

## Interface Formation in a Partially Miscible Polymer Blend.

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**Abstract.** – We have directly measured the interface formation and diffusion between two partially miscible polymers, SCPE and PMMA, using Rutherford backscattering spectrometry, as the temperature was varied from the glass transition into the two-phase region. As the temperature was increased, the interfacial width for a given diffusion time increased sharply, attaining a maximum value approximately 25 °C above the lower critical solution temperature and then dropped abruptly. The results are briefly discussed within the framework of the extended Flory-Huggins theory wherein nonlocal terms are included in the free energy.

There has recently been a great deal of activity, both experimentally and theoretically in trying to understand the mutual diffusion [1-7] of miscible polymer blends. On the other hand, due to their high molecular weights and low resultant combinational entropy of mixing, most polymer mixtures are not miscible over the entire temperature concentration range and will phase separate in the blend. In these systems the cooperative interdiffusion coefficient,  $D$ , approaches zero as the spinodal is approached, and shorter wavelength-dependent terms become important. As a result slowing-down of the interdiffusion is predicted as a function of temperature and concentration. Green and Doyle [8] observed a minimum in the rate of interdiffusion as a function of concentration in the one-phase region for a deuterated-hydrogenated blend of polystyrene. We would like to report on a direct observation of slowings-down as the temperature is varied from the glass transition into the

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two phase region for a blend of two chemically different polymers where a lower critical temperature is known to exist [9].

The polymers we studied [9]<sup>(1)</sup> were solution-chlorinated polyethylene (SCPE), an amorphous randomly chlorinated analogue of poly(vinylchloride) with a 66% (w/w) degree of chlorination and poly(methyl methacrylate) (PMMA), provided by Higgins and Fruitwallah. The characteristics of the polymers are summarized in table I.

TABLE I.

Polymer <sup>(1)</sup>	$M_w$	$M_w/M_n$	$T_g$
PMMA	$1.07 \cdot 10^5$	1.1	$105 \pm 2$
SCPE (66% Chlorinated)	$1 \cdot 10^5$	$\sim 2$	$70 \pm 1$

A sharp interface between SCPE and PMMA was established by spin casting approximately 400 nm and 2  $\mu$ m thick films of SCPE and PMMA, respectively, and floating them (with the SCPE film on top) onto polished carbon backings. The couples were then annealed for various specified times and temperatures at a pressure of  $10^{-3}$  Torr in an evacuated oven. Interdiffusion across the interface was measured via the Rutherford backscattering (RBS) technique wherein 2 MeV  $\alpha$ -particles are scattered from the various polymer components and are detected in a Si surface barrier detector at  $135^\circ$  to the incoming beam direction. Both incoming and outgoing  $\alpha$ -particles suffer inelastic energy losses in the polymer material and their detected energies can be converted into a depth scale from tabulated  $dE/dX$  values [10, 11]. RBS is well suited for this system, since the chlorine component is a natural label which can easily be detected at back angles without interference from the lighter elements. An intrinsic experimental resolution of  $\sim 25$  nm can be obtained. This is particularly useful for studying interface formation and other diffusion phenomena where small diffusion coefficients are expected. In the present case the experimental resolution was mainly limited by uncertainties in the thickness of the SCPE films which were estimated to be approximately 50 nm from measurements of various unannealed samples.

Since PMMA is very sensitive to ionizing radiation, great care was taken to minimize radiation damage during data acquisition. A flow of liquid nitrogen was maintained through the sample holder and the beam current was kept below 2 particle nA. The stoichiometric ratio of chlorine to carbon was continuously monitored and only runs where it stayed constant to within (5  $\div$  10)% were considered. Further details of the experimental procedure will be published elsewhere [12].

Figure 1 shows the profiles obtained for an unannealed couple and for two couples annealed for 9.2 hours at 147 °C and 18 hours at 181.5 °C, respectively. The solid line is a fitted spline function to guide the eye. From the figure it can clearly be seen that though the profile at 147 °C is diffuse, no measurable diffusion occurs at 181 °C. Preliminary neutron scattering data<sup>(1)</sup> on these polymers indicate the existence of a lower critical point at approximately 120 °C with an SCPE concentration of 25% and a point on the spinodal at

<sup>(1)</sup> The characterization data for the polymers used in these experiments were privately communicated by J. S. Higgins and H. Fruitwallah.

