BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 19, pp. 3687–3695, 1995

0032-3861/95/$10.00+0.00

Limited-supply non-Fickian diffusion in glassy polymers

P. F. Nealey*†, R. E. Cohen*‡ and A. S. Argon§
**Department of Chemical Engineering, and §Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
(Received 26 October 1994; revised 10 March 1995)

Non-Fickian diffusion of a flame-retardant plasticizer, resorcinol bis(diphenyl phosphate) (RDP), in a glassy poly(ether imide), Ultem^{TM}, was measured with Rutherford backscattering spectroscopy (RBS). Volume fraction *versus* depth profiles were obtained as a function of time, temperature and externally applied stress in experiments where a limited supply of RDP was initially present on the surface of the Ultem. The profiles of the plasticizer in the glassy polymer in all samples had sharp diffusion fronts with constant volume fraction behind the front. The limited-supply boundary condition requires that the volume fraction, ϕ, of RDP in the plastized zone decreases as penetration depth increases. Isochronal values of ϕ decrease with increasing temperature. At long times, ϕ approaches a value such that the material in the plasticized zone has a glass transition temperature equal to the temperature of the experiment. At 140, 160 and 180°C, ϕ decreased in direct proportion to the logarithm of time. At 120°C, two regimes of diffusion behaviour were observed in a plot of ϕ *versus* log time. Short-time, high-ϕ behaviour corresponds to case II diffusion, and long-time, low-ϕ behaviour corresponds to anomalous diffusion. Only the regime of anomalous diffusion was observed at the higher temperatures. Externally applied biaxial tensile or compressive stresses of order 10 to 40 MPa in the plane of the sample had no effect on diffusion normal to the plane in experiments at 120°C lasting 1 or 72 h.

(Keywords: non-Fickian diffusion; glassy polymers; Rutherford backscattering)

INTRODUCTION

A central process in a recently reported toughening mechanism observed in blends of a few volume per cent low-molecular-weight polybutadiene rubber (PB) and high-molecular-weight glassy polystyrene (PS) is the diffusion of PB into PS in the immediate vicinity of crazes[1,2]. According to a previously proposed model, randomly dispersed pools of phase-separated PB approximately 0.1 μm in diameter are tapped by crazes as they grow. A limited supply of PB wets the PS craze surfaces, and mass transport of PB into the PS is accelerated by the positive mean normal stress that is present in these regions during the deformation process. The chemical potential of the PB dissolved in PS is altered by the presence of the stress field, and the solubility of PB in PS is increased[3,4]. Thus one effect of the stress field is to create a greater driving force for diffusion. The material that is drawn into crazes is plasticized and crazing occurs at a lower flow stress than in the homopolymer, ultimately resulting in larger strains to fracture and increased toughness by avoiding critical levels of stress that initiate craze matter breakdown from intrinsic or extrinsic imperfections. Diffusion is clearly the limiting process in this mechanism because the increased toughness of these blends disappears at high strain rate, low temperature, or when a higher-molecular-weight PB is used[5]. Based on measured[6] craze velocities at 25°C and a characteristic length in the system of 10 nm (the diameter of a craze fibril), the required diffusion coefficient for the PB in PS to account for the toughening mechanism must be of order 10^{-12} cm^2 s^{-1} at room temperature. Tracer diffusion coefficients for 3000 g mol^{-1} PB in PS do not attain this magnitude until the temperature of the system is approximately 115°C, well above the T_g of PS[7]. It is possible that a non-Fickian diffusion mechanism can account for the required level of local flux of PB into the PS craze matter. This scenario is closely related to the model of Brown[4] for environmental craze growth in polymers.

Many plasticizer–glassy polymer systems have been studied that exhibit non-Fickian diffusion behaviour. Experimental and theoretical developments in this field are documented quite well in a number of recent publications[8–13]. In these studies, the polymer is in contact with an infinite reservoir of the plasticizer at constant activity. Under this particular boundary condition, the transport is characterized by an induction period followed by the formation of a diffusion front with a steep concentration gradient between swollen and unswollen material. The front propagates at a constant velocity and the mass uptake of penetrant is linear with time. Essentially the concentration behind the diffusion front is constant and is fixed by the equilibrium swelling ratio. The process zone in non-Fickian diffusion lies

