

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 polystyrene (one $2 \times 10^7 M_w$ 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 rubber¹ and crack healing in glassy polymers^{2,3} to the kinetics of phase separation in polymer blends^{4,5}. Attention has also been drawn to diffusion problems by recent theoretical advances^{6,7}, 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 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 polyethylene⁸⁻¹⁰.

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 weight¹¹ and from couples of chemically different, but compatible, polymers¹², 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, Jouffroy and Levinson¹³, hereafter abbreviated as B JL. 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 polymers¹⁴ nor for concentrated alloys (the famous Kirkendall effect in brass–copper couples^{15,16}), 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 μ_A and the chemical potential of B be μ_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

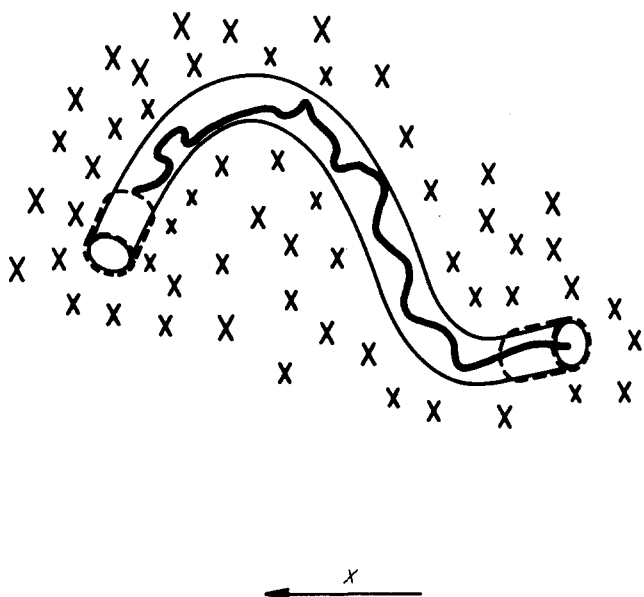


Figure 1 Schematic diagram of a polymer chain diffusing in the 'tube' defined by the topological constraints of neighbouring chains (crosses)

For this situation the Onsager relations can be written as follows:

$$J_A = -M_A \nabla(\mu_A - \mu_v) \quad (1a)$$

$$J_B = -M_B \nabla(\mu_B - \mu_v) \quad (1b)$$

$$J_v = +M_A \nabla(\mu_A - \mu_v) + M_B \nabla(\mu_B - \mu_v) \quad (1c)$$

where M_A and M_B are Onsager coefficients for the A and B molecules discussed and where the off-diagonal coefficients $M_{AB} = M_{BA}$ are assumed to be zero. Equation (1c) can be derived from the fact that lattice sites are conserved which means:

$$J_A + J_B + J_v = 0 \quad (2)$$

At this point B JL make the assumption that $J_v = 0$ which leads to a chemical potential gradient for vacancies given by:

$$\nabla \mu_v = (M_A \nabla \mu_A + M_B \nabla \mu_B) / (M_A + M_B) \quad (3)$$

and the Onsager relations:

$$J_A = -J_B = \frac{-M_A M_B}{M_A + M_B} \nabla(\mu_A - \mu_B). \quad (4)$$

The assumption of a zero J_v leads to an appreciable $\nabla \mu_v$ in the case when M_A and M_B are unequal. As M_A and M_B are strongly dependent on N_A and N_B as shown later, large gradients in the chemical potential of vacancies will arise from equation (3) even in the interdiffusion of two chemically identical polymers of different molecular weight. Finite $\nabla \mu_v$'s also imply the existence of a gradient in osmotic pressure:

$$\nabla \Pi = \nabla \mu_v / \Omega \quad (5)$$

where Ω is the volume of a quasi-lattice site assumed to be the same for both A and B molecules. In melts of linear

polymers, any such gradients in Π 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 $\nabla \mu_v = 0$, 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^{17,18} become:

$$J_A = -M_A \nabla \mu_A \quad (6a)$$

$$J_B = -M_B \nabla \mu_B \quad (6b)$$

$$J_v = M_A \nabla \mu_A + M_B \nabla \mu_B \quad (6c)$$

The vacancy flux will be detectable by marker movement experiments. Suppose an inert particle marker is placed in the diffusion couple where the gradients $\nabla \mu_A$ and $\nabla \mu_B$ are finite. The marker will move, relative to the origin of co-ordinate system, with a velocity given by:

$$v = \Omega J_v = \Omega (M_A \nabla \mu_A + M_B \nabla \mu_B) \quad (7)$$

CHEMICAL POTENTIAL GRADIENTS

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

$$F = k_B T \left(\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln (1-\phi) + \chi \phi (1-\phi) \right) \quad (8)$$

