Interdiffusion and marker movements in concentrated polymer-polymer diffusion couples

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Intrinsic and interdiffusion coefficients of binary polymer-polymer diffusion couples with initially large concentration gradients are markedly dependent on concentration, even when the polymers differ only in molecular weight. Assuming local thermal equilibrium of vacancies (or free volume) within the couple leads to different intrinsic diffusion coefficients for the two polymer species and to net vacancy fluxes. These fluxes should produce movement of inert markers in the couple relative to a point far from the initial interface. That such marker movements and vacancy fluxes actually occur is demonstrated by experiments in which the motion of 20 nm diameter Au islands is monitored by Rutherford backscattering spectrometry. The markers which are initially at the interface between thin films of monodisperse polystyrenes (one $2 \times 10^4 \ M_w$ and the other $1.1 \times 10^5 \ M_w$) are progressively displaced toward the lower molecular weight side of the couple. As expected the marker displacement is proportional to the square root of time at the diffusion temperature.

Keywords Polymer diffusion; marker movements; diffusion couples

INTRODUCTION

Interdiffusion of polymeric molecules is important in diverse areas of polymer science, ranging from 'tack' of rubber to crack healing in glassy polymers to the kinetics of phase separation in polymer blends. Attention has also been drawn to diffusion problems by recent theoretical advances, particularly the reptation model for polymer diffusion. For long chain polymer melts, each chain is imagined to crawl within a tube formed by the topological constraints of all of the other polymer chains. An important prediction of this model, that the diffusion coefficient, $D$, of a chain of degree of polymerization $N$ should decrease as $N^{-2}$, has been verified by experiments in which a very dilute concentration of deuterated polyethylene chains is allowed to diffuse into undeuterated polyethylene.

Most diffusion problems of practical interest in polymers, however, involve concentrated diffusion couples. Here, the experimental evidence, both from concentrated couples formed from homopolymers of different molecular weight and from couples of chemically different, but compatible, polymers, shows large deviations from the $N^{-2}$ dependence of $D$ expected from the naive application of the reptation model.

A possible reason for these deviations has been recently discovered by BROCHARD, JOLIFFREY and LEVINSON, hereafter abbreviated as BJL. They showed that the strongly non-ideal entropy of mixing of concentrated polymer solutions could produce both large deviations from the $N^{-2}$ dependence of $D$ found from the reptation model at infinite dilution and a $D$ which depends markedly on concentration. They made the assumption, however, that the fluxes of the diffusing species are equal and opposite. This assumption is not correct for small molecules diffusing into polymers nor for concentrated alloys (the famous Kirkendall effect in brass-copper couples), and evidence is presented here to show that it is not correct for polymer-polymer interdiffusion either. The primary purpose of this paper is to develop a theory for the interdiffusion of polymer molecules which does not rely on cancellation of fluxes of the diffusing species.

DIFFUSION FLUXES

Consider a diffusion couple between pure polymer A with degree of polymerization $N_A$ and pure polymer B with degree of polymerization $N_B$. Let the chemical potential of A be $\mu_A$ and the chemical potential of B be $\mu_B$. Construct a co-ordinate system $x, y, z$ such that the origin of this system is in a region of the couple where the chemical potential gradients of A and B are negligible. Consider a single chain of A as shown in Figure 1, diffusing by the reptation mechanism. An elementary step in the diffusion consists of linear diffusion of the A molecule along its tube 'creating' a certain length of new tube at one end and 'destroying' it at the other. For this diffusion to occur a certain volume of vacant space (a certain number of cells in the quasi-lattice) must be created at one end of the A molecule and destroyed at the other. This creation and destruction of volume corresponds to a flux of vacancies (holes or free volume) from one end of the molecule to the other. Thus, there are three fluxes involved in the interdiffusion problem: the flux of segments of A molecules $J_A$, the flux of segments of B molecules $J_B$, and a net flux of vacancies $J_v$.

* Each segment occupies one site on the quasi-lattice
polymers, any such gradients in \( \Pi \) might be expected to be relaxed rather rapidly, if not by vacancy diffusion, then by viscous flow of the melt.

