian process of $W(t) \propto t^{1/2}$. As the opposite of phase separation, the mixing takes place via interdiffusion driven by thermodynamic forces. The transport phenomena in the bilayer were found to depend strongly on thermodynamic conditions such as temperature, interaction parameters between polymers A and B, and molecular weights of A and B. In the experiment of ref 4, where interfacial relaxation took place between a polymer A-rich and polymer B-rich layers prepared with coexisting compositions, a scaling law $W(t) \propto t^{\alpha}$ was found with α considerably smaller than the Fickian exponent 1/2, falling between 0.25 and 0.5. But the experiment could not exclude the possibility that deeper in the two-phase region the exponent α might be smaller than 0.25, since the experiment was performed not far away from the critical temperature for miscibility.

The value of α also strongly depends upon the definition by which the width W of the interface is measured. The definition of maximal gradient adopted in refs 3 and 4 is most sensitive to local structure of the interface. A second meaningful characterization of interdiffusion is defining the amount of material $M(t)$ of species A transported across the initial boundary separating A and B as a function of time: $M(t) \propto t^{\beta}$. This definition is most insensitive to the local structure of the composition profile and describes an interdiffusion process in the most unambiguous way. In addition, it permits the highest precision in the experimental determination of exponent β. There have been relatively few theoretical investigations in conjunction with experiments mentioned above. The recent works of de Gennes,[10] Harden,[11] and Puri and Binder[12] are the representative attempts at rationalizing the experimental observations of Klein and his co-workers.[3,4] In order to linearize the highly nonlinear diffusion equation, the calculation of ref 11 was performed just below the critical miscibility point, whereas the experimental temperatures were clearly inside the two-phase region. Puli and Binder[12] used a definition for W, different from that adopted in refs 3 and 4, that is bound to produce the exponent α equal to 0.5. From a simple dimensional analysis, one tends to conclude that the exponent α has to fall between 1/4 (the Cahn–Hilliard[13] term dominant) and 1/2 (Fickian characteristic). But a competition and balance between

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interfacial and thermodynamic forces may lead to a much smaller α than the "lower bound" 0.25.

Interdiffusive behaviors of polymer mixtures can be characterized by following temporal change of both maximal gradient in spatial distribution of composition and mass transport across the interface. Due to theoretical difficulties, we focus on the situation studied in ref 3 and provide a semiquantitative analysis for the experiment. Thus, we consider interdiffusion between *pure* polymer A and *pure* polymer B and assume the polymer layers are infinitely thick. We believe that both interfacial width $W(t)$ and kinetics of mass transport $M(t)$ are required in order to have a reasonable description of interdiffusion between partially miscible polymer blends. In section II, the theoretical model is discussed and formulated in terms of a kinetic equation for the composition field. Numerical results are given in section III. The paper ends with a conclusion.

II. Model

It is known that equilibrium properties of a polymer mixture of spatially uniform composition can be approximately described by the Flory–Huggins type lattice thoery. When the mixture phase separates, interfaces are created between two or more phases. At phasic boundaries, polymer chains rearrange their conformations and repel chains of dissimilar species. This leads to an increase in free energy of both entropic and enthalpic origins. Now the total free energy will take a generalized form

$$F = \int \mathrm{d}V\, [f_0(\phi) + (\kappa/4)(\nabla\phi)^2] \tag{1}$$

where f_0 is the free energy density of the system and the second term involving $(\nabla\phi)^2$ accounts for the Cahn–Hilliard interfacial energy associated with the spatial variation of the composition. The phenomenological parameter κ has the dimension of length squared and plays an important role in control and formation of interfaces. It is generally a function of concentration ϕ and should also depend upon specific properties of both polymer species as well as ambient temperature. In the Flory–Huggins theory for incompressible polymer mixtures of lengths N_A and N_B, f_0 is given by the familiar expression

$$f_0(\phi) = (\phi/N_A)\ln(\phi) + [(1-\phi)/N_B]\ln(1-\phi) + \chi\phi(1-\phi) \tag{2}$$

with ϕ being the volume fraction of polymer A. Since N_A and N_B are large and the entropy of mixing is small, the thermodynamic driving force for mixing is very weak and a relatively small, positive Flory χ parameter is sufficient to make A and B phase-separate into A-rich and B-rich phases.

