

# Mutual diffusion studies of polystyrene and poly(xylenyl ether) using Rutherford backscattering spectrometry

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The concentration versus depth profile in diffusion couples initially consisting of layers of pure polystyrene (PS) and poly(xylenyl ether) (PXE) were measured. To reveal the profile, the PXE molecules (after diffusion) were preferentially stained in the glass by exposing the couple to a solution of 2 mol% Br in methanol; the covalently bound Br nuclei serve as heavy nuclear tags which permit a sensitive determination of the PXE depth profile by Rutherford backscattering spectrometry (RBS). The samples were annealed at temperatures,  $T$ , ranging from 177–210 °C that are above the glass transition temperature,  $T_g$ , of the pure PS (105 °C) but below the  $T_g$  of pure PXE (216 °C). The measured concentration versus depth profile is markedly asymmetric, with a low slope at low values of the volume fraction of PXE,  $\phi_{\text{PXE}}$ , but with a much greater slope at high values of  $\phi_{\text{PXE}}$ . These results are in qualitative agreement with the variation in the mutual diffusion coefficient,  $D$ , expected as  $\phi_{\text{PXE}}$  increases, causing the  $T_g$  of the blend to increase towards, and finally exceed, the diffusion temperature. Values of  $D$  extracted from these concentration versus depth profiles at low values of  $\phi_{\text{PXE}}$  using the Boltzmann–Matano analysis are in good agreement with those measured by forward recoil spectrometry (FRES) in deuterated-PS: PXE couples with only small composition differences.

## 1. Introduction

Mutual diffusion of chemically dissimilar yet compatible blends has received much theoretical and experimental attention recently [1–10]. Several groups [4–6] have shown that the most powerful way to test the current theories is to use diffusion couples consisting of two polymer blends with a slight composition difference. Because of the small jump in composition at the interface, the mutual diffusion can be assumed to be governed by a single mutual diffusion coefficient,  $D$ , corresponding to the average composition,  $\phi$ , of such a couple<sup>†</sup>. Although diffusion between polymer blends of slightly different composition provides a convenient way to test mutual diffusion theories, many practical problems, such as polymer–polymer adhesion and melt blending, are concerned with the interdiffusion between two pure polymers. In this case, the mutual diffusion coefficient,  $D(\phi)$ , is strongly composition dependent and therefore the diffusion profile at the interface will be non-Fickian [7]. Thus it is important to be able to measure, directly, the concentration profile between films of pure polymers.

While a wide variety of techniques [11] can be used to measure diffusion in polymer melts, most do not

have the resolution necessary to directly determine the asymmetric concentration versus distance profile expected. One technique that does, Rutherford backscattering spectrometry (RBS) [12] normally requires the labelling of one of the diffusing species with heavy nuclei before diffusion [13, 14], a requirement that would rule it out for use on most blend systems. However, if one of the components of the blend can be preferentially stained after diffusion in the glassy state, RBS can be used to differentiate between the two components. In this paper, we demonstrate that bromine can be used to stain only the poly(xylenyl ether) (PXE) component in the miscible blend polystyrene (PS): PXE [15, 16]. Because of its large Rutherford scattering cross-section and heavy mass, bromine is an excellent stain for RBS. After calibrating the bromine staining, we interdiffuse unlabelled films of pure PS and pure PXE, stain the couple and then directly measure the concentration profile of the PXE component. We are thus able to study both the position of the PS/PXE interface as a function of diffusion time and also the details of the concentration profile. In addition, the mutual diffusion coefficient,  $D(\phi)$ , is estimated from the shape of the concentration profile by the Boltzmann–Matano method; these  $D$ s are then

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<sup>†</sup>Strictly, the mutual diffusion coefficient varies continuously with  $\phi$ . However, if the diffusion couple consists of two deuterated PS: PXE blends which differ by 10% in concentration, a single mutual diffusion coefficient associated with the average composition at the interface of the couple can be measured.

compared with those calculated from forward recoil spectroscopy (FRES) experiments.

## 2. Experimental procedure

To calibrate the bromine staining of the poly(xylenyl ether) (PXE): polystyrene (PS) blends, 2  $\mu\text{m}$  thick films of uniform composition were stained in a bromine solution. These films were prepared by pulling a 2 cm  $\times$  2 cm silicon wafer, at a constant rate, from a blend of PS:PXE dissolved in chloroform. After drying, all blends were placed in the same 2 mol % solution of bromine in methanol [15, 16] for 24 h at room temperature, washed for 3 h in a methanol bath and then heated to 40  $^{\circ}\text{C}$  under a vacuum of  $10^{-3}$  torr (1 torr =  $1.333 \times 10^2$  Pa) for several hours. These last two steps were undertaken in order to remove any excess bromine on the surface of the sample.

Diffusion couples, consisting of one pure PS layer in contact with a top layer of pure PXE, were prepared by a procedure similar to that above. A base layer of PS ( $\sim 2 \mu\text{m}$  thick) was prepared by drawing a silicon wafer, at a constant rate, from a solution of PS and toluene. A second film was cast by drawing a glass slide, at a constant rate, from a solution of PXE and chloroform. This film, about 1  $\mu\text{m}$  thick, was then floated off the glass slide onto the surface of a distilled water bath and then carefully picked up with the PS-coated silicon wafer. In both the staining and diffusion experiments, the weight average molecular weight,  $M_w$ , and polydispersity of the PS were 390 000 and 1.1, whereas the  $M_w$  and polydispersity of the PXE were 35 000 and 2.3.

Each diffusion couple was scribed along the back of the silicon substrate and subsequently broken into several identical samples. All but one of these samples were heated to a temperature,  $T$ , under a vacuum of  $10^{-3}$  torr for various diffusion times,  $t$ . The remaining sample was given a low-temperature heat treatment of 1 h at a temperature of 105  $^{\circ}\text{C}$ , just above the glass transition temperature of PS, a temperature just high enough to promote adequate bonding of the couples but not high enough for much interdiffusion to have occurred. As shown in Fig. 6a (see later) the concentration profile of this standard showed no appreciable diffusion broadening due to this treatment. The diffused samples and the standard were then placed in a 2 mol % solution of bromine in methanol for 24 h. To remove any excess bromine, the diffusion couples were treated in the same way as the uniform PS:PXE blend films used for the calibration.