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

$$\nabla \mu_A = \frac{k_B T}{\phi} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \nabla \phi \quad (9a)$$

$$\nabla \mu_B = \frac{k_B T}{1-\phi} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \nabla \phi \quad (9b)$$

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

INTERDIFFUSION COEFFICIENT

The total flux J_A^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.,

$$J_A^T = -M_A \nabla \mu_A + \phi (M_A \nabla \mu_A + M_B \nabla \mu_B) \\ J_A^T = -(1-\phi) M_A \nabla \mu_A + \phi M_B \nabla \mu_B \quad (10)$$

Conservation of A segments leads to:

$$\frac{1}{\Omega} \frac{\partial \phi}{\partial t} = \nabla (-J_A^T) \quad (11)$$

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

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

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

$$\tilde{D} = \Omega k_B T \left(\frac{1-\phi}{\phi} M_A + \frac{\phi}{1-\phi} M_B \right) \times \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad (13)$$

This expression is different from the one found by BJL using the assumption $J_v = 0$, i.e.:

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

INTRINSIC DIFFUSION COEFFICIENTS

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

$$J_A = \frac{-D_A}{\Omega} \nabla \phi \quad (14a)$$

$$J_B = \frac{+D_B}{\Omega} \nabla \phi = \frac{-D_B}{\Omega} \nabla(1-\phi) \quad (14b)$$

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

$$D_A = \Omega k_B T \frac{M_A}{\phi} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad (15a)$$

$$D_B = \Omega k_B T \frac{M_B}{(1-\phi)} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad (15b)$$

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

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

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

$$v = \Omega k_B T \left(\frac{M_A}{\phi} - \frac{M_B}{1-\phi} \right) \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \nabla \phi \quad (16)$$

Measurements of v plus $\phi(x, t)$ should allow D_A , D_B and \tilde{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 these 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 $(Ne)_A$ and $(Ne)_B$, 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 $(Ne)_A$ and $(Ne)_B$. In the short chain limit:

$$B_A = \bar{B}_A \quad (17)$$

$$B_B = \bar{B}_B$$

whereas in the long chain limit:

$$B_A = \bar{B}_A (Ne)_A / N_A \quad (18)$$

$$B_B = \bar{B}_B (Ne)_B / N_B$$

where \bar{B}_A and \bar{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:

$$M_A = B_A \phi / \Omega \quad (19)$$

$$M_B = B_B (1-\phi) / \Omega$$

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

Short chain limit ($N_A < N_B < Ne = (Ne)_A = (Ne)_B$)

In this limit $\bar{B}_A = \bar{B}_B = B_0$ and $M_A = B_0 \phi / \Omega$, $M_B = B_0 (1-\phi) / \Omega$. The interdiffusion coefficient \tilde{D} is given by:

$$\tilde{D} = B_0 k_B T \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \quad (20)$$

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

$$D_A = D_B = B_0 k_B T \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \quad (21)$$

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 ($N_B > N_A > Ne$)

In this limit $\bar{B}_A = B_0 Ne / N_A$, $\bar{B}_B = B_0 Ne / N_B$ and $M_A = \phi B_0 Ne / (N_A \Omega)$, $M_B = (1-\phi) B_0 Ne / (N_B \Omega)$. The interdiffusion coefficient is:

$$\tilde{D} = Ne B_0 k_B T \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right)^2 \quad (22)$$

D_A and D_B are given by:

$$D_A = Ne B_0 k_B T \left(\frac{1-\phi}{N_A^2} + \frac{\phi}{N_A N_B} \right) \quad (23)$$

$$D_B = Ne B_0 k_B T \left(\frac{\phi}{N_B^2} + \frac{1-\phi}{N_A N_B} \right)$$

and the velocity of the marker, by:

$$v = NeB_0k_B T \left(\frac{1}{N_A} - \frac{1}{N_B} \right) \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \nabla \phi \quad (24)$$