---

† Present address: Chemistry Dept, Harvard University, Cambridge, MA 02138, USA

‡ To whom correspondence should be addressed

immediately ahead of the sharp interface. In this zone, entangled polymer chains are constrained in the unperturbed glassy polymer but are in close proximity to very mobile chains in the swollen plasticized material. Stresses on the order of the yield stress of the polymer can be generated in the glassy material just ahead of the diffusion front. The stress drives the diffusion and the time-dependent mechanical response of the polymer is the rate-controlling step[14]. The critical roles that stress and plasticization play in non-Fickian diffusion motivated us to explore the possible relevance of this mechanism to the diffusion process in the locally plasticized toughened PB/PS blends mentioned above.

Non-Fickian diffusion has been modelled by a number of groups for the boundary condition of an infinite supply of plasticizer in contact with a glassy polymer[8-15]. We will discuss the results of our experiments in relation to models based on the work of Thomas and Windle[9,10,13,14] because the parameters of these models are directly comparable to our measurements, and the models seem to capture the fundamental aspects of non-Fickian transport. The Thomas and Windle model successfully incorporates the ideas that the diffusion is driven by the stress generated ahead of the diffusion front and is controlled by the creep deformation of the polymer. The stress is calculated via an osmotic pressure analogy and the creep deformation of the polymer is considered to be dependent on the elongational viscosity, η. Both the viscosity and the diffusion coefficient in the flux equation are strongly dependent on the local volume fraction of penetrant. Thus the diffusion coefficient and the physical properties of the polymer change dramatically across the narrow interface between the swollen, plasticized material and the unswollen glassy substrate.

Hui *et al.*[9,10] developed a model based on the work of Thomas and Windle[14] for the infinite-supply-reservoir boundary condition; the Hui model is particularly useful for comparison to our limited-supply non-Fickian diffusion problem. It is useful because many of the observable non-Fickian diffusion characteristics are described in terms of the volume fraction of the plasticizer, ϕ, in the plasticized zone, a parameter that we measure directly in our experiments. In the present study with a limited supply of plasticizer, ϕ is a function of penetration depth. Hui *et al.*[9,10] described in detail the initial stages of non-Fickian diffusion, and defined a critical volume fraction, ϕ_c, below which the characteristic diffusion front will not form. They calculate that the natural logarithm of the diffusion front velocity increases rapidly for values of ϕ slightly greater than ϕ_c; however, the rate of increase drops off at higher values of ϕ. Hui *et al.* compared their model to diffusion profiles of iodohexane in polystyrene that were determined using Rutherford backscattering spectroscopy.

A Deborah number, originally introduced by Vrentas *et al.*[16], and later used by Durning[15] and Wu and Peppas[13], provides an insightful means to understand transitions in diffusion behaviour in polymer–plasticizer systems. Qualitatively, the integral sorption Deborah number, *De*, as defined by Wu and Peppas[13], is the ratio between the characteristic relaxation time of the glassy polymer and the characteristic time for diffusion in the plasticized zone. If $De \ll 1$, then the diffusion mechanism will be Fickian. Non-Fickian diffusion behaviour occurs when *De* is of order 1 and greater. *De* of order 1 is called anomalous diffusion, and $De \gg 1$ is called case II diffusion.

The goal of the present work is to observe non-Fickian diffusion of a plasticizer in a glassy polymer when the plasticizer is present in limited supply. The system we have chosen to investigate consists of a stable non-volatile plasticizer, resorcinol bis(diphenyl phosphate) (RDP), and a glassy poly(ether imide), Ultem$^{\mathrm{TM}}$. Experiments were performed in the range of 120 to 160°C, which is 95 to 55°C below the 215°C T_g of Ultem. At the end of each experiment the specimen was quenched to room temperature to 'freeze' the concentration *versus* depth profiles. The concentration profiles were determined via Rutherford backscattering spectroscopy in which the phosphorus atoms of the RDP provide an excellent tag to monitor the plasticizer volume fraction as a function of depth. The diffusion was measured as a function of time, temperature, matrix properties and externally applied biaxial compressive and tensile stresses. The results for the limited-supply boundary condition experiments are interpreted in terms of the above-mentioned theories of non-Fickian diffusion.