The bromine depth profile was measured in these samples by RBS [12]. Fig. 1 shows the geometry of the RBS experiment. In this technique, a beam of monoenergetic helium ( $\text{He}^{2+}$ ) ions with an energy of  $E_0$  strikes the sample at normal incidence. A small fraction of the incident ions collide elastically with nuclei in the film and are backscattered towards an energy-sensitive detector. If the incoming ion with mass,  $m$ , collides with a target nucleus of mass,  $M$ , at the surface of the sample, this ion will be backscattered with an energy,  $E_1$ , given by

$$E_1 = K_M E_0 \quad (1)$$

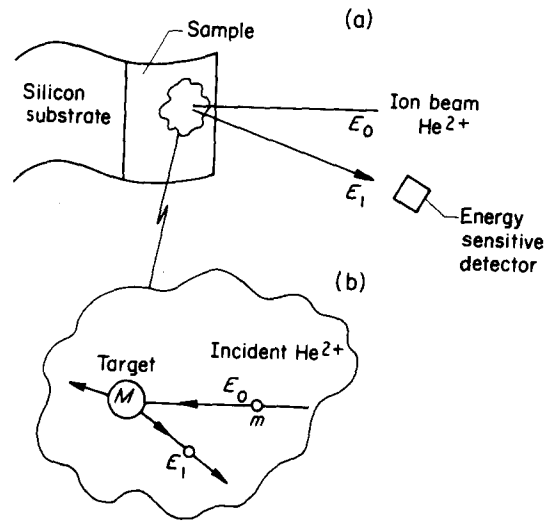


Figure 1 (a) Schematic drawing of the PS:PXE sample on a silicon substrate showing the geometry of the Rutherford backscattering experiment. (b) Elastic collision between a He ion of mass  $m$ , and a target nucleus of mass  $M$ .

where, for a scattering angle of  $180^{\circ}$ , the kinematic factor,  $K_M$ , is

$$K_M = [(M - m)/(M + m)]^2 \quad (2)$$

Thus the energy,  $E_1$ , of the backscattered ions provides a sensitive means for distinguishing between the atomic masses of the elements in a sample. For example, a  $\text{He}^{2+}$  ion backscattered from a heavy bromine nucleus retains a larger fraction of its initial energy ( $K_{\text{Br}} = 0.8185$ ) than an ion scattered from the lighter oxygen or carbon nuclei ( $K_{\text{O}} = 0.3598$  and  $K_{\text{C}} = 0.2498$ ) in the PXE and PS. Note that because hydrogen is lighter than  $\text{He}^{2+}$ , it cannot give rise to backscattering.

In addition to being mass sensitive, RBS is a powerful method for determining the depth profile of an element. As the beam traverses the sample, the  $\text{He}^{2+}$  ion will lose energy via electronic excitations on its inward and outward passage through the sample. Thus the energy,  $E_1$ , of a  $\text{He}^{2+}$  ion emerging from the sample after being scattered from a nucleus a depth,  $x$ , below the surface is

$$E_1 = K_M E_0 - [S]x \quad (3)$$

where  $[S]$ , the energy loss factor, is given by

$$[S] = K_M (dE/dx)_{\text{in}} + (1/\cos\theta)(dE/dx)_{\text{out}} \quad (4)$$

where  $(dE/dx)_{\text{in}}$  and  $(dE/dx)_{\text{out}}$  are the mean energy losses per unit depth of the ion travelling into, and out of, the film, respectively. One can compute  $dE/dx$  knowing only the atomic composition and density of the sample. Using the computed values of  $dE/dx$  [12, 18, 19], the energy scale in the RBS spectrum can be transformed into a depth scale by using Equation 3. For polymers  $(dE/dx)^{-1}$  is typically 2 nm keV $^{-1}$ . Thus for our detector resolution of 15 keV, the depth resolution at normal incidence is 30 nm.

## 4. Results and discussion

### 4.1. Fundamentals of staining in the glassy state

To calibrate the bromine staining of PXE, PS:PXE films of uniform composition and various volume fractions,  $\phi$ , of PS were stained simultaneously in a bromine solution. Fig. 2 shows RBS spectra from films of pure PXE ( $\phi = 0.0$ ) and a PS:PXE blend ( $\phi = 0.50$ ) at  $E_0 = 2.20$  MeV. The steps in the backscattering yield at 0.85 MeV in Fig. 2a and 0.80 MeV in Fig. 2b are due to  $\text{He}^{2+}$  ions scattered by silicon substrate beneath the polymer films, while the step at 0.545 MeV, which is superimposed on the silicon background, is due to scattering from carbon nuclei at the surface of the film. Note that a small step at 0.79 MeV due to the oxygen content is barely distinguishable from the silicon background in the PXE/Si sample. Thus, because of the similarity between the composition of a PXE ( $\text{C}_8\text{H}_8\text{O}_1$ ) and PS ( $\text{C}_8\text{H}_8$ ) mer unit, the backscattering spectrum due to pure PXE, as shown in Fig. 2a, is indistinguishable from that of a blend, as shown in Fig. 2b. However, by labelling the PXE with a heavy element, it is possible to produce a strong contrast between PS and PXE chains in a blend. The sharp step in yield at 1.76 MeV is due to  $\text{He}^{2+}$  ions scattered from the bromine at the surface. Note that the bromine portion of the RBS spectrum is shifted to much higher energies than the portions of the spectrum due to scattering from the