It is worth examining an assumption representing the opposite limiting case, not \( J_v = 0 \) but rather \( V_{\mu v} = 0 \), i.e., that the vacancy concentration is nearly at equilibrium everywhere. This assumption in fact provides a good description of the results of interdiffusion experiments in solid alloys, where one might imagine that vacancy creation or destruction (operation of vacancy sources and sinks) would be more difficult than in a polymeric fluid. Under this assumption the Onsager relations\(^{17,19}\) become:

\[
\begin{align*}
J_A &= -M_A V_{\mu A} \\
J_B &= -M_B V_{\mu B} \\
J_v &= M_A V_{\mu A} + M_B V_{\mu B}
\end{align*}
\]  

(6a)  
(6b)  
(6c)

The vacancy flux will be detectable by marker movement experiments. Suppose an inert particle marker is placed in the diffusion couple where the gradients \( V_{\mu A} \) and \( V_{\mu B} \) are finite. The marker will move, relative to the origin of co-ordinate system, with a velocity given by:

\[
v = \Omega J_v = \Omega (M_A V_{\mu A} + M_B V_{\mu B})
\]  

(7)

### CHEMICAL POTENTIAL GRADIENTS

In the Flory–Huggins theory the free energy per quasi-lattice site of an A–B mixture is given by:

\[
F = \frac{k_B T}{N_A} \phi \ln \phi + \frac{1}{N_B} \ln (1 - \phi) + \chi \phi (1 - \phi)
\]  

(8)

where \( \phi \) is the volume fraction of sites occupied by A and \( \chi \) is the Flory–Huggins interaction parameter. The chemical potential gradients then can be found from equation (8) in terms of the gradient in \( \phi \) to yield:

\[
\begin{align*}
V_{\mu A} &= \frac{k_B T}{\phi} \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi)|z| \right] \nabla\phi \\
V_{\mu B} &= \frac{k_B T}{1 - \phi} \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi)|z| \right] \nabla\phi
\end{align*}
\]  

(9a)  
(9b)

where \(|z|\) has been assumed to be either negative or zero. (Positive \( \chi \) will produce negligible mutual solubility for large values of \( N_A \) and \( N_B \)).

### INTERDIFFUSION COEFFICIENT

The total flux \( J_v^T \) of A across a plane fixed with respect to the co-ordinate system (but not with respect to the inert markers) is the sum of the diffusion flux of A plus the A transported by the vacancy flux, i.e.,

\[
\begin{align*}
J_A^T &= -M_A V_{\mu A} + \phi (M_A V_{\mu A} + M_B V_{\mu B}) \\
J_A^T &= -(1 - \phi) M_A V_{\mu A} + \phi M_B V_{\mu B}
\end{align*}
\]  

(10)

Conservation of A segments leads to:

\[
\frac{1}{\Omega} \frac{\partial \phi}{\partial t} = \nabla (-J_A^T)
\]  

(11)
and combining equations (9)-(11) gives:

$$\frac{\partial \phi}{\partial t} = -\nabla \left\{ \Omega k_B T \left( \frac{1 - \phi}{\phi} M_A + \frac{\phi}{1 - \phi} M_B \right) \times \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right] \nabla \phi \right\} \quad (12)$$

Since $\frac{\partial \phi}{\partial t} = -\nabla (D \nabla \phi)$, the interdiffusion coefficient is given by:

$$D = \Omega k_B T \left( \frac{1 - \phi}{\phi} M_A + \frac{\phi}{1 - \phi} M_B \right) \times \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right]$$

using the assumption $J_0 = 0$, i.e.:

$$D = \frac{\Omega k_B T}{\phi(1 - \phi) M_A + M_B} \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right]$$

This expression is different from the one found by BJL:

$$D = \frac{\Omega k_B T}{\phi(1 - \phi) M_A + M_B} \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right]$$

**INTRINSIC DIFFUSION COEFFICIENTS**

The intrinsic or chemical diffusion coefficients $D_A$ and $D_B$ defined by:

$$J_A = -\frac{D_A}{\Omega} \nabla \phi$$
$$J_B = +\frac{D_B}{\Omega} \nabla \phi = -\frac{D_B}{\Omega} \nabla (1 - \phi)$$

may also be determined from equations (6) and (9) to be:

$$D_A = \Omega k_B T \left[ \frac{M_A}{\phi} \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right] \right]$$
$$D_B = \Omega k_B T \left[ \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right) \right]$$

By comparing equations (13), (15a) and (15b) it is evident that:

$$D = (1 - \phi)D_A + \phi D_B$$

**MARKER VELOCITY**

The marker velocity is proportional to the difference between $D_A$ and $D_B$, i.e.:

$$v = (D_A - D_B) \nabla \phi$$

or

$$v = \Omega k_B T \left( \frac{M_A}{\phi} - \frac{M_B}{1 - \phi} \right) \left[ \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1 - \phi) \right] \nabla \phi$$

Measurements of $v$ plus $\phi(x, t)$ should allow $D_A, D_B$ and $D$ to be extracted.