EXPERIMENTAL

Materials

The glassy polymer employed in this study is a poly(ether imide) known as Ultem$^{\mathrm{TM}}$ 1000 (Ultem). The polymer was supplied by General Electric Co. in pellet form. The chemical structure is shown in *Figure 1*. Ultem was chosen because it has a high glass transition temperature (~ 215°C) and is resistant to crazing[17]. The selected plasticizer is resorcinol bis(diphenyl phosphate) (RDP). This flame-retardant plasticizer, known as Fyrolflex RDP, was supplied by Akzo Chemicals Inc. in the form of a viscous liquid (~ 600 cP at 20°C). The chemical structure of the compound is shown in *Figure 2*. Approximately 70% of the material is the dimer where $n = 1$, and the rest is higher-order oligomers and a few per cent triphenyl phosphate. This product is non-volatile (vapour pressure < 1 mmHg at 37.8°C) and is stable to 370°C.

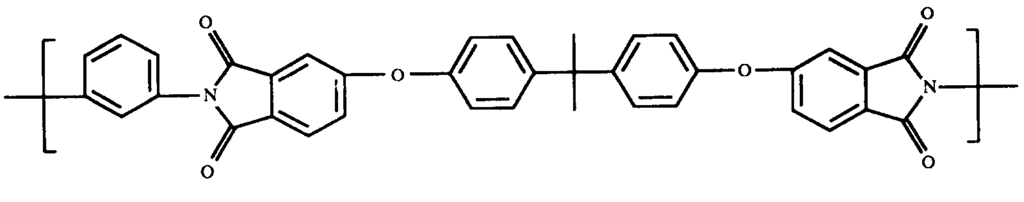

Figure 1 Chemical structure of Ultem

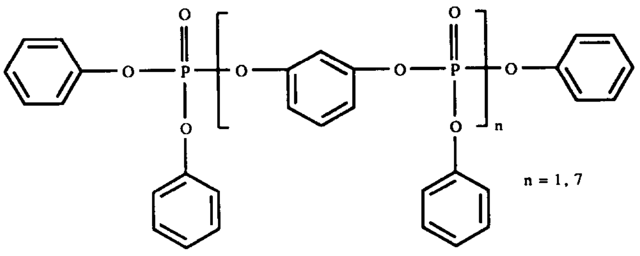

Figure 2 Chemical structure of RDP

Sample preparation

Most of the samples were prepared in the following manner. A uniform film of Ultem greater than 2 μm in thickness was deposited on a piece of silicon wafer via spin coating at 1500 rpm from a 15% by weight solution of Ultem in anisole. These films were dried in a vacuum oven for 8 h at room temperature and then for 24 h at approximately 220°C, a temperature 5°C above the T_g of Ultem. The oven was then allowed to cool slowly to room temperature over the course of about 4 h. We tried to ensure that each sample would experience the same thermal history. Samples that were part of the same series of experiments were processed together in a single batch. Films approximately 70 nm thick which consisted of a 4:1 blend of RDP and Ultem were deposited on a clean glass slide via spin coating from a solution that was 4% by volume RDP and 1% by volume Ultem in anisole. Transmission electron microscopy performed on one of these films did not reveal phase separation, and for the purposes of this study we consider the 4:1 blend to be homogeneous. The blended film was floated off the glass slide onto the surface of a water bath and picked up with the Ultem coated wafer. The bilayer samples were dried in a vacuum oven overnight at room temperature prior to placement in a thin-walled copper chamber, which was subsequently immersed in an oil bath for a specific period of time. The minimum time period for diffusion in the experiments was 30 min; this period is long enough to eliminate any significant effects of temperature transients and fluctuations that arise as the sample chamber initially heats up and the oil bath regains its steady-state temperature.

