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Modulated differential scanning calorimetry: 8. Interface development between films of polyepichlorohydrin and poly(vinyl acetate)

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A thermal method with the potential to determine the weight fraction and the interfacial thickness in multiphase polymer materials is described. The extent of interdiffusion, and hence the development of an interface between two miscible polymers, polyepichlorohydrin and poly(vinyl acetate), with time at 100°C has been studied by means of modulated-temperature differential scanning calorimetry. This polymer pair is known to be miscible. By measurement of the change of increment of heat capacity in the glass transition region, the total interface content can be determined. With increasing time, the interfacial thickness increases. The average interfacial thickness is about 0.1 mm after a diffusion time of 4180 min. The interfacial thickness grows at $t^{1/2}$, where t is the diffusion time, and the interdiffusion coefficient is about $6.25 \times 10^{-11}\,\mathrm{cm^2\,s^{-1}}$, assuming that the diffusion rates of the two polymers are equal. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

For the blending of two miscible polymers, the free energy of mixing, ΔF, arising from the classical Flory–Higgins[1,2] model, is shown in equation (1).

$$\Delta F/kT = \phi_A/N_A \ln\phi_A + \phi_B/N_B \ln\phi_B + \chi\phi_B\phi_B \quad (1)$$

N_A, N_B and ϕ_A, ϕ_B are the degrees of polymerization and mean volume fractions, respectively, of the two components A and B. χ is the net repeat unit A–repeat unit B interaction energy. The first two terms represent the translational entropy of mixing and are much smaller than the values for monomeric mixing. The third term, which represents enthalpic interactions, retains its regular solution value in that it is uninfluenced by N. This is because the intimate mutual interpenetration of the chains is such that the number of repeat unit A–repeat unit B contacts remains large. The net result is that the role of entropy in driving the mixing may be heavily suppressed relative to the enthalpic contribution. When two species are placed in contact, it is convenient to represent the interdiffusion coefficient (D_m) across the interface between them as a product of a term involving their intrinsic diffusivity and a thermodynamic term representing the driving force for mixing[3,4].

$$D_m = (\phi_B N_A D_A + \phi_A N_B D_B)(\phi_B/N_A + \phi_A/N_B - 2\phi_A\phi_B\chi) \quad (2)$$

D_A and D_B are the diffusion coefficients of polymer A and B. There are two limits here: where χ is large and negative, the coefficient D_m is magnified greatly relative to either diffusion coefficient. This is referred to as accelerated interdiffusion[5]. The other limit is where χ is positive. The latter is the most common case for polymer mixtures[6]. The interactions between A and B repeat units are dispersive in nature. In this case, phase separation occurs[7]. In an incompatible system, the equilibrium interfacial thickness is attained when the entropy effect equals the enthalpy effect[8–11], giving a thickness of 1–20 nm typically, depending on the degree of compatibility[8–11]. The formation of a diffuse interface is important in adhesion[8,12], phase separation and morphology in polymer blends[13–15], welding and crack healing[16,17] and co-extrusion[18].

Many techniques have been used in attempts to determine the fraction of materials contained in the mixed regions between microphases. Small angle X-ray scattering (SAXS) or neutron scattering techniques[19] can be used to analyse the width of the interface. The experimental difficulties of these methods have been discussed[20,21] fully by a number of authors. Dynamic mechanical[22] data can be modelled by assuming inter-

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Table 1 Source and characterisation data for the polymers

Polymer	Source	$M_w \times 10^{-5}$	M_w/M_n
PVAc	Aldrich	5.2	3.8
PECH	Aldrich	1.98	2.5