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

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

In this limit $(Ne)_B$ for the B chains diluted with short A chains should become $Ne/(1-\phi)$ where Ne is the number of segments between entanglements in the undiluted polymer B. Thus, for $(1-\phi) > Ne/N_B$, $\bar{B}_B = B_0 Ne / [(1-\phi)N_B]$, $\bar{B}_A = B_0$ and $M_B = B_0 Ne / N_B \Omega$, $M_A = \phi B_0 / \Omega$, the interdiffusion coefficient \bar{D} is:

$$\bar{D} = B_0 k_B T \left(1 - \phi + \frac{\phi Ne}{(1-\phi)N_B} \right) \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \quad (25)$$

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

$$D_A = B_0 k_B T \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \quad (26)$$

$$D_B = \frac{B_0 k_B T Ne}{N_B (1-\phi)} \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \quad (27)$$

for $(1-\phi) > Ne/N_B$ and $D_B = D_A$ for $(1-\phi) < Ne/N_B$.

The marker velocity is:

$$v = B_0 k_B T \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right) \left(1 - \frac{Ne}{N_B (1-\phi)} \right) \quad (28)$$

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

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

Short chain limit ($N = N_A = N_B < (Ne)_A$ or $(Ne)_B$)

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

$$\bar{D} = k_B T \bar{B}(\phi) \left[\frac{1}{N} + \phi(1-\phi)|\chi| \right] \quad (29)$$

The intrinsic diffusion coefficients are:

$$D_A = k_B T \bar{B}_A \left[\frac{1}{N} + \phi(1-\phi)|\chi| \right] \quad (30a)$$

$$D_B = k_B T \bar{B}_B \left[\frac{1}{N} + \phi(1-\phi)|\chi| \right] \quad (30b)$$

* This is the same assumption made by BJL but may not be a good one if T_g of the blend varies appreciably with composition

and the marker velocity is:

$$v = k_B T (\bar{B}_A - \bar{B}_B) \left[\frac{1}{N} + \phi(1-\phi)|\chi| \right] \nabla \phi \quad (31)$$

In the limit $\bar{B}_A = \bar{B}_B$ these results reduce to those found by BJL.

Long chain limit ($N = N_A = N_B > (Ne)_A$ or $(Ne)_B$)

In this case $M_A = \bar{B}_A (Ne)_A \phi / (N \Omega)$ and $M_B = \bar{B}_B (Ne)_B (1-\phi) / (N \Omega)$ so that the interdiffusion coefficient is given by:

$$\bar{D} = \frac{k_B T \bar{B}_\infty(\phi)}{N} \left(\frac{1}{N} + 2\phi(1-\phi)|\chi| \right) \quad (32)$$

where $\bar{B}_\infty(\phi) \equiv (1-\phi)\bar{B}_A(Ne)_A + \phi\bar{B}_B(Ne)_B$. The intrinsic diffusion coefficients are:

$$D_A = \frac{k_B T \bar{B}_A(Ne)_A}{N} \left(\frac{1}{N} + 2\phi(1-\phi)|\chi| \right) \quad (32a)$$

$$D_B = \frac{k_B T \bar{B}_B(Ne)_B}{N} \left(\frac{1}{N} + 2\phi(1-\phi)|\chi| \right) \quad (33b)$$

and the marker velocity is:

$$v = \frac{k_B T}{N} (\bar{B}_A(Ne)_A - \bar{B}_B(Ne)_B) \left(\frac{1}{N} + 2\phi(1-\phi)|\chi| \right) \nabla \phi \quad (34)$$

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

INTERDIFFUSION OF CHEMICALLY DIFFERENT POLYMERS OF DIFFERENT MOLECULAR WEIGHT

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

In this case $M_A = \bar{B}_A \phi / \Omega$ and $M_B = \bar{B}_B (1-\phi) / \Omega$ so that the interdiffusion coefficient is given by:

$$\bar{D} = k_B T \bar{B}(\phi) \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + \phi(1-\phi)|\chi| \right] \quad (35)$$