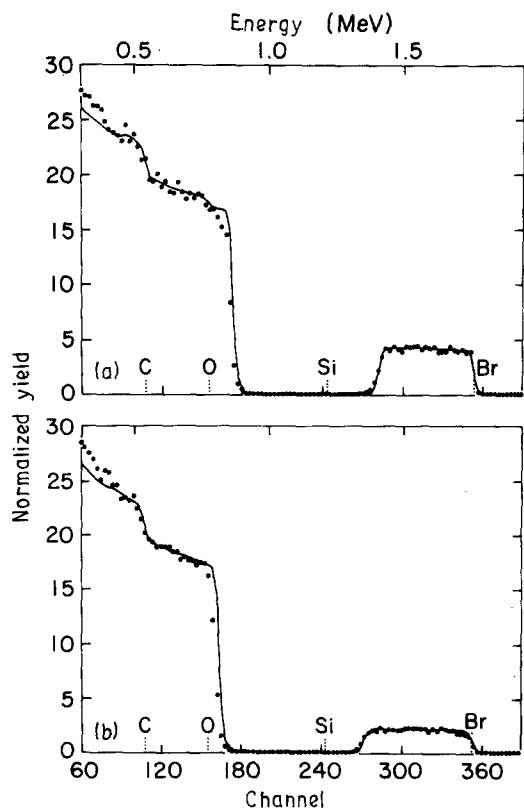


Figure 2 RBS spectra ( $\bullet$ ) of 2.20 MeV He ions backscattered from (a) pure PXE ( $\phi = 0.0$ ) and (b) a PS:PXE blend ( $\phi = 0.5$ ). Both samples are stained in a bromine and methanol solution for 24 h. (—) Simulated spectra where the thickness and mer unit of PXE are 915 nm and  $\text{C}_8\text{H}_{7.70}\text{OBr}_{0.30}$  whereas the thickness and mer unit of the blend are 1060 nm and  $\text{C}_8\text{H}_{7.86}\text{OBr}_{0.14}$ . The energies at which the He ions would be backscattered by C, O, Si and Br nuclei at the surface are marked.

lighter elements in the sample (i.e. silicon, oxygen, carbon). Thus, one can distinguish between the backscattering spectrum due to PXE and that due to PS. To determine if bromine preferentially reacts with PXE, but not PS, a relationship between the normalized yield and the concentration of bromine at a particular depth is needed.

It is convenient to plot the  $y$ -axis of an RBS spectrum as the normalized yield  $H/(Q\Lambda\Omega)$  where  $H$  is the number of counts per channel,  $Q$  is the integrated or total charge ( $\mu\text{C}$ ) of the ions hitting the sample,  $\Lambda$  is the energy width (keV) of each channel, and  $\Omega$  is the solid angle (milliradians, msr) subtended by the detector. For bromine or carbon nuclei at the surface of the sample,  $H$  is given by [12]

$$H = \sigma(E_0)Q\Omega N\tau \quad (5)$$

where  $N$  is the density of atoms of a particular nuclear species,  $\tau$  is the thickness of the layer traversed that corresponds to one energy channel on the multi-channel analyser and  $\sigma$  is the Rutherford cross-section [12], i.e.

$$\sigma(E_0) = (Z_1 Z_2 e^2 / 4E_0)^2 [\sin^4(\theta/2)]^{-1} \quad (6)$$

where  $Z_1$  and  $Z_2$  are the atomic numbers of the incident ions ( $Z_1 = 2$ ) and target atom, respectively. Thus, the scattering cross-section for 2.20 MeV  $\text{He}^{2+}$  ions incident on a bromine nucleus ( $\sigma_{\text{Br}} = 0.33 \times 10^{-24} \text{ cm}^2$ ) is much larger than the cross-section for the lighter elements in the sample ( $\sigma_{\text{O}} = 0.02 \times 10^{-24} \text{ cm}^2$  and  $\sigma_{\text{C}} = 0.01 \times 10^{-24} \text{ cm}^2$ ). This large cross-section for scattering from bromine is advantageous because it allows many counts (good statistics) to be accumulated in a fairly short analysis time ( $\sim 5$  min).

Successive RBS spectra taken at room temperature show a progressive loss of bromine from the high-energy edge (i.e. near surface region) of the bromine RBS spectrum. The inelastic collisions of the ions with the electrons in the polymer causes radiation damage leading to the formation of HBr, which readily diffuses out of the sample. One way to prevent this diffusion of HBr is to cool the sample to liquid nitrogen temperatures (77 K) during the analysis [13, 14]. The RBS spectra of the samples taken at 77 K showed no evidence of Br loss or Br redistribution between successive spectra. Thus all stained polymer samples were analysed at 77 K.

Doolittle [20, 21] has developed a computer program which simulates the RBS spectrum to be expected for a certain composition versus depth profile of a sample. In our case, the PS:PXE blend film can be described as having a uniform composition and an average mer unit of  $\text{C}_8\text{H}_{8-n}\text{O}_{1-\phi_{\text{PS}}}\text{Br}_n$ , where  $n$  is the number of bromine atoms per average mer and  $\phi_{\text{PS}}$  is the volume fraction of PS. The simulation program was used to produce the solid lines in Fig. 2a and b where  $n$  and the film thickness are given by 0.30 and 915 nm, respectively, for pure PXE and 0.14 and 1060 nm, respectively, for the PS:PXE blend ( $\phi = 0.50$ ). Note that the concentration of bromine has decreased by 50% upon increasing  $\phi_{\text{PS}}$  from 0.0–0.50. Note also that the fits of the simulated spectra to the experimental spectra are quite good. Fits of similar

quality were obtained for various uniform PS:PXE blend films ranging from pure PS to pure PXE.

As shown in Fig. 3, the number,  $n$ , of bromine atoms per average mer unit decreases linearly with increasing volume fraction,  $\phi_{PS}$ , of PS in the PS:PXE blends. The solid line is a best fit to the data given by  $n = 0.294(1 - \phi_{PS})$ . Under our experimental staining conditions, these results suggest that only the PXE component in the blend is stained by bromine. However, only about one-third of all the PXE mers in a given blend are brominated. Previous studies [16] on the bromination of PXE in solution suggest that  $n = 1$  if there is no steric hindrance to the bromination reaction. To determine if similar results are obtained under our staining conditions, the bromination of PXE was carried out in solution by adding a stoichiometric amount of Br to a PXE/chloroform solution. This brominated polymer ( $C_8H_{8-n}O_1Br_n$ ) was then precipitated with methanol, redissolved in a chloroform solution and then cast on a silicon wafer. After analysing this film with RBS and then simulating the spectrum, a composition of  $C_8H_7O_1Br_1$  was found to produce the best fit to the experimental spectrum, as expected. Thus it appears that the reduced free volume in a glass prohibits the complete bromination of the glassy PXE.