In general, depending on the initial conditions, polymers A and B may either demix through spinodal decomposition or interdiffuse into each other. Phase separation cannot be perfect when the system is not too far from the critical point for miscibility. By the same token, partial mixing via interdiffusion will occur when a layer of pure polymer A is put in contact with a layer of pure B. But the diffusion is not free in the sense of Fickian transport, and anomalous behaviors are anticipated. Since a complete mixing is prevented by thermodynamics, the interface between A and B presents a diffusion barrier where the composition crosses over from its coexistence value of one phase to that of the other. Consequently, the diffusion constant is negative at the middle of the interface where the interfacial effect stabilizes the interdiffusion process. It is possible to describe this transport process by simply applying the law of mass conservation. In our situation, the initial arrangement is a sharp contact between two unmixed polymer species A and B. The thermodynamic driving forces, both from the bulk and interfacial region, compel the system to mix through the interfacial region.

According to the conservation law, the temporal change of composition in space is described by the dynamic equation

$$\partial\phi/\partial t + \nabla\cdot J = 0 \tag{3a}$$

where the mass flux is given by

$$J = -\Lambda(\phi)\nabla\mu \tag{3b}$$

In (3b), $\Lambda(\phi)$ is a concentration-dependent mutual mobility coefficient and the exchange chemical potential[14] μ is the functional derivative of the free energy F given in eq 1. One topic in studies of interdiffusion is to derive the functional form of $\Lambda(\phi)$ at a phenomenological level by setting the off-diagonal Onsager coefficients to zero.[15–18] Some Monte Carlo simulations also have recently been carried out.[19] There has not been any attempt at formulating a molecular-level, statistical mechanical theory for the transport coefficient $\Lambda(\phi)$. In any event, the subject of $\Lambda(\phi)$ is beyond the scope of the present work. Here for simplicity we consider only the symmetric case where $N_A = N_B = N$ and A and B have the same molecular mobility. In this case, $\Lambda(\phi)$ takes the simple form[15–17]

$$\Lambda(\phi) = \Lambda_0\phi(1-\phi) \tag{3c}$$

where Λ_0 is independent of the composition field $\phi(r,t)$. The equilibrium theory of Helfand and others[20,21] for the interfacial structure of incompatible polymer blends also produces a simple expression for the parameter $\kappa(\phi)$ in (1)

$$\kappa(\phi) = a^2/\phi(1-\phi) \tag{4}$$

where a is a monomer length. Equations 1, 2, 3a–c, and 4 constitute the dynamic model for spinodal decomposition in polymer blends, first proposed by de Gennes.[15,17,22]

Combining (3b) with (3c) and using (1) together with (4), we obtain the local current J associated with the diffusion of species A

$$J = -\Lambda_0\phi(1-\phi)\nabla\frac{\delta F}{\delta\phi(r,t)} = D\{[1 - 2N\chi\phi(1-\phi)]\nabla\phi - K\nabla^3\phi\} \tag{5}$$

where the mutual diffusion coefficient D, given by $D = \Lambda_0/N$, is of the magnitude of the self-diffusion coefficient in an entangled polymer melt and the interfacial parameter K has the magnitude of the square of the radius of gyration: $K = Na^2$. In arriving at (5), we have neglected nonlinear terms involving $(\nabla\phi)^3$ and $(\nabla\phi)\nabla^2\phi$. These terms are unimportant at late stages of interdiffusion when the interface has sufficiently broadened. Apart from the absence of a noise term, eq 3a plus (5) has the same form as that of a time-dependent Ginzburg–Landau equation for conserved order parameter systems, which is also known as model B according to the classification scheme of Hohenberg and Halperin.[23] A more detailed theory for the mutual mobility Λ of (3c) may lead to a ϕ-dependent D in (5).[18] Experiment also showed that the form of (3c) can be rather complicated.[24–26] For an excellent review on this subject, see Kausch and Tirrell's article.[27] This additional nonlinearity is neglected based on the assumption that the properties of the diffusion equation given by (3a) and (5) is dominated by the factor $[1 - 2N\chi\phi(1-\phi)]$, which changes its sign across the interface. Linearization of (5), as performed in ref 11, will remove this important characteristic. We now write our model in dimensionless form before discussing its solutions in the next section. Consider the interdiffusion taking place between two thin sheets of polymers A and B. For such a bilayer arrangement, the analytical description reduces to a one-dimensional space denoted by the x-axis. Scale length by the natural length $K^{1/2}$ in the problem and make the conversion $x \rightarrow x/K.^{1/2}$ Scale time with the unit $\tau = 2K/D$, which is on the order of the reptation time of a single chain in a melt, and make the transformation $t \rightarrow t/\tau$. Finally, it is convenient to redefine the composition variable around its value at the critical point $\phi_c = 1/2$ as $\psi = 2(\phi - \phi_c)$, so that the order parameter ψ takes values between +1 and −1 as composition ϕ drops from 1 to zero. Substituting (5) into (3a) and writing the resulting equation in terms of the rescaled variables, we find