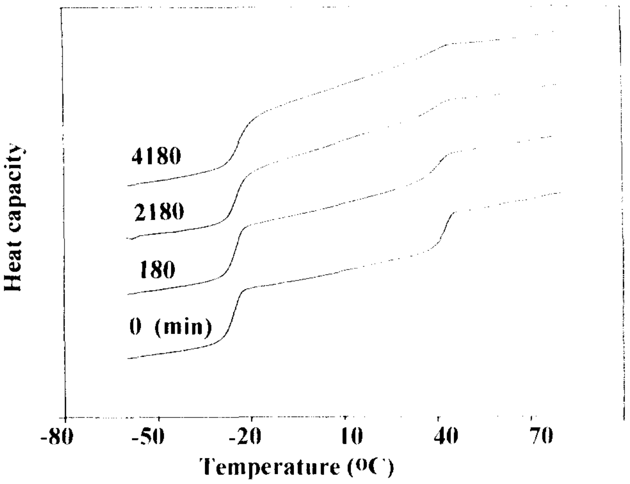

Figure 1 Heat capacity vs temperature at different diffusion times

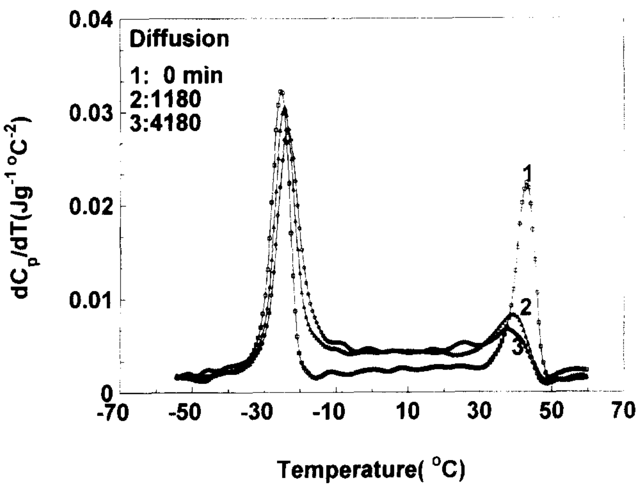

Figure 2 Differential of heat capacity vs temperature at different diffusion times

facial profiles, but this method requires large interfacial volume fractions. A technique that can yield both interfacial width and profile is transmission electron microscopy (TEM), and results from highly ordered systems have been obtained that are in good agreement with SAXS, dynamic mechanical[23] and ellipsometric measurements[24]. However, preparation of samples for which TEM techniques may be used can be difficult. However, it has been shown to be possible[25] to estimate the weight fraction of interfacial materials by means of modulated-temperature differential scanning calorimetry (m.t.d.s.c.)[26].

In this work, the interfaces formed by thermal diffusion between two compatible polymers[27], polyepichlorohydrin (PECH) and poly(vinyl acetate) (PVAc) films, have been studied by means of m.t.d.s.c. This is a new method for studying interfaces. The total quantity of interface, interfacial thickness and macromolecular interdiffusion coefficient have been calculated.

EXPERIMENTAL

Materials and preparation

The characteristics and sources of the polymers used are given in *Table 1*. The average molecular weights and polydispersities were determined by gel permeation chromatography (g.p.c.) relative to polystyrene standards. The films used in the diffusion studies had a thickness of 0.2 mm for PVAc and 0.24 mm for PECH. The PVAc and PECH film was initially superimposed and put into a m.t.d.s.c. pan. The samples were annealed for different times at 100°C under a N_2 flux, and then cooled to −80°C at a cooling rate of 10°C min^{-1}. The samples were then scanned using the conditions below.

Instrumentation

A m.t.d.s.c. manufactured by TA Instruments was used. An oscillation amplitude of 1.5°C and a period of 60 s were used with a heating rate of 3°C min^{-1}. The calorimeter was calibrated with an indium standard.

RESULTS AND DISCUSSION

Heat capacity in the glass transition region determined by conventional d.s.c. yields only an apparent value[28], because the total heat flow includes a relaxation content. However, m.t.d.s.c. can separate the relaxation signal from the total heat flow, so that the true heat capacity can be obtained in the glass transition region[28]. Heat capacity data can reflect the interfacial development by interdiffusion. *Figure 1* shows the changes of heat capacity with temperature at four diffusion times. In the glass transition region, the heat capacity traces are different for the different diffusion times. However, it is difficult to draw more detailed conclusions. The differential of heat capacity signal, dC_p/dT, shows clearly that an interface is formed by thermal diffusion (see *Figure 2*). This is shown by the increase in the dC_p/dT signal between the two glass transitions. With increasing diffusion time, the concentration of the interface will change and its thickness will increase.