If free volume is indeed crucial to the staining of a PXE glass, physical ageing of this glass before staining should have a marked effect on the concentration of bromine atoms in the stained film. Fig. 4 shows how the ratio  $n(t)/n(t=0)$  varies with ageing time,  $t$ , for pure PXE films heated to 6 and 17.5°C below the glass transition temperature of PXE, 216°C. Regardless of temperature, the ratio  $n(t)/n(t=0)$  decreases by 50% after 1 h and then remains constant. This result suggests that bromine staining reactions are profoundly affected by the initial decrease in free volume caused by physical ageing at these temperatures.

During these ageing experiments a slight amount of oxidation was observed at the near surface region of PXE. Fig. 5 shows the high energy edge of the bromine spectrum for two samples of PXE, one annealed in a low vacuum ( $10^{-3}$  torr) oven for 12 h at 210°C and one annealed in a medium vacuum ( $10^{-6}$  torr) oven for 12 h at 210°C. When a low vacuum was used

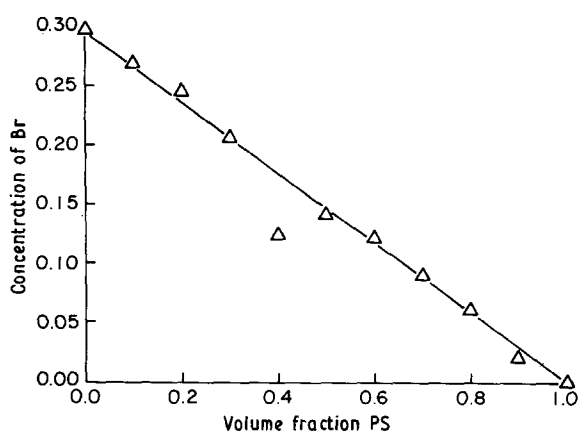


Figure 3 Number,  $n$ , of bromine atoms per average mer versus the volume fraction,  $\phi$ , of PS in a PS:PXE blend. (—) Linear fit to the data given by  $n = 0.294(1 - \phi_{PS})$ .

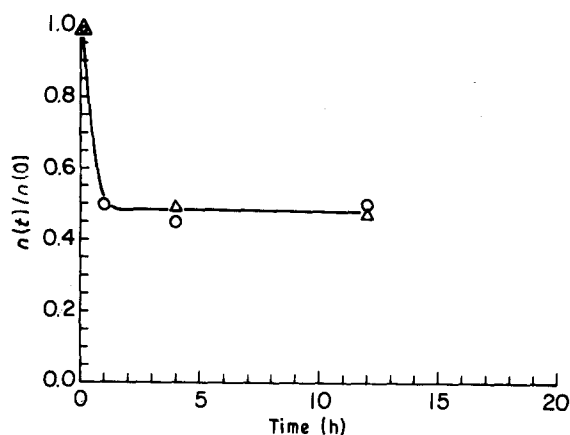


Figure 4 Relative bromine concentration  $n(t)/n(0)$  in pure PXE as a function of ageing time,  $t$ , at two annealing temperatures, where  $n(t)$  and  $n(0)$  are the number of bromine atoms per mer unit for an aged and unaged sample, respectively. Data at annealing temperatures of ( $\Delta$ ) 210°C and ( $\circ$ ) 198.5°C, respectively. (—) A guide for the eye.

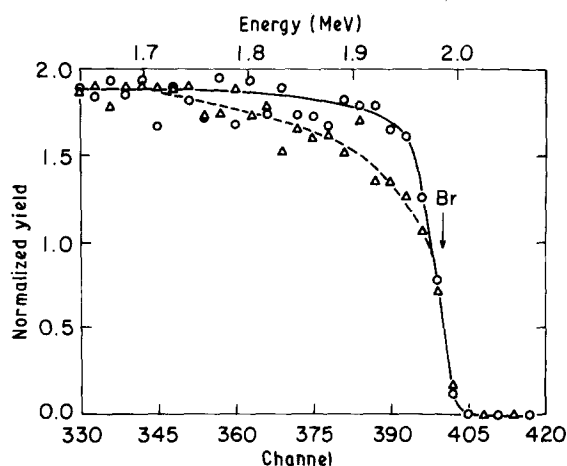


Figure 5 Blow-up of the high-energy RBS spectrum of bromine in pure PXE samples which have been aged for ( $\Delta$ , ---) 12 h in a low-vacuum oven triangles, and ( $\circ$ , —) 12 h in a medium-vacuum oven. Both samples were heated to 210°C and then stained in a bromine/methanol solution for 24 h.

during the annealing, the front edge of the bromine yield was not sharp (----) suggesting that PXE near the skin is more difficult to stain than PXE below the surface. On the other hand, after a similar annealing treatment in a medium vacuum, no such dip was observed. To determine if these results could be attributed to the oxidation of PXE, samples were heated for 24 h at 200°C under three atmospheric conditions: no vacuum (air), low vacuum and medium vacuum. While the sample heated in air showed a strong increase in the infrared absorption peak corresponding to C=O (i.e. carbonyl group), no such increase was observed for the other vacuum-annealed samples when compared with an unannealed standard. In agreement with these infrared spectroscopy results, Kelleher *et al.* [22] found similar absorption bands for PXE heated to 125°C in air, while Madorsky [23] and Madorsky and Straus [24] observed that PXE annealed under vacuum was stable at 320°C. Thus it appears that the decrease in bromine yield near the surface of PXE (see Fig. 5) can be attributed to the deactivation of the phenylene ring due to an oxidation

reaction. However, this oxidation can be avoided if a medium vacuum ( $10^{-6}$  torr) oven is used.