Some samples were subjected to an externally applied stress in addition to being held for 1 h or 72 h at 120°C. These samples were prepared from injection-moulded Ultem discs 4 inches (~ 102 mm) in diameter and 1/8 inch (~ 3.2 mm) thick supplied by General Electric Co. The polymer discs were sanded down to thicknesses of 0.5 to 1 mm and then polished with successively smaller diamond grit solutions starting with a 15 μm grit and ending with 1 μm. In this way bulk samples could be prepared with high-quality surfaces suitable for ion beam analysis. The samples were stressed biaxially in a concentric ring arrangement depicted in *Figure 3*. A load is applied to the smaller ring with radius R on one side of the disc and the other side of the sample is held by a larger concentrically placed ring with radius A. The biaxial stress, σ_{biaxial}, arises inside the smaller ring in the plane of the disc and is either compressive or tensile depending on which side of the sample is considered; σ_{biaxial} is calculated as a function of R, A, the load L, the reciprocal Poisson ratio n, and the sample thickness t, with the following equation[18]:

$$\sigma_{rr} = \sigma_{\theta\theta} = \sigma_{\text{biaxial}}$$

$$= -\frac{3L}{2\pi n t^2}\left[0.5(n-1)(n+1)\log\left(\frac{A}{R}\right) - (n-1)\frac{R^2}{2A^2}\right] \tag{1}$$

where σ_{biaxial} is the surface stress in both the radial and tangential directions in the plane of the sample at distances less than R from the sample centre. The stress normal to the plane of the sample, σ_{zz}, is zero. Two sample chambers, one with R and A equal to 11.1 and 23.8 mm, and the other with R and A values of 14.4 and 45.6 mm, were designed in which samples could be subjected to biaxial stresses while immersed in an oil bath for temperature control. With these devices, loads of a few kilograms produce values of σ_{biaxial} as high as 40 MPa. The large sample holder was used for samples in which the diffusion surface was held in tension, and the small sample holder for samples in which the diffusion surface was held in compression.

Rutherford backscattering spectroscopy

All of the samples were analysed with Rutherford backscattering spectroscopy (RBS) at the Cambridge Accelerator for Materials Science located at Harvard University. The model system of RDP and Ultem was chosen to allow the determination of the phosphorus concentration as a function of depth, which can be directly correlated to the volume fraction RDP in Ultem based on knowledge of the chemical formulae and densities of the species involved. We employed a 2 mm diameter beam of 2 MeV alpha particles ($^4He^+$), which was directed normal to the sample surface. The backscattered alpha particles were counted in a subtended solid angle of 14.2×10^{-3} steradians centred at 176° from the incident beam as a function of energy using an annular silicon surface barrier detector and a multichannel analyser. The beam dose for all of the samples was 15 μC. The resolution in the experiments was 20 keV. Details of this experimental technique are described elsewhere[5,19,20].

Differential scanning calorimetry

Blends that contained from 0 to 30% by weight RDP in Ultem were prepared via evaporation of solvent from solutions of RDP and Ultem in methylene chloride.

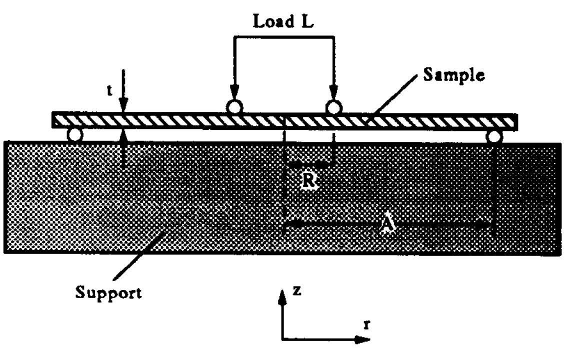

Figure 3 Configuration of concentric ring stress experiments (cross-sectional view)

Solutions of approximately 10% by weight polymer were poured into 1 inch (~ 25 mm) diameter weighing pans and allowed to evaporate slowly over the course of a week in a partially sealed chamber. The samples were then dried in air for a few days, and finally in a vacuum oven at room temperature for more than one week. The specimens had thicknesses of approximately 0.5 mm. Glass transition temperatures for the blends were determined from differential scanning calorimetry (d.s.c.) experiments on a Perkin–Elmer model DSC7 operated at 20°C min^{-1} in scans from 50 to 250°C.

RESULTS

Figure 4 shows the results from the d.s.c. experiments on static cast homogeneous blends of RDP and Ultem. As the volume fraction of RDP increases from 0 to 0.3, the single glass transition temperature of the blended RDP/Ultem material decreases monotonically from 215 to 90°C.