**ONSAGER COEFFICIENTS**

The Onsager coefficients $M_A$ and $M_B$ may be expressed in terms of polymer segment mobilities $B_A$ and $B_B$ which relate the diffusional velocities of those segments to their chemical potential gradients. There are two cases of interest: the long chain limit where $N_A$ and $N_B$ are much larger than $\langle Ne \rangle_A$ and $\langle Ne \rangle_B$, the number of segments of A and B, respectively, per entanglement length, and the short chain limit where $N_A$ and $N_B$ are less than $\langle Ne \rangle_A$ and $\langle Ne \rangle_B$. In the short chain limit:

$$B_A = B_A$$
$$B_B = B_B$$

whereas in the long chain limit:

$$B_A = B_A \langle Ne \rangle_A/\langle N \rangle$$
$$B_B = B_B \langle Ne \rangle_B/\langle N \rangle$$

where $B_A$ and $B_B$ are the curvilinear Rouse mobilities of the A and B segments, respectively. The mobilities in short chain/long chain diffusion couples can also be found by selecting the appropriate members of equations (17) and (18).

As the flux of a particular species is the product of the concentration of that species and its diffusional velocity:

$$M_A = B_A \langle \phi \rangle$$
$$M_B = B_B \langle 1 - \phi \rangle$$

**INTERDIFFUSION OF CHEMICALLY IDENTICAL POLYMERS ($\chi = 0$) OF DIFFERENT MOLECULAR WEIGHT**

**Short chain limit ($N_A < N_B < N$)**

In this limit $B_A = B_B = B_0$, and $M_A = B_0 \langle \phi \rangle$, $M_B = B_0 \langle 1 - \phi \rangle$. The interdiffusion coefficient $D$ is given by:

$$D = B_0 k_B T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)$$

the intrinsic diffusion coefficients $D_A$ and $D_B$ from equation (15) are given by:

$$D_A = D_B - B_0 k_B T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)$$

and the velocity of the inert marker is identically zero since $D_A - D_B = 0$. In the case the results are identical to those found by BJL.

**Long chain limit ($N_B > N_A > N$)**

In this limit $B_A = B_A \langle Ne \rangle N_A$, $B_B = B_B \langle Ne \rangle N_B$, and $M_A = \phi B_A N_A/\langle N \rangle$, $M_B = (1 - \phi) B_B N_B/\langle N \rangle$. The interdiffusion coefficient is:

$$D = Ne B_A k_B T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)^2$$

$D_A$ and $D_B$ are given by:

$$D_A = Ne B_A k_B T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)$$
$$D_B = Ne B_B k_B T \left( \frac{\phi}{N_B} + \frac{1 - \phi}{N_A} \right)$$
and the velocity of the marker, by:

$$v = N e B_0 k_T \left( \frac{1}{N_A} - \frac{1}{N_B} \right) (1 - \phi) \frac{\phi}{N_A} \frac{\phi}{N_B} \nabla \phi$$

(24)

If $N_A < N_B$ the markers will move to the A-rich side of the diffusion couple.

Short chains diffusing into long chains ($N_A < N_e < N_B$)

In this limit ($N_e$) for the B chains diluted with short A chains should become $N/e(1 - \phi)$ where $N$ is the number of segments between entanglements in the undiluted polymer B. Thus, for $1 - \phi > N/e/N_B$,

$$B_0 = B_0 N/e[1 - (1 - \phi) N_B], B_A = B_0$$

and

$$M_A = B_0 N/e/N_A \Omega, M_B = B_0 N/e/N_B \Omega$$

the interdiffusion coefficient $\bar{D}$ is:

$$\bar{D} = B_0 k_T \left( \frac{1 - \phi}{N_A} \right) \frac{\phi}{N_B} \left( 1 - \phi + \frac{\phi}{N_A} + \frac{\phi}{N_B} \right)$$

(25)

For $(1 - \phi) < N/e/N_B$ both A and B chains are no longer entangled and equation (20) applies. The intrinsic diffusion coefficients are:

$$D_A = B_0 k_T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)$$

(26)

$$D_B = B_0 k_T \frac{N/e}{N_B} \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)$$

(27)

for $(1 - \phi) > N/e/N_B$ and $D_a = D_A$ for $(1 - \phi) < N/e/N_B$.