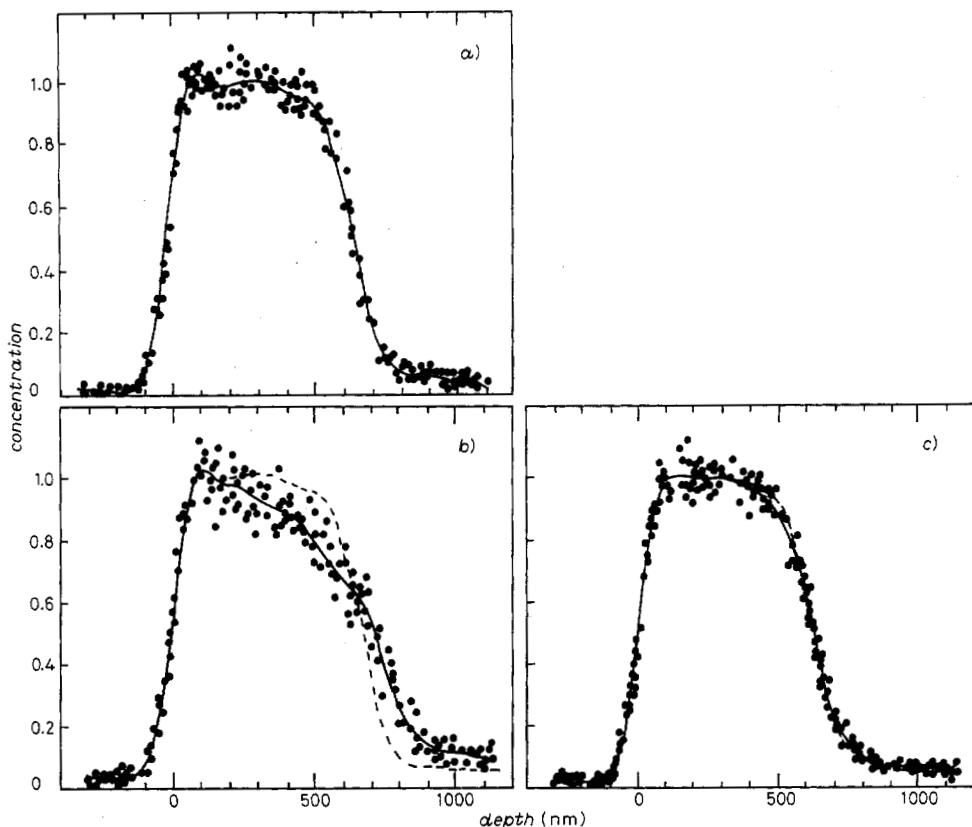


Fig. 1. – Typical RBS spectra of chlorine concentration *vs.* depth for SCPE/PMMA couples. *a)* Unannealed, *b)* annealed for 9.2 h at 147 °C, *c* annealed for 18 h at 181.5 °C. The solid lines are a spline to guide the eye. The broken line in *b*) and *c*) is the step function from the unannealed sample *a*).

140 °C having an SCPE concentration of 50%. Consequently, the profiles we observe for  $T > 120$  °C include regions of diffusion through a miscibility gap. The diffusion in this case is non-Fickian, since the equilibrium state is not a uniform composition in space, but rather two compositions separated by an interfacial zone whose width  $w$ , in the Flory-Huggins model [13-16], is proportional to

$$w \sim (\chi(T)/\chi(T_c) - 1)^{-1/2}, \quad (1)$$

where  $\chi(T)$  is a temperature-dependent interaction parameter between the two polymers and  $T_c$  is the critical temperature for phase separation. A quantitative interpretation of the dynamics must include terms proportional to the square of the concentration gradient in the free energy and wavelength-dependent terms in the diffusion coefficient [13-16]. No satisfactory theoretical model exists as yet for our initial conditions. The data were, therefore, quantified in terms of an «average» diffusion coefficient, defined in analogy to that obtained for standard Fickian diffusion where the coefficient is a constant

$$D^{\text{avg}} = \sigma^2/3.64t \text{ (cm}^2/\text{s)} , \quad (2)$$

where  $\sigma$  is the interquartile distance corrected for the initial film width, and  $t$  is the annealing time<sup>(2)</sup>.

Figure 2 is a plot of  $D^{\text{avg}}$  as a function of temperature. From the figure one can see that the  $D^{\text{avg}}$  increases sharply above the glass transition, followed by a steep decline, with the temperature at the maximum  $D^{\text{avg}}$  being higher than  $T_g$ . Auxiliary measurements, using the

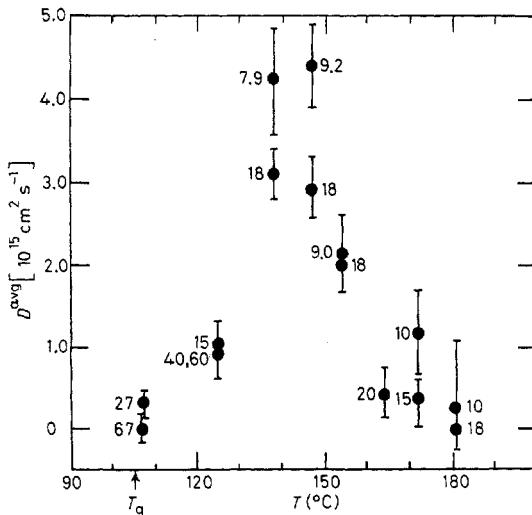


Fig. 2. – Effective diffusion coefficient,  $D^{\text{avg}}$ , defined in eq. (2), as a function of annealing temperature. The numbers next to the data points are the annealing times, in hours, of the SCPE/PMMA couples.