One possible technique for increasing the staining efficiency of bromine might be to increase the concentration of bromine in the staining solution. While Hobbs and Watkins [15] found that a 20% bromine and methanol solution would etch the surface of a PS:PXE blend, no such etching was observed for 15% solutions. Nevertheless, the good sensitivity of RBS to high  $Z$  atoms means that the minimum detectable bromine concentration based on a signal-to-noise ratio of 2 is about 500 p.p.m. for  $Q = 5 \mu\text{C}$ . Taking the worst case, one out of every six PXE mers will be brominated and therefore the smallest detectable PXE concentration is about 3000 p.p.m. which is much lower than concentrations of interest in our diffusion experiments.

#### 4.2. Diffusion

As we can now preferentially stain the PXE molecules in a blend, this staining will be used to investigate the interdiffusion of PS/PXE couples. Fig. 6 shows RBS spectra from three different PS/PXE couples: the standard couple and couples heated to  $184^\circ\text{C}$  in a low-vacuum oven for 4.0 and 16.0 h. The low-energy edge of the bromine RBS spectrum moves progressively to higher energies indicating that the thickness of the pure PXE layer decreases as the diffusion time increases. As shown in Fig. 6b, the bromine profile above the low-energy edge is quite uniform except for the sharp decrease in yield at the high-energy edge due to the previously noted oxidation of PXE.\* Because the interdiffusion process takes place deep within the sample, this surface effect should not influence our results significantly. It is informative to transform the bromine RBS spectrum into a concentration profile for PXE. This transformation is accomplished by using the tabulated energy loss factors,  $[S]$ , to rescale the RBS spectrum into a plot of atomic fraction of bromine versus depth [20]. Given that the volume fraction of PXE,  $\phi_{\text{PXE}}$ , in an undiffused region is 1.0, one can simply normalize the bromine concentration profile in this region so that it is also 1.0.

Fig. 7 shows the volume fraction versus depth profile of PXE for PS/PXE diffusion couples which were heated to  $184^\circ\text{C}$  for diffusion times,  $t$ , of 1.0, 4.0 and 16.0 h. As time increased, the interface between the PS layer and the PXE layer moved towards the PXE side of the diffusion couple. Defining the interface position,  $x_i$ , as the depth at which  $\phi_{\text{PXE}} = 0.5$ , the interface shift,  $\Delta x_i$ , relative to the position of the interface at  $t = 0$  was followed. Fig. 8 shows a plot of  $\Delta x_i$  versus  $t^{1/2}$  for couples heated to temperatures ranging from  $177.5$ – $210^\circ\text{C}$ . To verify that the interface shift did not depend on sample geometry, the experiment at  $199^\circ\text{C}$  was carried out with an interdiffusion couple which consisted of a PS top layer and a PXE bottom layer. As expected, the interface moved towards the PXE for all experiments. As shown by the linear least squares

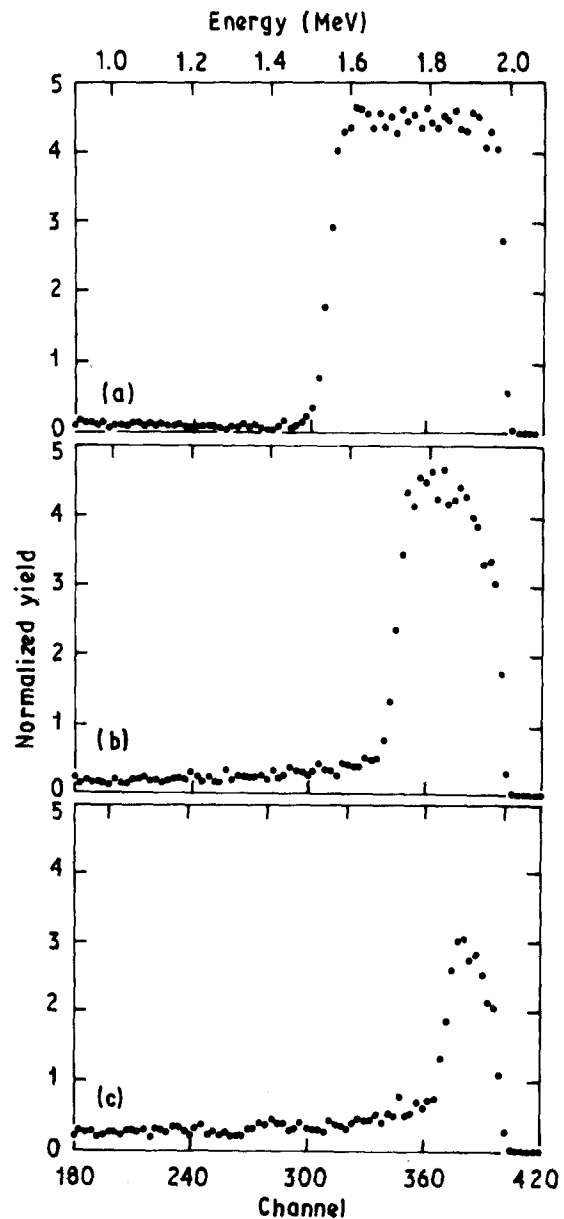


Figure 6 Energy spectra of 2.4 MeV  $\text{He}^{2+}$  ions backscattered from a PS/PXE diffusion couple annealed for (a) 0.0 h, (b) 4.0 h and (c) 16.0 h, at  $184^\circ\text{C}$  followed by staining with bromine.

fits to the data, the interface shift increased linearly with  $t^{1/2}$  at all diffusion temperatures. Note, however, that these lines do not quite extrapolate to  $\Delta x_i = 0$  when  $t = 0$ . In addition to showing that the thickness of the pure PXE layer decreased with increasing diffusion times, Fig. 7 demonstrates that the concentration profile does not vary smoothly with depth. It decreases rapidly with depth from pure PXE ( $\phi_{\text{PXE}} = 1.0$ ) to a value  $\phi_{\text{PXE}} \leq 0.2$  but then much more slowly with depth as  $\phi_{\text{PXE}}$  decreases further. As discussed below, this non-Fickian profile must be due to the strong concentration dependence of the mutual diffusion coefficient,  $D(\phi)$ .