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

$$D_A = k_B T \bar{B}_A \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + \phi(1-\phi)|\chi| \right] \quad (36a)$$

$$D_B = k_B T \bar{B}_B \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + \phi(1-\phi)|\chi| \right] \quad (36b)$$

and the marker velocity is:

$$v = k_B T (\bar{B}_A - \bar{B}_B) \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + \phi(1-\phi)|\chi| \right] \nabla \phi \quad (37)$$

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

In this case $M_A = \bar{B}_A (Ne)_A \phi / N_A \Omega$ and

$M_B = \bar{B}_B(Ne)_A(1-\phi)/N_B\Omega$ so that \bar{D} is given by:

$$\bar{D} = k_B T \left(\frac{(1-\phi)\bar{B}_A(Ne)_A}{N_A} + \frac{\phi\bar{B}_B(Ne)_B}{N_B} \right) \times \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right) \quad (38)$$

The interdiffusion coefficients are:

$$D_A = \frac{k_B T \bar{B}_A(Ne)_A}{N_A} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad (39a)$$

$$D_B = \frac{k_B T \bar{B}_B(Ne)_B}{N_B} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad (39b)$$

and the marker velocity is:

$$v = k_B T \left(\frac{\bar{B}_A(Ne)_A}{N_A} - \frac{\bar{B}_B(Ne)_B}{N_B} \right) \times \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right) \nabla\phi \quad (40)$$

Short chains diffusing into long chains ($N_B > (Ne)_B$ and $(Ne)_A > N_A$)

Here $M_A = \bar{B}_A\phi/\Omega$ and $M_B = \bar{B}_B(Ne)_B/N_B\Omega$ for $(1-\phi) > (Ne)_B/N_B$ and $M_B = \bar{B}_B(1-\phi)/\Omega$ for $(1-\phi) < (Ne)_B/N_B$ so the interdiffusion coefficient is:

$$\bar{D} = k_B T \left[(1-\phi)\bar{B}_A + \frac{\phi\bar{B}_B(Ne)_B}{(1-\phi)N_B} \right] \times \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad \text{for } (1-\phi) > (Ne)_B/N_B \quad (41)$$

and

$$\bar{D} = k_B T \bar{B}(\phi) \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad \text{for } 1-\phi < (Ne)_B/N_B$$

The intrinsic diffusion coefficients are:

$$D_A = k_B T \bar{B}_A \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] \quad (42a)$$

$$D_B = \begin{cases} \frac{k_B T \bar{B}_B(Ne)_B}{(1-\phi)N_B} \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] & \text{for } 1-\phi > (Ne)_B/N_B \\ k_B T \bar{B}_B \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_B} + 2\phi(1-\phi)|\chi| \right] & \text{for } 1-\phi < (Ne)_B/N_B \end{cases} \quad (42b)$$

and the marker velocity is:

$$v = k_B T \left(\bar{B}_A - \frac{\bar{B}_B(Ne)_B}{(1-\phi)N_B} \right) \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_A} + 2\phi(1-\phi)|\chi| \right] \nabla\phi \quad \text{for } 1-\phi > (Ne)_B/N_B$$

and (43)

$$v = k_B T (\bar{B}_A - \bar{B}_B) \left[\frac{1-\phi}{N_A} + \frac{\phi}{N_A} + 2\phi(1-\phi)|\chi| \right] \nabla\phi \quad \text{for } 1-\phi < (Ne)_B/N_B$$

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 $J_v=0$ assumption of B JL or the $\nabla\mu_v=0$ assumption of the present treatment, is valid. If the B JL 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_m relative to the origin. Define a second co-ordinate system x_o using the particle as the origin so that:

$$x = x_o + x_m \quad (44)$$

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

$$\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial x_o} \left(\bar{D}(\phi) \frac{\partial\phi}{\partial x_o} \right) \quad (45)$$

For the infinite diffusion couple it is useful to make the Boltzmann transformation¹⁹ and define the variable:

$$u = x_o/\sqrt{t} \quad (46)$$

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

$$-\frac{1}{2}u \frac{d\phi}{du} = \frac{d}{du} \left[\bar{D}(\phi) \frac{d\phi}{du} \right] \quad (47)$$