During conventional d.s.c. studies of a partially miscible polymer blend, Fried[29] found that the increment of heat capacity, ΔC_p, in the glass transition region changed in magnitude. He attributed this behaviour to the presence of a large amount of interfacial material and postulated that the amount of this material could be determined by the ratio F shown below.

$$F = (\omega_{10}\Delta C_{p1} + \omega_{20}\Delta C_{p2})/(\omega_{10}\Delta C_{p10} + \omega_{20}\Delta C_{p20}) \tag{3}$$

ΔC_{p10} is the increment of heat capacity at T_{g1} before mixing. ω_{10} and ω_{20} are the weight fractions of polymer 1 and polymer 2, respectively. ΔC_{p1} and ΔC_{p2} are the increments of heat capacity at T_{g1} and T_{g2} for polymer 1 and polymer 2, respectively, after mixing. When there exists no interface, the value of F is equal to 1.0. The Fried ratio, F, provides a qualitative measure of interfacial material in polymer blends.

For an immiscible polymer blend, the total ΔC_p is the linear addition of the ΔC_p values of two constituent polymers[30].

$$\Delta C_p = \omega_{10}\Delta C_{p10} + \omega_{20}\Delta C_{p20} \quad (4)$$

When the system exhibits an interface, the following equation applies.

$$\Delta C_p = \Delta C_{pl} + \Delta C_{p2} + \Delta C_{pi} \quad (5)$$

$$\Delta C_{pl} = \omega_1\Delta C_{p10} \quad (6)$$

$$\Delta C_{p2} = \omega_2\Delta C_{p20} \quad (7)$$

ΔC_{pi} is the increment of heat capacity of the interface in its glass transition region. ω_1 and ω_2 are the weight fractions of polymer 1 and polymer 2, respectively, after mixing. The weight fractions, δ_1 and δ_2, in the polymer 1–polymer 2 interfacial regions can be obtained.

$$\delta_1 = \omega_{10} - \Delta C_{pl}/\Delta C_{p10} \quad (8)$$

$$\delta_2 = \omega_{20} - \Delta C_{p2}/C_{p20} \quad (9)$$

One of the major problems in the study is how to calculate the increment of heat capacity. Based on the differential of heat capacity signals, increment of heat capacity, ΔC_p, can be calculated. The value of the apparent heat capacity, ΔC_p^n, determined directly by m.t.d.s.c. can be presented as follows.

$$\Delta C_p^n = A_0 + A + BT + f(t) \quad (10)$$

A_0 is the system state constant. Different state constants result in shifts of the base line. A and B are constants and $f(T)$ is a function of temperature. Out of the transition region, $f(T)$ is zero.

Consider the value of the differential of the apparent heat capacity with respect to temperature.

$$\mathrm{d}C_p^n/\mathrm{d}T = B + \mathrm{d}f(T)/\mathrm{d}T \quad (11)$$

The effect of the state of the system on a themodynamic quantity can be eliminated.

To obtain the required value of heat capacity, it is necessary to integrate the signal over the region of interest, which in this case is the glass transition region.

$$\Delta C_p^n = \int_{C_{p(i)}^n}^{C_{p(e)}^n} (\mathrm{d}C_p^n/\mathrm{d}T)\mathrm{d}T \quad (12)$$

$C_{p(i)}^n$ and $C_{p(e)}^n$ are the initial and final values of the apparent heat capacity in the glass transition region. If it is assumed that the calibration constant of heat capacity if K_1 at the onset point of the glass transition and is K_2 at the final point, then the increment of heat capacity at glass transition region is as follows

$$\Delta C_p = K_2C_{p(e)}^n - K_1C_{p(i)}^n \quad (13)$$

Consider

$$K = (K_1 + K_2)/2 \quad (14)$$

$$K = K_1 + \lambda = K_2 - \lambda \quad (15)$$

where λ is a small increment. Then equation (13) can be rewritten as follows

$$\Delta C_p = K[\Delta C_p^n + \lambda/K(C_{p(e)}^n + C_{p(i)}^n)] \quad (16)$$

According to our experimental results, the magnitude of λ/K is approximately 10^{-3}. Thus, the following equation holds.

$$\Delta C_p = K\Delta C_p^n \quad (17)$$

The difference between the results from equations (16) and (17) is small at about 3%. Thus, equations (8) and (9) can be rewritten as follows

$$\delta 1 = \omega 10 - \Delta C_{pl}^n/\Delta C_{p10}^n \quad (18)$$

$$\delta 2 = \omega 20 - \Delta C_{p2}^n/\Delta C_{p20}^n \quad (19)$$

Figure 3 shows the change of weight fraction of interface with time. The weight fraction of interface was calculated using equations (18) and (19) and clearly increases with time.