Although there can be several contributions to the concentration dependence of  $D$  [5, 25], the dominant one is surely the large difference between the  $T_g$  of PS ( $105^\circ\text{C}$ ) on one side of the couple and that of PXE ( $216^\circ\text{C}$ ) on the other. As shown in Fig. 9, the glass

\*We find that the oxidation process at the surface also removes a PXE layer. However, this layer is much smaller than the  $\Delta x_i$ s measured in our experiments.

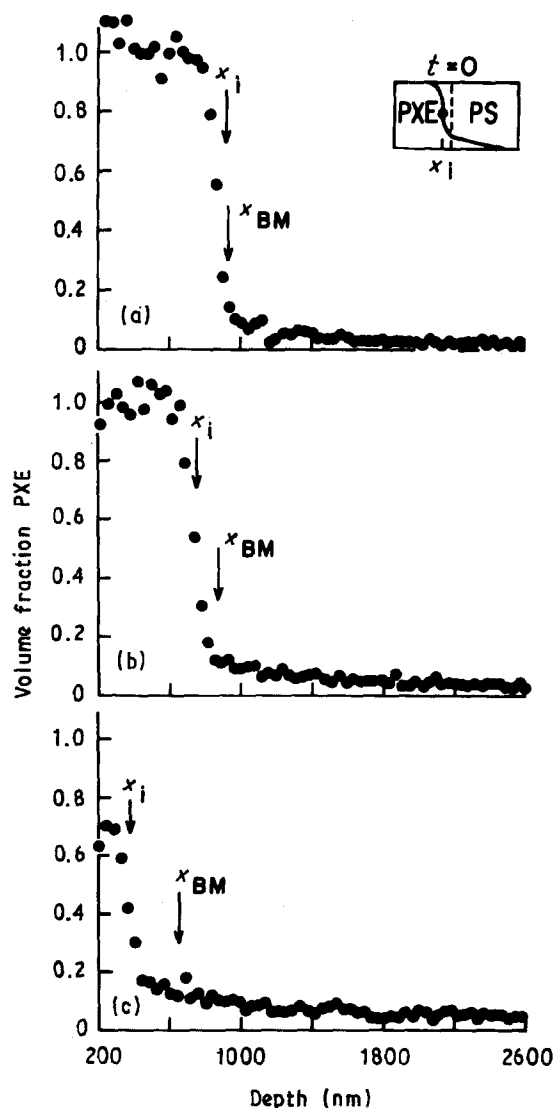


Figure 7 Volume fraction profile of PXE in the PS/PXE diffusion couple. The couples are heated to 184°C for (a) 1.0 h, (b) 4.0 h and (c) 16.0 h. The interface position,  $x_i$ , at which  $\phi_{\text{PXE}} = 0.5$  is represented along with the Boltzmann–Matano interface,  $x_{\text{BM}}$ .

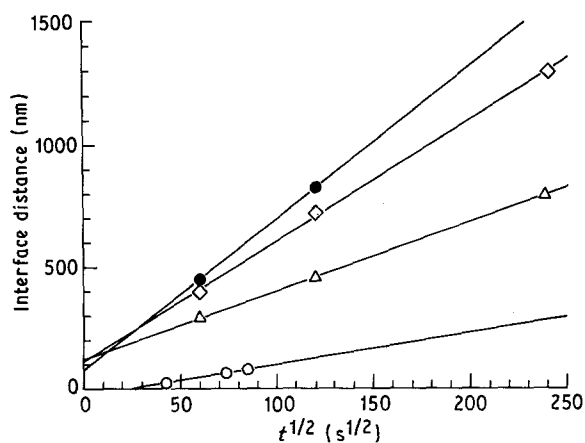


Figure 8 Interface displacement versus square root of diffusion time for a PS/PXE diffusion couple. Couples annealed at (●) 210°C, (◇) 199°C, (△) 184°C, (○) 177°C. (—) Least square fits to the data.

transition temperature for pure PXE is greater than any of the diffusion temperatures used in this study [25, 26]. Thus no diffusion is possible in the PXE rich blends, i.e. the regions  $\phi_{\text{PS}} < 0.25$  at 177°C or  $\phi_{\text{PS}} < 0.03$  at 210°C. Moreover, for typical diffusion

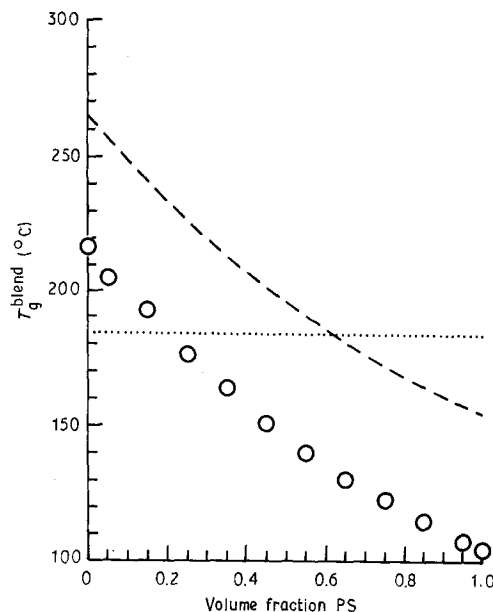


Figure 9 Glass transition temperature,  $T_g$ , of PS:PXE blends as a function of volume fraction of PS. (···) 184°C, (---) 50°C above the  $T_g$  of each blend.

times used in this study, a diffusion temperature roughly 50°C above  $T_g$  is necessary to cause large enough diffusion distances (about 200 nm) to be measured by RBS. Take for example a couple heated to 184°C. In our approximation, only blends containing a volume fraction of PS less than 0.60 are at high enough  $T - T_g$  to allow the polymer chains to diffuse over measurable distances.