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

Define $D_A(\phi) - D_B(\phi)$ as $\Delta D(\phi)$. The marker velocity may be written as:

$$v = \Delta D(\phi_o) \frac{\partial\phi}{\partial x} \Big|_{x_m} = \Delta D(\phi_o) \frac{\partial\phi}{\partial x_o} \Big|_{x_o=0} \quad (48)$$

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

$$v = \Delta D(\phi_o) \Phi'(0) t^{-1/2} \quad (49)$$

The change in marker position Δx_m may be determined by integration to yield:

$$\Delta x_m = 2\Delta D(\phi_o) \Phi'(0) t^{1/2} \quad (50)$$

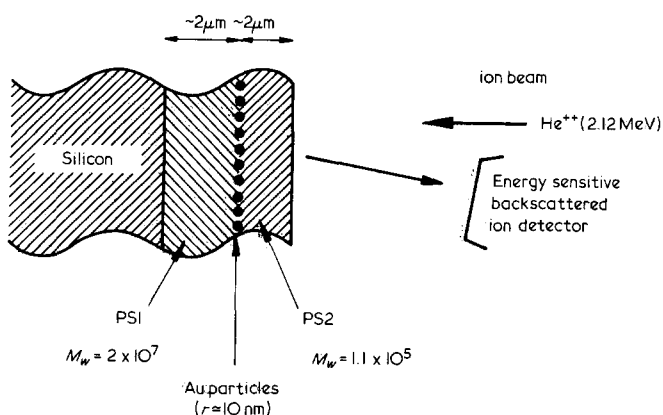


Figure 2 Configuration of Rutherford backscattering experiment to determine gold marker movements

Thus, regardless of the composition dependence of $D_A - D_B$ the marker should move as \sqrt{t} .

In general, as $\bar{D}(\phi)$ 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_A and D_B are almost constant with ϕ and not too different, the error function solution is a reasonable approximation, i.e.:

$$\Phi(u) \cong \left[\frac{\phi^+ - \phi^-}{2} \right] \left[1 + \operatorname{erf} \frac{u}{2(\bar{D})^{1/2}} \right] + \phi^- \quad (51)$$

where $\bar{D} = \bar{D}(\phi_0 = (\phi^+ - \phi^-)/2 + \phi^-)$ and ϕ^+ and ϕ^- are the original concentrations of A on right and left sides of the couple, respectively. Under these conditions $\Phi'(0)$ is given by:

$$\Phi'(0) \cong -\frac{\phi^+ - \phi^-}{2} (\pi \bar{D})^{-1/2} \quad (52)$$

and

$$\Delta x_m \cong (\phi^+ - \phi^-) \Delta D(\phi_0) \left[\frac{t}{\pi \bar{D}(\phi_0)} \right]^{1/2} \quad (53)$$

Large differences between D_A and D_B will lead to a strong asymmetric ϕ dependence of $\bar{D}(\phi)$ and a decrease in $\Phi'(0)$ over that predicted by equation (53).

Experiment

To test the validity of the B JL assumption, $J_v = 0$, 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 $\approx 1.3 \times 10^{-3}$ Pa. The gold nucleates in small islands which subsequently grow in size to ≈ 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 ($M_w = 1.1 \times 10^5$, $M_w/M_n = 1.03$) was deposited on a glass slide. The thickness of this film was uniform and $\approx 2 \mu\text{m}$. 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 sample²⁰. Whereas Au at the surface of the sample would produce a peak in the backscattered He ion energy spectrum at 1.956 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_g and after annealing for progressively longer times at 170°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°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 ($M_w = 110\,000$) and away from the slower diffusing PS1 ($M_w = 20\,000\,000$)). From the energy-depth calibration the observed peak shift corresponds to ≈ 130 nm of marker movement toward the surface. Other results for the same annealing temperature, 170°C, are plotted in Figure 4. It is evident that the marker shift Δx_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 but the peak would remain stationary in energy.