The marker velocity is:

$$v = B_0 k_T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right) \left( 1 - \phi + \frac{\phi}{N_A} + \frac{\phi}{N_B} \right)$$

(28)

for $(1 - \phi) > N/e/N_B$ and $v = 0$ for $(1 - \phi) < N/e/N_B$.

**INTERDIFFUSION OF CHEMICALLY DIFFERENT POLYMERS ($\chi \neq 0$) OF IDENTICAL MOLECULAR WEIGHT**

**Short chain limit ($N_A = N_B < (N_e)_A$ or $(N_e)_B$)**

In this limit $M_A = B_0(B_e) \Omega$ and $M_B = B_0(1 - \phi) \Omega$ where the Rouse mobilities of A and B segments are assumed to be independent of composition. If an average mobility $\bar{B} = B_A(1 - \phi) + B_B(\phi)$ is defined, the interdiffusion coefficient is:

$$\bar{D} = k_T \bar{B} \left[ \frac{1 - \phi}{N} + \phi(1 - \phi) / |x| \right]$$

(29)

The intrinsic diffusion coefficients are:

$$D_A = k_T \bar{B}_A \left[ \frac{1 - \phi}{N_A} + \phi(1 - \phi) / |x| \right]$$

(30a)

$$D_B = k_T \bar{B}_B \left[ \frac{1 - \phi}{N_B} + \phi(1 - \phi) / |x| \right]$$

(30b)

These only reduce to the results found by BJL when $\bar{B}_A(N_e)_A = \bar{B}_B(N_e)_B$.

**INTERDIFFUSION OF CHEMICALLY DIFFERENT POLYMERS OF DIFFERENT MOLECULAR WEIGHT**

**Short chain limit ($N_A < N_B < (N_e)_A$ or $(N_e)_B$)**

In this case $M_A = B_0 \phi/\Omega$ and $M_B = B_0(1 - \phi) / \Omega$ so that the interdiffusion coefficient is given by:

$$\bar{D} = k_T \bar{B} \left[ \frac{1 - \phi}{N} + \phi(1 - \phi) / |x| \right]$$

(35)

where $\bar{B}(\phi) = B_A(1 - \phi) + B_B(\phi)$. The intrinsic diffusion coefficients are:

$$D_A = k_T \bar{B}_A \left[ \frac{1 - \phi}{N_A} + \phi(1 - \phi) / |x| \right]$$

(36a)

$$D_B = k_T \bar{B}_B \left[ \frac{1 - \phi}{N_B} + \phi(1 - \phi) / |x| \right]$$

(36b)

and the marker velocity is:

$$v = k_T (\bar{B}_A(N_e)_A + \bar{B}_B(N_e)_B) \left[ \frac{1 - \phi}{N} + \phi(1 - \phi) / |x| \right] \nabla \phi$$

(37)

Long chain limit ($N_A > N_B > (N_e)_A$ or $(N_e)_B$)

In this case $M_A = \bar{B}_A(N_e)_A \phi / N_A \Omega$ and
\[ M_b = \overrightarrow{B}_b(Ne)_b(1 - \phi)/N_b\Omega \text{ so that } \overrightarrow{B} \text{ is given by:} \]

\[ \overrightarrow{B} = k_b T \left( \frac{(1 - \phi)\overrightarrow{B}_a(Ne)_a + \phi\overrightarrow{B}_b(Ne)_b}{N_a} \right) \times \left( \frac{1 - \phi}{N_a} + \frac{\phi}{N_b} + 2\phi(1 - \phi)\|\vec{x}\| \right) \] (38)

The interdiffusion coefficients are:

\[ D_a = k_b T \left( \frac{\overrightarrow{B}_a(Ne)_a}{N_a} \right) \left[ 1 - \phi + \frac{\phi}{N_a} + 2\phi(1 - \phi)\|\vec{x}\| \right] \] (39a)

\[ D_b = k_b T \left( \frac{\overrightarrow{B}_b(Ne)_b}{N_b} \right) \left[ 1 - \phi + \frac{\phi}{N_a} + 2\phi(1 - \phi)\|\vec{x}\| \right] \] (39b)

and the marker velocity is:

\[ v = k_b T \left( \frac{\overrightarrow{B}_a(Ne)_a}{N_a} - \frac{\overrightarrow{B}_b(Ne)_b}{N_b} \right) \times \left( \frac{1 - \phi}{N_a} + \frac{\phi}{N_b} + 2\phi(1 - \phi)\|\vec{x}\| \right) \nabla \phi \] (40)