One can more clearly see the relationship between the mutual diffusion coefficient and the shape of the diffusion profile if  $D(\phi)$  at a constant temperature is plotted against the volume fraction of PS,  $\phi_{\text{PS}}$ . In previous forward recoil spectrometry (FRES) experiments [5], the tracer diffusion coefficients of PS and PXE,  $D_{\text{PS}}^*$  and  $D_{\text{PXE}}^*$ , were measured for a series of PS:PXE blends at a constant  $T - T_g$  of the blend. Using the WLF equation and the reptation prediction ( $D^* \propto M^{-2}$ ), these  $D^*$ s were scaled to a temperature of 184°C and a weight average molecular weight,  $M_{\text{PS}}$ , of 390 000 for the PS component (the same  $M_{\text{PXE}}$  was used in both studies). The mutual diffusion coefficient is related to the  $D^*$ s of the individual components by the equation [2, 3, 5]

$$D = [D_{\text{PS}}^* N_{\text{PS}} \phi_{\text{PXE}} + D_{\text{PXE}}^* N_{\text{PXE}} \phi_{\text{PS}}] \left( \frac{\phi_{\text{PXE}}}{N_{\text{PS}}} + \frac{\phi_{\text{PS}}}{N_{\text{PXE}}} - 2\phi_{\text{PS}}\phi_{\text{PXE}}\chi \right) \quad (7)$$

where  $N_{\text{PS}}$  and  $N_{\text{PXE}}$  are the degrees of polymerization of PS and PXE, respectively, and  $\chi(184^\circ\text{C}) = -0.022$ . As shown in Fig. 10,  $D$  (◇) is predicted to decrease by over an order of magnitude as  $\phi_{\text{PS}}$  is decreased from 1.0 ( $T_g = 105^\circ\text{C}$ ) to 0.6 ( $T_g = 140^\circ\text{C}$ ), suggesting that diffusion should be much faster in the high  $\phi_{\text{PS}}$  (or low  $\phi_{\text{PXE}}$ ) regime, in agreement with the profiles shown in Fig. 7; at high  $\phi_{\text{PXE}}$  the steep wall is a result of the high  $T_g$  whereas at very low  $\phi_{\text{PXE}}$  the diffuse tail shows that the mutual diffusion coefficient is much higher.

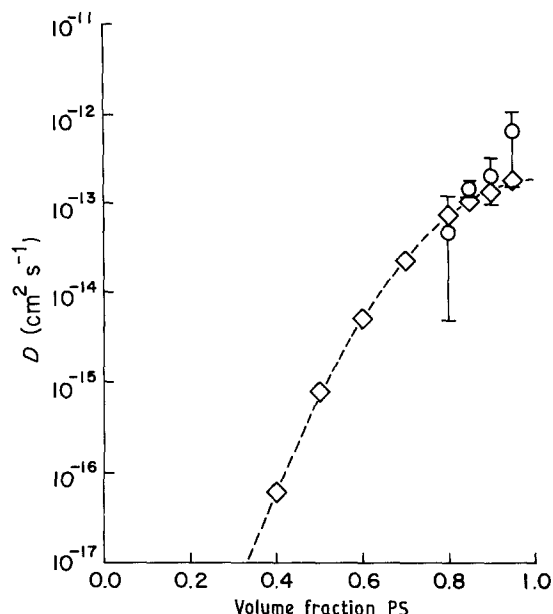
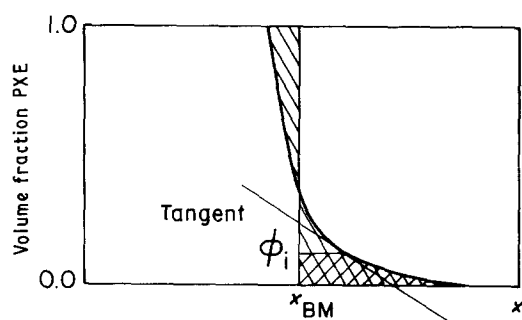


Figure 10 Mutual diffusion coefficient of a PS:PXE blend as a function of the volume fraction of PS. (—◇—) Calculated from FRES experiments, (○) from the Boltzmann–Matano analysis. The error bars were determined from the error in measuring the tangent of the volume fraction profile shown in Fig. 12. The diffusion temperature is 184 °C.



$$\text{Cross-hatched area} = \int_0^{\phi_i} (x - x_{\text{BM}}) d\phi$$

$$\text{Tangent} = \left. \frac{d\phi}{dx} \right|_{\phi_i}$$

Figure 11 Schematic diagram of the volume fraction versus depth profile in a diffusion couple. The Boltzmann–Matano interface,  $x_{\text{BM}}$ , is defined so that the hatched areas to the left and right of  $x_{\text{BM}}$  are equal. The cross-hatched area and tangent at  $\phi_i$  are used to derive the mutual diffusion coefficient,  $D(\phi_i)$ .

The Boltzmann–Matano method ((○) Fig. 10) provides a graphical technique for estimating  $D$  from the shape of the concentration profile, i.e.

$$D(\phi_i) = \frac{-1}{2t} \left. \frac{dx}{d\phi} \right|_{\phi_i} \int_0^{\phi_i} \phi dx \quad (8)$$

where the tangent and integral are defined in Fig. 11. The Boltzmann–Matano interface,  $x_{\text{BM}}$ , is defined