Now, consider that the average value of density of PECH and PVAc in the interface is ρ. The volume of interface, V, is as follows

$$V = W/\rho \quad (20)$$

$$W = \phi(W_{\mathrm{PECH}} + W_{\mathrm{PVAc}}) \quad (21)$$

W is the weight of polymers in the interface. W_{PECH} and W_{PVAc} are the weights of PECH and PVAc, respectively in the pure phases before mixing. ϕ is the weight fraction

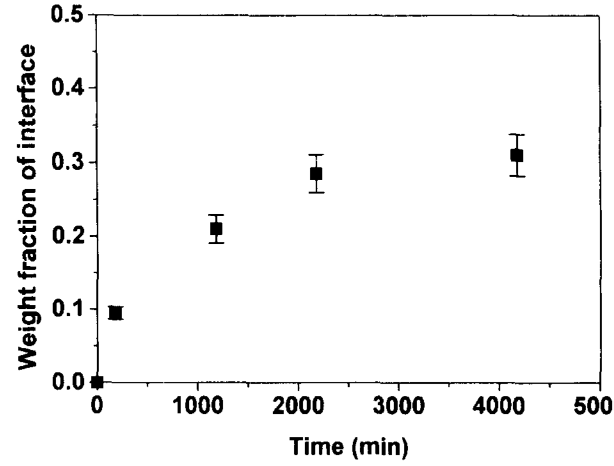

Figure 3 Weight fraction of the interface vs diffusion time

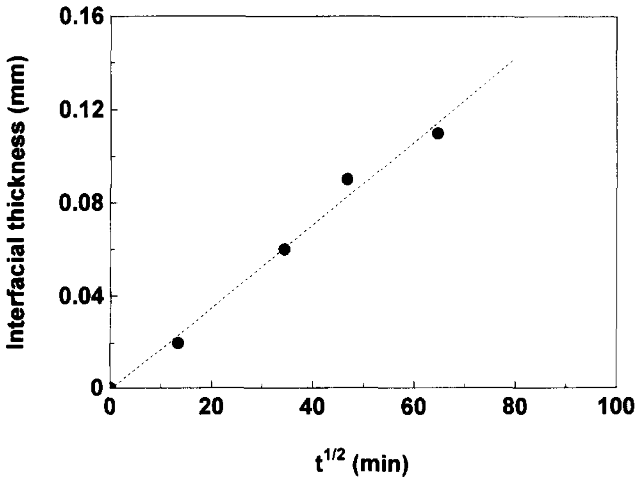

Figure 4 Average thickness of the interface vs square root of diffusion time

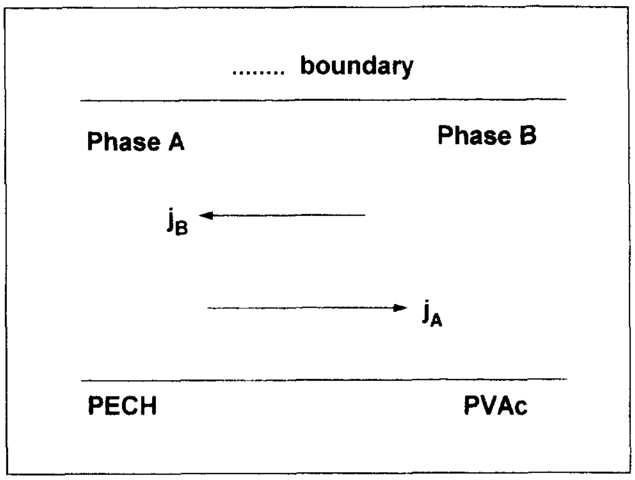

Figure 5 Schematic diagram of interdiffusion fluxes

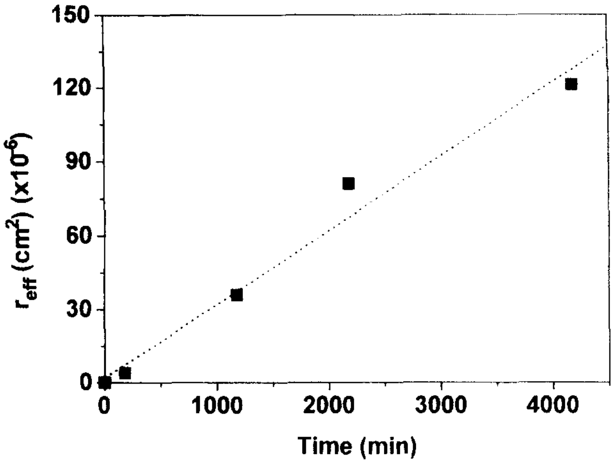

Figure 6 Plot of mean-square interfacial thickness vs diffusion time

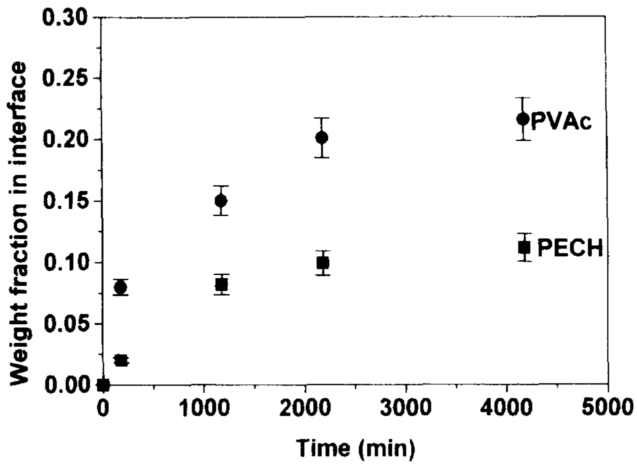

Figure 7 Weight fraction of PECH and PVAc in the interface vs diffusion time

of interface. The average thickness of the interface, d, can be obtained:

$$d = \phi(W_{\rm PECH} + W_{\rm PVAc})/(S\rho) \quad (22)$$

S is the area of the sample, and, therefore, also of the interface. The change of thickness of the interface with diffusion times is shown in *Figure 4*. Here, the densities of PECH and PVAc at room temperature were used to calculate the average density ρ. Obviously, the thickness of interface is a function of diffusion time, t. The interfacial thickness increases in the following way:

$$d \propto t^{1/2} \quad (23)$$

This is consistent with the reptation (2) analysis of Kim and Wool (16), Prager and Tirrell[31], Adolf and co-workers[32,33] and Wu and Chaung[34].

For interdiffusion, consider the following two cases.

Case 1

The diffusion rates for polymer 1 and polymer 2 are equal[35,36]. Consider the interdiffusion of two phases A (PECH) and B (PVAC) in a quasilattice, with respect to fixed coordinates (*Figure 5*). The total fluxes are given by the following equations[34–37].

$$J_A = -\Lambda_A\Delta\mu_A + \Pi_A(\Lambda_A\Delta\mu_A + \Lambda_B\Delta\mu_B) \quad (23)$$

$$J_B = -\Lambda_B\Delta\mu_B + \Pi_B(\Lambda_A\Delta\mu_A + \Lambda_B\Delta\mu_B) \quad (24)$$

where Π_k is the fraction of k sites. Λ is the Onsager coefficient and μ the chemical potential. Conservation of A and B sites gives the following equations

$$(1/\Omega)\partial\Pi_A/\partial t = -D_m J_A \quad (25)$$

$$(1/\Omega)\partial\Pi_B/\partial t = -D_m J_B \quad (26)$$

where Ω is the volume per lattice site. In terms of the D_m, the total mass flux W_A of component A is given by[34,37]

$$W_A = -\rho D_m \partial w_A/\partial_x \quad (27)$$

where ρ is the density at x and w_A is the weight fraction of A in the interface. The equation of continuity is given by

$$\partial W_A/\partial_x + \rho_A/\partial t = 0 \quad (28)$$

Equations (27) and (28) can be solved analytically to give the usual solutions[37].