**Short chains diffusing into long chains \((Ne)_a/(Ne)_b\)**

Here \(M_a = \overrightarrow{B}_a\phi/\Omega\) and \(M_b = \overrightarrow{B}_b(Ne)_b/N_b\Omega\) for \((1 - \phi) > (Ne)_b/N_b\) and \(M_b = \overrightarrow{B}_b(1 - \phi)/\Omega\) for \((1 - \phi) < (Ne)_b/N_b\) so the interdiffusion coefficient is:

\[ \overrightarrow{B} = k_b T \left[ (1 - \phi)\overrightarrow{B}_a + \phi\overrightarrow{B}_b(Ne)_b \right] \times \left( \frac{1 - \phi}{N_a} + \frac{\phi}{N_b} + 2\phi(1 - \phi)\|\vec{x}\| \right) \]

for \((1 - \phi) > (Ne)_b/N_b\) (41)

and

\[ \overrightarrow{B} = k_b T \overrightarrow{B}(\phi) \left[ \frac{1 - \phi}{N_a} + \frac{\phi}{N_b} + 2\phi(1 - \phi)\|\vec{x}\| \right] \]

for \(1 - \phi < (Ne)_b/N_b\)

The intrinsic diffusion coefficients are:

\[ D_a = k_b T \overrightarrow{B}(\phi) \left[ \frac{1 - \phi}{N_a} + \frac{\phi}{N_b} + 2\phi(1 - \phi)\|\vec{x}\| \right] \] (42a)

\[ \frac{k_b T \overrightarrow{B}(\phi)(Ne)_b}{(1 - \phi)N_b} \left[ 1 - \phi + \frac{\phi}{N_a} + 2\phi(1 - \phi)\|\vec{x}\| \right] \]

for \(1 - \phi > (Ne)_b/N_b\)

\[ D_b = \left\{ \begin{array}{ll}
\frac{k_b T \overrightarrow{B}_b(Ne)_b}{(1 - \phi)N_b} \left[ 1 - \phi + \frac{\phi}{N_a} + 2\phi(1 - \phi)\|\vec{x}\| \right] \\
(1 - \phi)N_b \left[ 1 - \phi + \frac{\phi}{N_a} + 2\phi(1 - \phi)\|\vec{x}\| \right] 
\end{array} \right. \]

for \(1 - \phi < (Ne)_b/N_b\)

and the marker velocity is:

\[ v = k_b T \left( \overrightarrow{B}_a - \frac{\overrightarrow{B}_b(Ne)_b}{(1 - \phi)N_b} \right) \left[ 1 - \phi \overrightarrow{B}_a + \phi \overrightarrow{B}_b(Ne)_b \right] \nabla \phi \]

for \(1 - \phi < (Ne)_b/N_b\)

and

\[ v = k_b T (\overrightarrow{B}_a - \overrightarrow{B}_b) \left[ \frac{1 - \phi + \phi}{N_a} + 2\phi(1 - \phi)\|\vec{x}\| \right] \nabla \phi \]

for \(1 - \phi < (Ne)_b/N_b\)

**MARKER MOVEMENTS**

**Theory**

As indicated previously, experiments in which the movement of inert markers in the diffusion couple are monitored offer the best way of distinguishing which of two assumptions, the \(J_k = 0\) assumption of Bjal or the \(\nabla \mu_k = 0\) assumption of the present treatment, is valid. If the Bjal assumption is correct the marker(s) should not move relative to the origin of the co-ordinate system whereas the present treatment predicts a marker velocity equal to the product of the difference of the intrinsic diffusion coefficients \(D_a - D_b\) and the gradient in composition \(\nabla \phi\). The direction of movement is toward the side of the couple richest in the fastest diffusing species, i.e., if \(D_a > D_b\), \(v\) is toward the A-rich side.

Consider a linear infinite diffusion couple containing a marker in the initial interface at a position \(x_0\) relative to the origin. Define a second co-ordinate system \(x_0\) using the particle as the origin so that:

\[ x = x_0 + x_m \] (44)

As \(\partial/\partial x_0 = \partial/\partial x\), the diffusion equation [equation (12)] can be written as:

\[ \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x_0} \left( \overrightarrow{B}(\phi) \frac{\partial \phi}{\partial x_0} \right) \] (45)

For the infinite diffusion couple it is useful to make the Boltzmann transformation* and define the variable:

\[ u = x_0/\sqrt{t} \] (46)

In terms of this variable the diffusion equation may be written as:

\[ -\frac{1}{2} \frac{du}{dt} \frac{\partial \phi}{\partial u} = \frac{d}{du} \left[ \overrightarrow{B}(\phi) \frac{\partial \phi}{\partial u} \right] \] (47)

The concentration \(\phi = \Phi(u)\) is now the solution to an ordinary differential equation. Moreover, as the particle is always at \(x_0 = 0\), \(u = 0\), it always stays at a constant composition \(\phi = \Phi(0)\), as time increases.