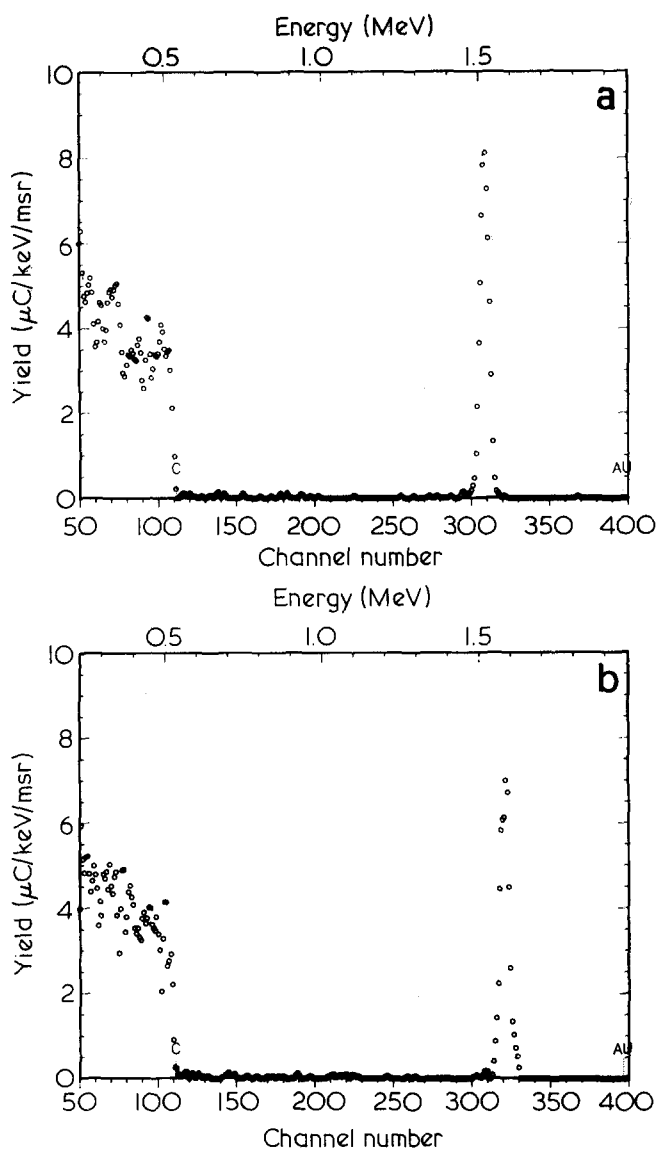


Figure 3 Rutherford backscattering spectra from (a) PS1-Au-PS2 sandwich before annealing; (b) PS1-Au-PS2 sandwich annealed 1 h at 170°C in vacuum

DISCUSSION

The marker movement experiments show clearly that vacancy fluxes during polymer-polymer interdiffusion cannot be ignored. Whether these fluxes are as large as that required to maintain local equilibrium of vacancies, i.e., $\nabla\mu_v=0$, is yet to be established. Unfortunately, an accurate estimate of $\Phi'(0)$ and thus Δx_m requires a numerical solution of equation (47) which has not yet been attempted. A crude overestimate of Δx_m may be made using equation (50), which, strictly, is not applicable as D_A and D_B differ by as much as 5 orders of magnitude. Let D_A^* represent the infinite dilution (or self) diffusion coefficient of PS2, i.e.:

$$D_A^* = \frac{NeB_0k_B T}{N_A^2} \quad (54)$$

Then

$$\Delta D(\phi_0) \cong D_A(\phi_0) = (1 - \phi_0)D_A^* \quad (55)$$

and

$$\bar{D}(\phi_0) \cong (1 - \phi_0)^2 D_A^* \quad (56)$$

and from equation (53)

$$\Delta x_m \cong \left(\frac{D_A^* t}{\pi} \right)^{1/2} \quad (57)$$

From both self diffusion measurements in 110 000 M_w PS at a slightly lower temperature, 150°C¹¹, and theoretical extrapolations²¹, D_A^* is estimated to be $\approx 3 \times 10^{-13}$ cm² s⁻¹. The slope of the estimated Δx_m versus $t^{1/2}$ plot, $(D_A^*/\pi)^{1/2}$ is 31 nm s^{-1/2} whereas the slope of the experimental Δx_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 $\nabla\mu_v$. 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 $\nabla\Pi$ fully, a $\nabla\mu_v$ 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 Briscoe⁹ and Klein⁸ measured the concentration