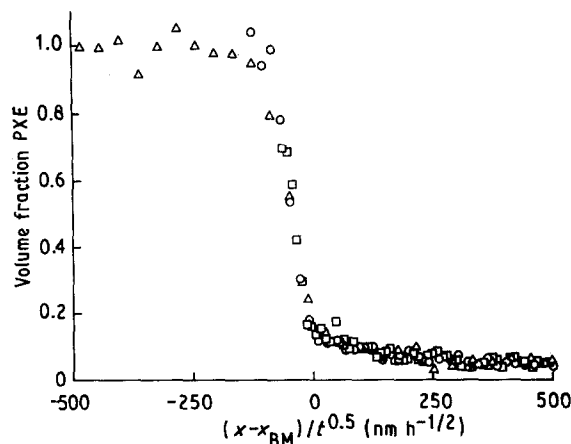


Figure 12 Volume fraction of PXE versus reduced depth profile for the couples shown in Fig. 7. (△) 1.0, (○) 4.0 and (□) 16.0 h anneals.

such that the PXE on the left-hand side of this interface is equal to the PXE depleted from the right-hand side, so that

$$\int_0^1 (x - x_{\text{BM}}) d\phi = 0 \quad (9)$$

i.e. conservation of PXE such that the hatched areas in Fig. 11 are equal. Applying the Boltzmann–Matano method to the PS/PXE profiles shown in Fig. 7, the Boltzmann–Matano interface must be positioned in the low  $\phi_{\text{PXE}}$  region at  $\phi_{\text{PXE}} \approx 0.15$  in order for Equation 9 to be satisfied. Thus the PS/PXE interface ( $\phi_{\text{PXE}} = 0.50$ ) moves away from  $x_{\text{BM}}$  so as to compensate for the steepness in the volume fraction versus depth profile at high  $\phi_{\text{PXE}}$ . Note that this interface shift is due to the decrease in  $D$  caused by the increase of  $T_g$  with  $\phi_{\text{PXE}}$  and not to any mismatch in the tracer diffusion coefficients.<sup>‡</sup>

By plotting the data in the volume fraction versus depth profiles of Fig. 7 as  $\phi_{\text{PXE}}$  versus the variable  $\eta = (x - x_{\text{BM}})/t^{1/2}$  one can obtain the single master diffusion profile shown in Fig. 12.<sup>§</sup> Measuring the tangents and integrals from this figure, several values for  $D$  were calculated at low values of  $\phi_{\text{PXE}}$  using Equation 8. These results are shown in both Table I and Figure 10 (○) along with the values of  $D$  determined from FRES using Equation 7. Considering that the error in measuring  $dx/d\phi$  at low  $\phi_{\text{PXE}}$  can be as large as  $\pm 400\%$ , the agreement between the two different measurements is quite good. It is worth noting here that the FRES technique can measure the  $D$ \*s to  $\pm 20\%$  and therefore the values of  $D$  calculated from Equation 7 are more accurate than those found using the Boltzmann–Matano analysis at low  $\phi_{\text{PXE}}$ .

In the forward recoil spectrometry experiments,  $D$  can be affected by the deuterium labelling because  $\chi_{\text{d-PS:PXE}}$  may not be equal to  $\chi_{\text{PS:PXE}}$ .  $D$  measured by RBS, however, must be the mutual diffusion coefficient of PS:PXE itself, because the PXE was not

<sup>‡</sup> Actually  $D$  is dominated by the PS component because  $N_{\text{PS}} \gg N_{\text{PXE}}$ . In addition the  $D$ \*s in this system are roughly equivalent at low  $\phi_{\text{PXE}}$  and therefore the diffusion couples used in our experiments cannot be used to test the current mutual diffusion theories (i.e. the “fast” versus “slow” theories).

<sup>§</sup> A different  $x_{\text{BM}}$  was used for each profile in Fig. 7 because the PXE surface loss depended on annealing time. This PXE loss is responsible for the apparent motion of the Boltzmann–Matano interface,  $x_{\text{BM}}$ , towards the PXE side of the couple.

TABLE I Mutual diffusion coefficient for a PS/PXE diffusion couple at 184°C determined by RBS (Boltzmann–Matano analysis) and FRES

Volume fraction PXE	RBS (cm <sup>2</sup> s <sup>-1</sup> )	FRES <sup>a</sup> (cm <sup>2</sup> s <sup>-1</sup> )
0.05	$7 \times 10^{-13}$	$1.9 \times 10^{-13}$
0.10	$2 \times 10^{-13}$	$1.4 \times 10^{-13}$
0.15	$1.5 \times 10^{-13}$	$1.1 \times 10^{-13}$
0.20	$5 \times 10^{-14}$	$7.6 \times 10^{-14}$

<sup>a</sup>Calculated from the measured tracer diffusion coefficients,  $D_{PS}^*$  and  $D_{PXE}^*$ , and  $\chi(184^\circ\text{C}) = -0.022$  using Equation 7.

labelled until after diffusion had occurred. The agreement between the two different results thus signifies that the deuterium labelling effect on  $\chi$  of this blend must be relatively small.

## 5. Conclusions

1. RBS is a sensitive technique for measuring the shape of the concentration profile between two pure polymer layers if one of the polymers can be stained after diffusion with a molecule containing a heavy nucleus.

2. In uniform blends of glassy PS:PXE which are stained in a bromine methanol solution, the number  $n$  of bromine atoms per average mer decreases as the volume fraction of PS in the blend increases indicating that only the PXE is stained and that the staining efficiency does not depend on composition.

3. Because of steric hindrance effects, only about one-third of the mers in a freshly prepared PXE glass are stained with bromine, i.e. the staining efficiency is  $\sim 0.3$ . After the physical ageing of PXE, the staining efficiency decreases by 50% because of the decrease in free volume which increases the steric hindrance.

4. For PS/PXE diffusion couples heated to temperatures  $177.5^\circ\text{C} < T < 210^\circ\text{C}$  for diffusion times,  $t$ , the displacement of the interface is towards the PXE-rich side of the couple and is observed to scale at  $t^{\frac{1}{2}}$ .

5. Because the diffusion temperatures are greater than the glass transition temperature of PS but less than that of PXE, the mutual diffusion coefficient,  $D$ , varies quite strongly across the couple and therefore the concentration profile is non-Fickian.  $D$  measured by the Boltzmann–Matano technique, is in reasonable agreement with the values calculated from forward recoil spectrometry experiments on d-PS:PXE diffusion couples.

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