Define \(D_a(\phi) - D_b(\phi) = \Delta D(\phi)\). The marker velocity may be written as:

\[ v = \Delta D(\phi_0) \frac{\partial \phi}{\partial x_0} = \Delta D(\phi_0) \frac{\partial \phi}{\partial x_0} \bigg|_{x_0=0} \] (48)

As \(\partial \phi/\partial x_0 \big|_{x_0=0} = \Phi'(0)t^{-1/2}\), where \(\Phi'(0) = (d\Phi(u)/du)_{u=0}\), the marker velocity becomes:

\[ v = \Delta D(\phi_0) \Phi'(0)t^{-1/2} \] (49)

The change in marker position \(\Delta x_n\) may be determined by integration to yield:

\[ \Delta x_n = 2\Delta D(\phi_0) \Phi'(0)t^{-1/2} \] (50)
Thus, regardless of the composition dependence of $D_1 - D_2$, the marker should move as $\sqrt{t}$.

In general, $D(\phi)$ is a very strong function of composition in polymer blends. Equation (47) must be solved numerically to find $\Phi(u)$ and $\Phi(0)$. If $D_1$ and $D_2$ are almost constant with $\phi$ and not too different, the error function solution is a reasonable approximation, i.e.:

$$\Phi(u) \approx \left[ \frac{\phi^+ - \phi^-}{2} \right] \left[ \frac{1 + \operatorname{erf} \left( \frac{u}{2D^{1/2}} \right)}{2} \right] + \phi^-$$

(51)

where $D$ is $D(\phi) = (\phi^+ - \phi^-)^2 + (\phi^-)$ and $\phi^+$ and $\phi^-$ are the original concentrations of $\phi$ on left and right sides of the couple, respectively. Under these conditions $\Phi(0)$ is given by:

$$\Phi(0) \approx \frac{\phi^+ - \phi^-}{2} (\pi D)^{-1/2}$$

(52)

and

$$\Delta x_m \approx (\phi^+ - \phi^-) \Delta D(\phi) \left[ \frac{t}{(\pi D(\phi))^1/2} \right]$$

(53)

Large differences between $D_1$ and $D_2$ will lead to a strong asymmetric $\phi$ dependence of $D(\phi)$ and a decrease in $\Phi(0)$ over that predicted by equation (53).

Experiment

To test the validity of the BJL assumption, $J_s = 0$, movements of small gold markers in polystyrene diffusion couples have been monitored. The experimental geometry is shown in Figure 2. A film of almost monodisperse ($M_w/M_n \approx 1.2$) high molecular weight PS ($M_w = 2 \times 10^7$) was cast on a smooth silicon single crystal substrate. A small amount of gold was then evaporated onto the surface of the polystyrene film (designated PS1) in a vacuum of $\approx 1.3 \times 10^{-2}$ Pa. The gold nucleates on small islands which subsequently grow in size to $\approx 10$ nm in radius. These islands form irregular clusters as large as $200$ nm in diameter. The gold occupies only a minor portion ($<10%$) of the surface area of the film. A second polystyrene film (PS2) of lower molecular weight ($M_w = 1.1 \times 10^7$, $M_w/M_n = 1.03$) was deposited on a glass slide. The thickness of this film was uniform and $\approx 2$ nm. The PS2 film was floated off the glass slide onto the surface of a water bath and carefully picked up on the Au decorated PS1/silicon wafer to form the sandwich shown in Figure 2.

Rutherford backscattering spectrometry (RBS) was used to measure the depth $x_m$ of the Au markers beneath the free surface. In this technique a He $^+ \^+$ ion beam at an energy of 2.12 MeV is directed at normal incidence to the surface. The ion beam is elastically back-scattered by heavy nuclei in the sample, in this case Au and C, but the ions rebounding from a heavy Au nucleus retain a much higher fraction $K$ of their original energy ($K = 0.9225$) than those scattered from a much lighter C nucleus ($K = 0.2526$). If the scattering nucleus is beneath the surface of the sample, however, the He ion loses energy both on the way into the sample and on the way out. This energy is lost by electronic excitations of the sample and may be computed based on the stopping power of the individual elements in the sample. Whereas Au at the surface of the sample would produce a peak in the backscattered He ion energy spectrum at 1.936 MeV for 2.12 MeV incident ion energy, a layer of Au particles beneath the surface will produce a peak at a lower energy. The relation between the Au depth and energy shift of the Au was determined to be approximately rectilinear over the range of interest at $11$ nm per channel of $2.2$ nm keV$^{-1}$ by measuring the shift produced by PS films of known thickness. These were measured by optical interferometry.