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial x}\left[(\chi_c - \chi + \chi\psi^2)\frac{\partial \psi}{\partial x} - \frac{\partial^3 \psi}{\partial x^3}\right] \qquad (6)$$

where we have also made a change of notation: $N\chi \rightarrow \chi$ and thus $\chi_c = 2$ corresponds to the critical point. The second term involving $\partial^3\psi/\partial x^3$ accounts for the presence of an interface separating two incompatible phases. The other major difference from an ordinary Fickian diffusion equation is that the factor in front of $\partial\psi/\partial x$ in the square brackets can turn negative, amounting to a negative diffusion constant and therefore "uphill diffusion". Notice this equation is identical in form to the Cahn–Hilliard equation used in ref 12.

Before proceeding to the next section for numerical results, we discuss briefly the limitations of such a model as given in (6) for interdiffusion and spinodal decomposition. At a given temperature, i.e, for a given χ, the two phases will coexist in equilibrium with compositions determined by two roots of the following equation:

$$\ln\left[\frac{1 + \psi_{\text{coex}}}{1 - \psi_{\text{coex}}}\right] - \chi\psi_{\text{coex}} = 0 \qquad (7)$$

Clearly, the dynamic equation (6) *does not* contain any information leading to eq 7. Thus, the kinetic theory (6) is unaware of the equilibrium state to which the system must approach by virtue of interdiffusion or spinodal decomposition depending on initial conditions. For example, start with an initial state of a step function with magnitude $\pm\psi_{\text{coex}}$ corresponding to an initial sharp interface between A-rich and B-rich layers that are prepared with coexisting compositions $\phi' = (1 - \psi_{\text{coex}})/2$ and $\phi'' = (1 + \psi_{\text{coex}})/2$. One expects to observe the interface broadening and eventual relaxing to its equilibrium dimension, as experimentally found in ref 4. But the diffusion process according to (6) will continue indefinitely and the amount of mass transported through the interface will increase with time without bound, resulting in an ever-changing composition profile. A similar theoretical difficulty should be recognized in the case of demixing. When a polymer mixture phase separates, the two phases will eventually reach their coexisting compositions ϕ' and ϕ''. But the three-dimensional version of (6) given by (3a) and (5) cannot determine what values of composition the phases should end up with at long times. As long as the mass transport has not approached the outer two boundaries of the thin film, the interdiffusion process can still be described by (6).

III. Numerical Solutions and Results

It is not feasible to seek the analytical solution of the nonlinear partial differential equation (6). But numerical solutions can be obtained by discretizing (6) with finite differences. Consider the situation examined experimentally in ref 3, namely, a bilayer of initially pure polymer A and polymer B. Regarded as a one-dimensional problem, the left-hand side is occupied by A and the right-hand side by B initially. 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 (6). In discretizing $\partial\psi(x,t)/\partial t$ as $(\psi_i^n - \psi_i^{n-1})/\Delta t$, $\partial\psi(x,t)/\partial x$ as $(\psi_{i+1}^n - \psi_{i-1}^n)/2\Delta x$, and similarly for its higher spatial derivatives, Δt is chosen as $\Delta t = 0.01$ and Δx as $\Delta x = 0.5$. We take 400 grid points so that the total thickness is $200K^{1/2}$. The boundary condition is $\partial\psi(x,t)/\partial x = 0$ and $\partial^3\psi(x,t)/\partial x^3 = 0$ at the two ends: $i = 0$ and $i = 400$. Starting with an initial interfacial width of a reasonable magnitude, we allow the system to evolve 10^5 time steps corresponding to $10^3\tau$ during which the boundary condition will remain valid.