FRS technique [17], of the tracer diffusion coefficients (for the deuterated species) of d-PMMA and 50%-50% d-PMMA/SCPE blends into H-PMMA and 50%-50% H-PMMA/SCPE blends showed them to be smaller than  $5 \cdot 10^{-16} \text{ cm}^2/\text{s}$  at temperatures  $T < 160 \text{ }^{\circ}\text{C}$  indicating that the diffusion is either enhanced in the blend as observed by Jones *et al.* [2] and/or dominated by the SCPE tracer diffusion. The  $D^{\text{avg}}$  data can be qualitatively interpreted as follows. In the one-phase region, the mutual diffusion coefficient,  $D^{\text{mut}}$ , for two polymers *A* and *B*, can be derived from the Flory-Higgins approximation for the free energy of mixing [5-7]. The expression obtained, which has also been experimentally verified [2, 3, 18] is given by

$$D^{\text{mut}} = 2\phi_A \phi_B (D_A^* N_A(\phi_B) + D_B^* N_B \phi_A)(\chi_s - \chi(T)) , \quad (3)$$

where

$$\chi_s = 0.5[(N_A \phi_A)^{-1} + (N_B \phi_B)^{-1}] \quad (4)$$

and

$$\phi_A + \phi_B = 1 . \quad (5)$$

<sup>(2)</sup> Numerical solution of the diffusion equation for cases where the concentration ( $\phi$ ) dependence of the mutual diffusion coefficient,  $D^{\text{mut}}(\phi)$ , is not too extreme shows that the expression for  $D^{\text{avg}}$  in eq. (2) is close to the value of  $D^{\text{mut}}$  ( $\phi = 0.5$ ), independent of the functional form of  $D^{\text{mut}}(\phi)$ . R. Ball, private communication and especially appendix IV in ref. [18].

$D_A^*$ ,  $D_B^*$  are the tracer coefficients and  $N_A$ ,  $N_B$  are the polymerization indices. From eqs. (3)-(5) one can see that at a given  $T > T_c$ , the macroscopic  $D^{\text{mut}}$  goes to zero as the concentration approaches the value on the spinodal line. (On a shorter scale, terms in the free energy proportional to  $(\nabla\phi_A)^2$  ensure that diffusion continues until the equilibrium interface is established between the two stable concentrations defined by the spinodal line) [13, 16]. As the temperature is increased several competing effects must be considered; *a*) above the glass transition the tracer coefficients,  $D_A^*$  and  $D_B^*$  in eq. (3) increase rapidly as described by the WLF approximation [19]; *b*) the concentration space in the miscible region is reduced as the two-phase region grows wider and *c*) the equilibrium interface width between the coexisting phases grows narrower according to eq. (1). The latter two effects compete and finally overcome the first, producing the sharp downturn in the  $D^{\text{avg}}$  coefficients observed in fig. 2. A more quantitative model must account for the dynamics of interface formation and diffusion through the interfacial region between the two coexisting concentrations on the spinodal. Several wave-vector-dependent theories [14-16] exist which predict in the spinodal region  $D(q)$  is positive for short wavelength, but negative for long ones. Application of these theories to ion scattering data would require Fourier inversion of the  $q$ -dependent equations into direct space. Further experiments are currently in progress using RBS, to measure formation of the interfacial width as a function of temperature. The present data for  $T > 160$  °C is consistent with the prediction of eq. (1) that the interfacial width should become narrower with increasing temperature. From fig. 1c) one can see that at 181.5 °C the width is less than the experimental resolution of 50 nm.

Another aspect of this explanation is that there is no *a priori* reason for  $D^{\text{avg}}$  to scale as  $\sigma^2/t$ . Rather as  $t \rightarrow \infty$ , the interquartile width is expected to approach a constant value which is a function of the coexisting phases on the spinodal and the intrinsic width of the interface. Qualitatively this is consistent with fig. 2, where the  $D^{\text{avg}}$  values at longer annealing times, for a given temperature, appear systematically lower as  $\sigma$  increases more slowly than  $\sqrt{t}$ .

In conclusion, we have observed the critical slowing-down of mutual diffusion as a function of temperature in a partly miscible polymer blend, and obtained an experimental estimate of the interfacial width for  $T \gg T_c$ . It is hoped that these results, coupled with the potential of RBS to obtain better spatial resolution, will stimulate theoretical efforts to produce a more complete theory of interface formation in direct space.

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