The RBS spectrum of the coated silicon wafer was determined before annealing above $T_c$ and after annealing for progressively longer times at $170^\circ$C. The ion beam was moved for each spectrum so that a fresh region of the PS film sandwich was analysed. This precaution is necessary because the ion beam cross-links the PS film and will change the subsequent interdiffusion radically.

Figure 3 shows two RBS spectra, one from before the PS1/Au/PS2 sandwich was annealed and one after this wafer was heated for $1$ h at $170^\circ$C. The back-scattered energies from C and Au nuclei at the surface of the sandwich are marked. It is apparent that the gold particles have moved towards the surface (i.e., towards the faster diffusing PS2 ($M_w = 110000$) and away from the slower diffusing PS1 ($M_w = 200000$)). From the energy-depth calibration the observed peak shift corresponds to $\approx 130$ nm of marker movement toward the surface. Other results for the same annealing temperature, $170^\circ$C, are plotted in Figure 4. It is evident that that the marker shift $\Delta x_m$ is approximately rectilinear with $\sqrt{t}$ as predicted by equation (50).*

Other experiments were carried out reversing the positions of PS1 and PS2. In all cases the markers moved towards PS1 (now away from the surface). These shifts, however, were consistently larger than those shown in Figure 4 and are thought to be partially due to the relaxation of biaxial orientation in the cast high molecular weight film which would cause a thickening of this film and apparent marker movements indistinguishable from true diffusional marker movement. Similar but smaller initial marker movements were observed for the samples shown in Figure 4 (the PS1/Au/PS2 sandwiches) and these results were corrected for this initial transient thickening.

* It is also noteworthy that this shift could not be due to an asymmetric Brownian motion of the particles themselves due to the very different viscosities of the different molecular weight layers. Such Brownian motion would lead to broadening of the peak but would remain stationary in energy.
and

\[ \tilde{D}(\phi_0) \approx (1 - \phi_0)^2 D_\lambda^* \]  

(56)

and from equation (53)

\[ \Delta x_m \approx \left[ \frac{D_\lambda^* r}{\pi} \right]^{1/2} \]  

(57)

From both self diffusion measurements in \( 110 \, 000 \, M_w \) PS at a slightly lower temperature, \( 150^\circ C \), and theoretical extrapolations, \( D_\lambda^* \) is estimated to be \( 3 \times 10^{-13} \) cm\(^2\) s\(^{-1}\). The slope of the estimated \( \Delta x_m \) versus \( t^{1/2} \) plot, \( (D_\lambda^* r/\pi)^{1/2} \), is 31 nm s\(^{-1/2}\) whereas the slope of the experimental \( \Delta x_m \) versus \( t^{1/2} \) curve in Figure 2 is 22 nm s\(^{-1/2}\).

While part of the discrepancy may be due to the approximations involved in deriving equation (57), part of the discrepancy may be due to a non-zero \( V \mu_\lambda \). The high molecular weight PS1 must swell greatly (create large numbers of vacancies) to accept the large volume of PS2 diffusing into it. Such swelling will ultimately require reptation of the high molecular weight chains to relax the osmotic pressure. If this reptation cannot occur rapidly enough to relax \( V \mu_\lambda \) fully, a \( V \mu_\lambda \) will develop and the marker movement velocity will not be as rapid as predicted by theory.

It seems useful also to discuss other recent polymer interdiffusion experiments in view of these results. Klein and Briscoe\(^4\) and Klein\(^5\) measured the concentration

\[ D_\lambda^* = \frac{N e B_0 k_B T}{N_\lambda^2} \]  

Then

\[ \Delta D(\phi_0) \approx D_\lambda(\phi_0) = (1 - \phi_0) D_\lambda^* \]  

(55)

\[ \Delta x_m \approx \left[ \frac{D_\lambda^* r}{\pi} \right]^{1/2} \]  

(57)

Figure 4 Gold marker movement \( \Delta x_m \) to the free surface (toward PS1) versus the square root of annealing time at \( 170^\circ C \). Results are corrected for initial thickening of the \( 10\mu \) PS2 film due to relaxation of biaxial orientation during the first half hour of annealing.