The distance from the critical point $\chi_c = 2$, represented by the factor $\chi - \chi_c$ in (6), completely determines the progress of interdiffusion. The thickness W_0 of the initial interface has some effect on the transport process in the early stage but has an insignificant influence after a time period of about one characteristic time $\tau = 2K/D$. Of course, the value of W_0 cannot be chosen to be larger than the saturated width W_∞ at long times. In fact, we take W_0 considerably smaller than W_∞ to start the interdiffusion process on the computer. We have considered three values of $\chi = 2.03$, 2.12, and 2.31, corresponding to the following three pairs of equilibrium coexisting compositions: $\phi' = 0.4$, $\phi'' = 0.6$; $\phi' = 0.3$, $\phi'' = 0.7$; and $\phi' = 0.2$, $\phi'' = 0.8$. One purpose is to systematically characterize how the "quenching depth" affects the pace with which the interfacial region grows as a result of mass transport. One anticipates that as the interdiffusion experiment is conducted further away from the critical temperature, the transport behavior will be more non-Fickian or anomalous.

As discussed in the Introduction, we need at least two quantities, one reflecting the local structure right at the middle of the interface and the other depicting the overall profile of the composition field, in order to provide a reliable description of the interdiffusion process between partially compatible polymer species. We adopt the definition of ref 3 for the sake of comparison; namely, we define $W(t)$ in terms of the maximal gradient of composition. For a symmetric case such as the present study, $W(t)$ is simply given by

$$W(t) = \left[\left(\frac{\partial\psi(x{=}200\Delta x,t)}{\partial x}\right)^{-2} - \left(\frac{\partial\psi(x{=}200\Delta x,t{=}0)}{\partial x}\right)^{-2}\right]^{1/2} \qquad (8)$$

where $W(t)$ is given in units of $K^{1/2}$. The second characteristic property is the mass $M(t)$ of polymer A transported from the left-hand side of the initial dividing surface to its right-hand side. The mass transport $M(t)$ is calculated according to

$$M(t) = C\int_{200\Delta x}^{400\Delta x} \mathrm{d}x\, [1 + \psi(x,t)] \qquad (9)$$

where C is a proportionality constant. It is expected that $M(t)$ will increase with time slower than $t^{1/2}$ for the partially miscible couples of polymer blends. It should be recognized that the definition (9) is only true in the symmetric case considered here.

Our numerical results are presented as follows. In Figure 1A–C, the composition profiles for $\chi = 2.03$, 2.12, and 2.31 are respectively plotted at four consecutive times $t = 63\tau$, 250τ, 500τ, and $10^3\tau$ after onset of the interdiffusion. Near the critical point, e.g., $\chi = 2.03$, the transport phenomenon