$$w_A(x,t) = 1/2\ \{1 - {\rm erf}\ [x(4D_m t)^{-1/2}]\} \quad (29)$$

$$w_B(x,t) = 1/2\ \{1 - {\rm erf}\ [x(4D_m t)^{-1/2}]\} \quad (30)$$

which give a symmetrical interfacial profile. The mean-square interfacial thickness is given by

$$r_{\rm eff} = (d)^2 = 4\int_{-\infty}^{\infty} x^2 P(x){\rm d}x \Big/ \int_{-\infty}^{\infty} P(x){\rm d}x \quad (31)$$

$$P(x) = \partial w(x)/\partial x \quad (32)$$

Then, the following relation can be obtained[37].

$$d = 2(2D_m t)^{1/2} \quad (33)$$

Thus, D_m can be calculated. *Figure 6* shows the change of $r_{\rm eff}$ with time. From *Figure 6*, it can be found that D_m is about 6.25×10^{-11} cm^2 s^{-1}. Wu and Chaung[34] reported that the interdiffusion coefficients of poly(methyl methacrylate) and poly(vinylidene fluoride) at 190°C were about 4.00×10^{-11} and $A \times 10^{-11}$ cm^2 s^{-1} (A is a constant depending on the molecular weight), respectively.

Case 2

The diffusion rates are unequal[4]. *Figure 7* shows the changes of weight fraction, w_A and w_E, of PECH and PVAc in the interface with time. Obviously, the change of w_A and w_B with time are different. This indicates that the diffusion of PVAc is faster than PECH. The interdiffusion coefficient value of $6.25 \times 10^{-11}\ \mathrm{cm^2\,s^{-1}}$ is only approximate.

In this case, equation (27) will become

$$W_A = -\rho D_A \partial w_A/\partial x + \rho^2 w_A (v_A D_A - v_B D_B)\partial w_A/\partial x \tag{34}$$

where v_A and v_B are the specific volumes of pure A and pure B. D_A and D_B are the interdiffusion coefficients of polymers A and B, respectively. Substitution of equation (34) into equation (28) gives[34,37] the following relations.

$$\begin{aligned} &-(\rho\partial w_A/\partial t + w_A \partial\rho/\partial x) \\ &= -\rho D_A \partial^2 w_A/\partial x^2 - D_A \partial w_A/\partial x \partial\rho/\partial x \\ &\quad - \rho^2 w_A (v_A D_A - v_B D_B)\partial^2 w_A/\partial x^2 \\ &\quad - \rho^2 w_A (v_A D_A - v_B D_B)(\partial w_A/\partial x)^2 \\ &\quad + 2\rho w_A (v_A D_A - v_B D_B)\partial w_A/\partial x \partial\rho/\partial x \end{aligned} \tag{35}$$

$$\begin{aligned} &-(\rho\partial w_B/\partial t + w_B \partial\rho/\partial x) \\ &= -\rho D_B \partial^2 w_B/\partial x^2 - D_B \partial w_B/\partial x \partial\rho/\partial x \\ &\quad - \rho^2 w_B (v_A D_A - v_B D_B)\partial^2 w_B/\partial x^2 \\ &\quad - \rho^2 w_B (v_A D_A - v_B D_B)(\partial w_B/\partial x)^2 \\ &\quad + 2\rho w_B (v_A D_A - v_B D_B)\partial w_B/\partial x \partial\rho/\partial x \end{aligned} \tag{36}$$

Assume that ρ is approximately the linear sum of ρ_A and ρ_B.

$$\rho = (\rho_A w_A W_{PECH} + \rho_B w_B W_{PVAc})/(w_A W_{PECH} + w_B W_{PVAc}) \tag{37}$$

Combining equations (35), (36) and (37), D_A and D_B can be obtained. However, they can only be solved numerically, and the interfacial profile will be asymmetrical.

CONCLUSIONS

It has been shown that the $\mathrm{d}C_p/\mathrm{d}T$ signal from m.t.d.s.c. can be used to study the interdiffusion of two compatible polymers. The interfacial thickness d increases as $t^{1/2}$, consistent with the results of reptation analysis and the interdiffusion coefficient has a value of about $6.25 \times 10^{-11}\ \mathrm{cm^2\,s^{-1}}$ for the PECH/PVAc pair, assuming that the two polymers have the same diffusion rates.

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