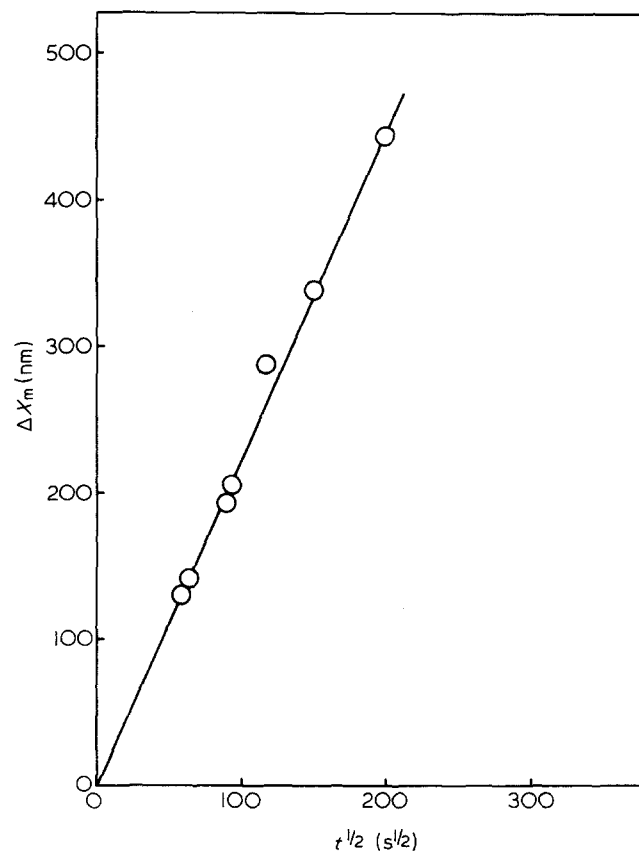


Figure 4 Gold marker movement Δx_m to the free surface (toward PS1) versus the square root of annealing time at 170°C. Results are corrected for initial thickening of the top PS2 film due to relaxation of biaxial orientation during the first half hour of annealing

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):

$$\bar{D} = NeB_0k_B T \left(\frac{1-\phi}{N_A} + \frac{\phi}{N_B} \right)^2$$

where ϕ 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 ϕ , i.e.

$$\bar{D} \approx D_A^* = \frac{NeB_0k_B T}{N_A^2}$$

and the error function solution to Fick's second law used by Klein is appropriate. Klein's experiments, which show that $\bar{D} \propto N_A^{-2}$, therefore, are excellent verification of the reptation model.

Gilmore and coworkers^{1,2} have measured interdiffusion in a compatible polymer blend of polyvinylchloride (PVC) and poly(ϵ -caprolactone) (PCL). Pure PVC was butted against pure PCL. Various average molecular weights (broad distribution $M_w/M_n \approx 2$) 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 $\bar{D} \propto 1/M_w$ which they said was inconsistent with the reptation model, which predicts $D_A^* \propto 1/N_A^2$. However, in a compatible blend, \bar{D} is given by equation (38):

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

As noted first by BJJL for compatible blends, χ must be strongly negative for any solubility so that over the intermediate range of ϕ , $2\phi(1-\phi)\chi \gg (1-\phi)/N_A + \phi/N_B$. Therefore, \bar{D} should go approximately as N_A^{-1} or N_B^{-1} as observed.*

Finally Kumagai *et al.*¹¹ have measured the interdiffusion of a thin film (2–3 μm thick) of narrow M_w PS, degree of polymerization N_A , into a thick film (30–40 μm s) 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 count rate was monitored as diffusion occurred. The results were analysed as if the interdiffusion coefficient \bar{D} were

* It is important to realize that for infinite dilution, $\phi \rightarrow 0$, $\bar{D} \rightarrow \frac{k_B T \bar{B}_A(Ne)_A}{N_A^2}$ as $\phi(1-\phi)|\chi|$ goes to zero

independent of composition. There are two problems with this analysis. First, as the $\bar{D}(\phi)$ varies markedly with ϕ 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 attenuation of the products of radioactive decay (β 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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