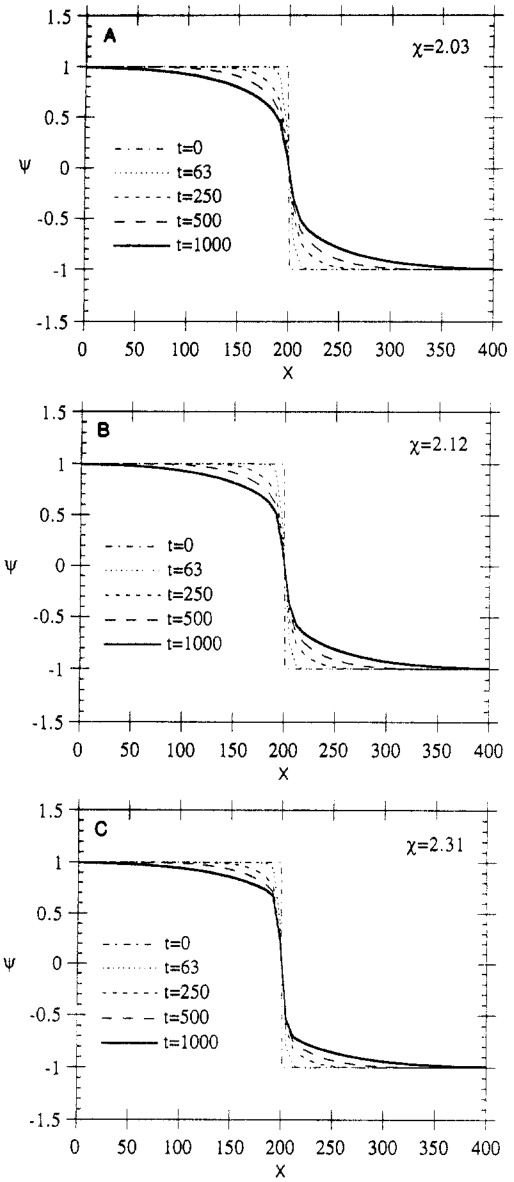

Figure 1. (A) Composition profiles for $\chi = 2.03$ at five different times. The time is expressed in units of $\tau = 2K/D$ and length in units of $0.5K^{1/2}$. (B) Composition profiles for $\chi = 2.12$ at five different times. The units are the same as in (A). (C) Composition profiles for $\chi = 2.31$ at five different times. The units are the same as in (A).

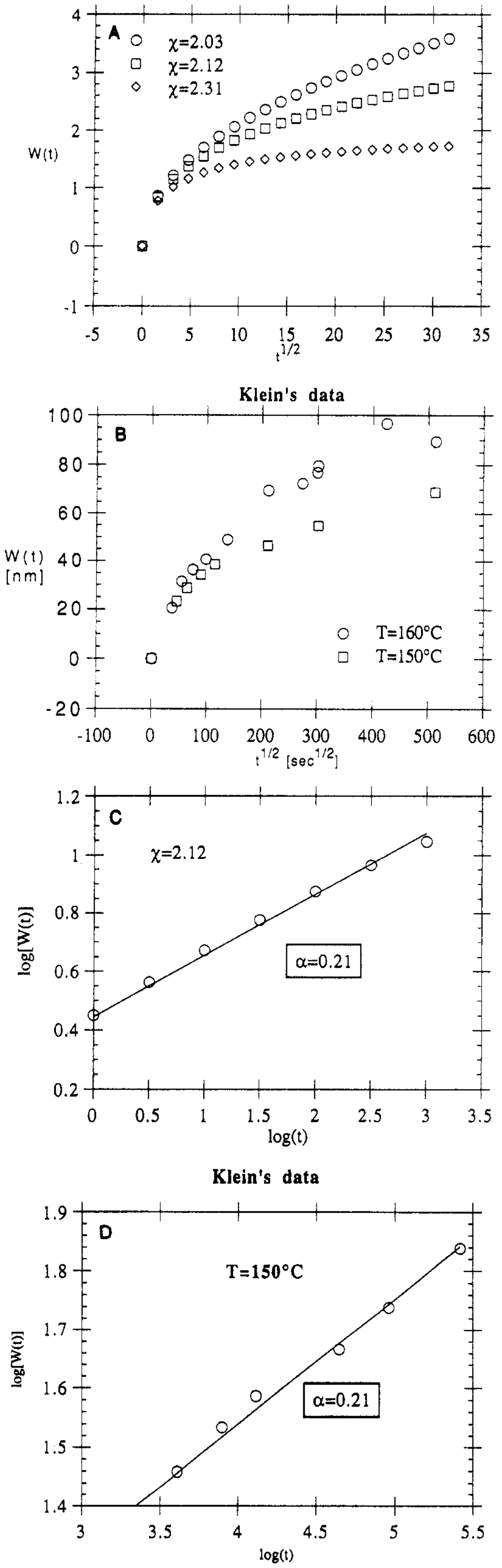

Figure 2. (A) Interfacial width $W(t)$ against the square root of time. The units are the same as in Figure 1A. (B) Data reproduced from ref 3. (C) One set of data ($\chi = 2.12$) in (A) replotted in double-logarithmic form; α is the slope. (D) One set of data ($T = 150$ °C) in (B) replotted in double-logarithmic form; α is the slope.