PLO YMER, 1984, Vol 25, April 479
profiles in diffusion couples made up of dilute (2% or less) concentrations of deuterated polyethylene (DPE) in protonated polyethylene (PE) initially in contact with protonated polyethylene. The concentration of DPE was measured using an i.r.-microdensitometry technique with a spatial resolution of \( \approx 100 \) \( \mu \text{m} \). The results should be described by equation (22):

\[
\bar{D} = N_e B A_0 T \left( \frac{1 - \phi}{N_A} + \frac{\phi}{N_B} \right)^2
\]

where \( \phi \) and \( N_A \) represent the volume fraction and degree of polymerization of DPE and \( N_B \) the degree of polymerization of PE. Under the dilute conditions used \( \bar{D} \) is independent of \( \phi \), i.e.

\[
\bar{D} \approx D^* = \frac{N_e B A_0 T}{N_A^2}
\]

and the error function solution to Hick's second law used by Klein is appropriate. Klein's experiments, which show that \( \bar{D} \propto N_A^{-1} \), therefore, are excellent verification of the reptation model.

Gilmore and coworkers\cite{12} have measured interdiffusion in a compatible polymer blend of polyvinylchloride (PVC) and poly(epsilon-caprolactone) (PCL). Pure PVC was butted against pure PCL. Various average molecular weights (broad distribution \( M_w/M_c = 2 \)) of each polymer were used. Concentration profiles were determined by finding the chlorine concentration using an electron microprobe with a spatial resolution of \( \approx 1 \) \( \mu \text{m} \). The data were fitted to an assumed error function solution and \( \bar{D}' \)s extracted. Gilmore et al. found \( \bar{D} \propto 1/M_c \) which they said was inconsistent, with the reptation model, which predicts \( D^* \propto 1/N_A^{-1} \). However, in a compatible blend, \( \bar{D} \) is given by equation (38):

\[
\bar{D} = k_B T \left[ \frac{(1 - \phi) \bar{D}_A(N_A)}{N_A} + \frac{\phi \bar{D}_B(N_B)}{N_B} \right] \left( 1 - \frac{\phi}{N_A} + \frac{\phi}{N_B} + 2 \phi(1 - \phi) \chi \right)
\]

As noted first by BJL for compatible blends, \( \chi \) must be strongly negative for any solubility so that the intermediate range of \( \phi \), \( 20(1 - \phi) \chi(1 - \phi)/N_A + \phi/N_B \). Therefore, \( \bar{D} \) should go approximately as \( N_A^{-1} \) or \( N_B^{-1} \) as observed.*

Finally Kumagai et al.\cite{11} have measured the interdiffusion of a thin film (2–3 \( \mu \text{m} \) thick) of narrow \( M_w \) PS, degree of polymerization \( N_A \), into a thick film (30–40 \( \mu \text{m} \)) of narrow \( M_w \) PS, degree of polymerization \( N_B \). The PS in the top film \( (N_A) \) was labelled with tritium and the decrease in the observed beta decay rate was monitored as diffusion occurred. The results were analysed as if the interdiffusion coefficient \( \bar{D} \) were independent of composition. There are two problems with this analysis. First, as the \( \bar{D}(\phi) \) varies markedly with \( \phi \) if \( N_A \) and \( N_B \) are more than slightly different, their assumed \( \phi(x,t) \) profile cannot be correct. As the observed radioactive decay should depend markedly on the form of the profile the \( \bar{D} \)'s extracted from the analysis are also incorrect. If \( \bar{D} \) really were independent of composition, whether the high or low \( M_w \) film was the thin film next to the counter should be irrelevant; \( \bar{D} \), however, was as much as a factor of 2 different for these two cases.

A second problem with such radioactive decay experiments in concentrated couples is that the entire concentration gradient moves toward or away from the free surface exactly as inert markers would move. Such motion would affect the attainment of the products of radioactive decay (\( \beta \) particles in this case) and thus the computed \( \bar{D} \). Thus, without a complete numerical solution for this diffusion problem no firm conclusions about possible conflicts with the reptation model are possible.

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* It is important to realize that for infinite dilution, \( \phi \to 0, \bar{D} \to k_B T B_A(N_A)^{-1} \) as \( \phi(1 - \phi) \chi \) goes to zero.