appears almost Fickian as shown in Figure 1A. To quantify our analysis and to compare with existing experimental data, we evaluate the interfacial width $W(t)$ as a function of time. First, $W(t)$ is plotted against the square root of time $t^{1/2}$ in Figure 2A for different values of χ. One set of experimental data was presented in a similar way in ref 3 and is reproduced here in Figure 2B. Our theoretical predictions strongly resemble the experimentally observed behaviors. This can be seen more clearly by searching for a scaling law $W(t) \propto t^{\alpha}$. In Figure 2c, $\log[W(t)]$ is drawn versus $\log(t)$ for $\chi = 2.12$, which corresponds to equilibrium coexistence compositions of $\phi' = 0.3$ and $\phi'' = 0.7$, and the exponent α is found to be $0.21 < 0.25$. This indicates that the "uphill" diffusion represented by the first term on the right-hand side of (6) is well balanced by the Cahn–Hilliard interfacial effect described by the second in (6). Next we plot the data from ref 3 in double-logarithmic form as shown in Figure 2D. The same value of 0.21 is found for the exponent α. Evidently, both experiment and theory allowed α to be smaller than 1/4, at least for the definition of interfacial width specified by (8). It is appropriate to note that this comparison is not exact because the experimental system[3] involved polymers A and B of different molecular weights and our calculation was for $N_A = N_B$. Three points are in order at this moment. First, we reiterate that all properties of the interdiffusion process

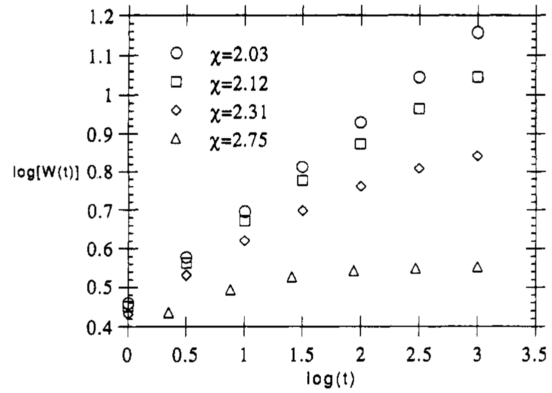

Figure 3. Interfacial width versus time plotted in double-logarithmic form. The units are the same as in Figure 1A.

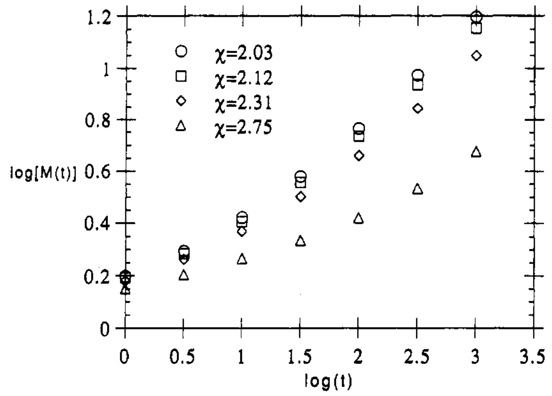

Figure 4. Mass transport $M(t)$ versus time plotted in double-logarithmic form. The units are the same as in Figure 1A.

are independent of the initial thickness W_0 of the interface after about one $\tau = 2K/D$. Second, evolution of the interfacial region starts to bifurcate for different values of χ only after one τ as clearly shown in Figure 2A. Third, from the crude comparison between theory and experiment, one can estimate the magnitude of the mutual diffusion constant D in the actual experiment conducted in ref 3. Taking $\tau \approx 2500$ s and $K \approx 10^{-11}$ cm^2, one finds $D = 2K/\tau \approx 8 \times 10^{-15}$ cm^2/s.

Now we contrast the two different quantities $W(t)$ and $M(t)$ that describe the same transport process. In Figure 3, log $[W(t)]$ versus log(t) is presented for the four different values of χ. Clearly, the interfacial width $W(t)$, defined in (8) by the local variation of composition with film thickness, approaches a stationary value at long times. The further away from the critical point given by $\chi_c = 2$, i.e., the larger χ, the faster $W(t)$ saturates. On the other hand, the mass $M(t)$ transported across the boundary continues to increase with time as shown in Figure 4. It is important to notice that the mass transport processes also begin to deviate from one another for different values of χ after a period of order τ. Thus we are able to demonstrate that behaviors associated with the interfacial dynamics are greatly different from those related to mass transport. Since the curves are not straight lines throughout the time interval in either Figure 3 or Figure 4, power laws such as $W(t) \propto t^\alpha$ and $M(t) \propto t^\beta$ hold only for a certain period during the interdiffusion. We can describe the two properties more quantitatively by finding the values of α and β during the same period. Take the cases of $\chi = 2.03$ and $\chi = 2.31$ for example. In Figure 5A for $\chi = 2.03$, a single value of 0.23 for α and 0.41 for β are identified over nearly two decades of time scale. Because of the suppressed diffusion due to the "spinodal barrier", it is expected that β does not exceed 0.5. Moreover, the value of α does not have to stay within 0.25 and 0.5 since existence of an optimal stationary interfacial width is plausible in a steady-state of interdiffusion. The fact that $\alpha = 0.23$ is smaller than 0.25 even though the system is near the critical point for complete mixing means that the exponent α alone cannot well characterize the entire transport process. It at best depicts how sharply the composition field varies across the A/B interface. Furthermore, $\beta = 0.41$ is notably smaller than 0.5 despite a small value of 2.03 for χ. That is, the diffusion is not free, with the system inside the two-phase region. Similarly, for $\chi = 2.31$ it is found in Figure 5B that $\alpha = 0.10$ and β 0.37, both smaller than those for $\chi = 2.03$ during the same time interval. Indeed, for $\chi = 2.31$ the system already begins to approach toward a stable interface of finite width at around 30τ as shown in Figure 3. This explains why the exponent α has become so small, far below 0.25.

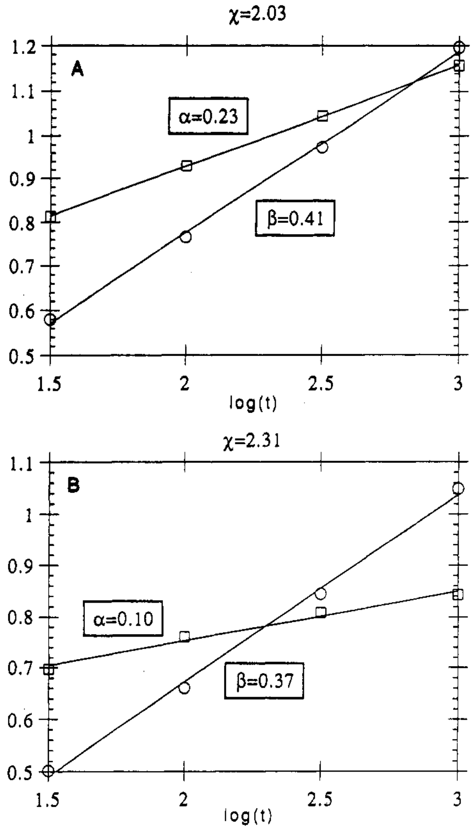

Figure 5. (A) Logarithm of W and M against logarithm of time for $\chi = 2.03$. Exponents α and β are obtained from the slopes. (B) Logarithm of W and M against logarithm of time for $\chi = 2.31$. Exponents α and β are obtained from the slopes.

IV. Conclusions

We have studied phenomena of interdiffusion between partially compatible polymer species from a theoretical viewpoint by applying the simplest dynamic model for collective interdiffusion and spinodal decomposition in polymeric materials. Our predictions agree well with available experimental data. Therefore the model should be taken more seriously in spite of its severe limitations concerning the simplistic form of the mutal mobility (3c). On the other hand, our calculation is based on a symmetric case and the experimental data of ref 3 are for asymmetric polymers. Nevertheless, we point out that the time dependent of the interfacial width $W(t)$ alone is not sufficient to fully characterize the transport process. We find in our calculations that $W(t)$ stops broadening at long times and loses its function as a monitor of the interdiffusion process. More specifically, during a certain period when a power law such as $W(t) \propto t^\alpha$ holds, it is found that

α is actually always smaller than 0.25, in agreement with the reproduced experimental data of ref 3 shown in Figure 2D. It is necessary to introduce other quantities such as the mass transport $M(t)$ that not only is a salient feature throughout the dynamic process but also replaces the function of $W(t)$ to provide an illustration of interdiffusive transport in the late stage. One benefit from comparison between theory and experiment would be that one can determine the magnitude of the mutual diffusion constant by identifying the time scales involved in the process. However, it is important to note that our calculations need improvement for a more reliable comparison. For example, we need to include higher nonlinear terms in the dynamic equation and to incorporate asymmetric conditions where polymers are of different molecular weights.

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