Typical RBS data from a sample held for 4.5 h at 140°C are shown in *Figure 5*. Helium ions backscattered from elastic collisions with phosphorus atoms on the surface of the sample in the configuration of our experimental set-up are detected at an energy of 1.19 MeV. The data at energies immediately lower than 1.19 MeV are from helium ions backscattered from phosphorus atoms below the surface of the sample; decreasing energy corresponds to increasing depth. Here an energy of 1.10 MeV in the phosphorus peak is equivalent to a depth of 275 nm (ref. 5). The data at energies below 0.75 MeV are a result of backscattered helium ions from oxygen, nitrogen and carbon atoms in the sample. Since RDP is the only species in the sample that contains phosphorus, the yield of backscattered helium ions from collisions with phosphorus is directly proportional to the volume fraction of RDP in the sample. Thus a volume fraction *versus* depth profile of RDP in Ultem is obtained in the RBS experiments. The profile in *Figure 5* shows that the limited supply of RDP initially on the surface has penetrated into the initially pure Ultem layer and a sharp diffusion front exists at a depth of 275 nm between swollen and unswollen material. The width of the interface is less than the 50 nm, the depth resolution[21] of the technique. The concentration of RDP in the plasticized zone is constant within the experimental error. The normalized yield of backscattered helium from phosphorus atoms corresponds[21] to a volume fraction of RDP in Ultem equal to 0.26 in the swollen layer. The existence of the sharp diffusion front with a constant concentration behind the front is indicative of non-Fickian diffusion[9,14]. If the diffusion were Fickian, the concentration *versus* depth profiles would resemble complementary error functions[7,22]. The shape of the profile shown in *Figure 5* is typical of all the samples analysed in this study.

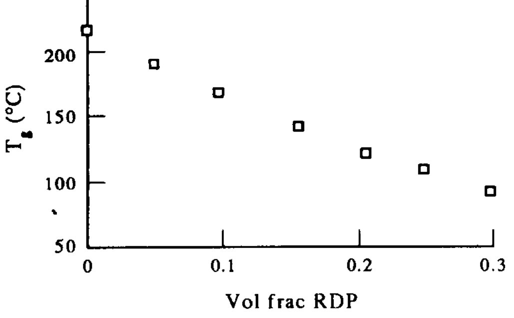

Figure 4 Glass transition temperature as a function of volume fraction RDP

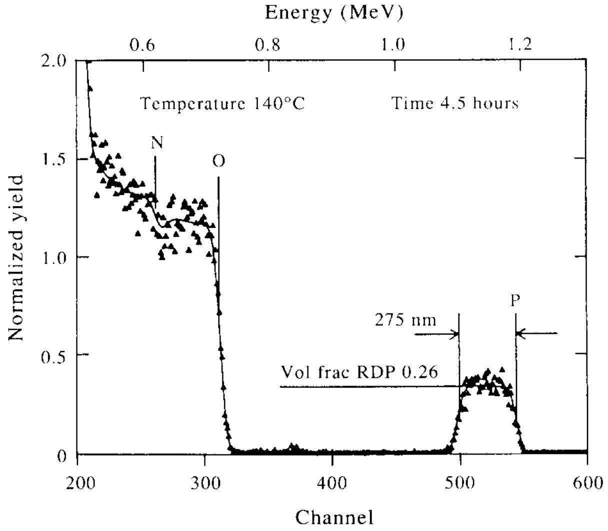

Figure 5 Typical RBS data for a sample held 4.5 h at 140°C. The energy (channel) and normalized yield axes are readily converted to depth and volume fraction RDP in Ultem respectively. Subsequent figures of RBS data omit the former units and the axes are labelled with relevant penetration depths and volume fractions

The full curve in *Figure 5* represents the best least-squares fit of a simple model to the data. The model assumes that a step function in RDP volume fraction is formed via diffusion into the initially pure Ultem substrate. The step function is convoluted with a Gaussian function whose full width at half-maximum is 20 keV, the known resolution of the experiment, and the result is fitted to the RBS data. The convolution with the Gaussian function is responsible for the rounding of the step function edges. The Gaussian function is determined and fixed independently[21] and should not be considered a fitting parameter. Only the penetration depth and the volume fraction of RDP in the step function are varied to obtain the best two-parameter fit. Data between about 0.5 and 0.7 MeV are used to normalize the yield or volume fraction axis for small errors in measured beam dose from sample to sample. These fits are performed with the aid of the RUMP software package developed at Cornell University[23,24]. The software was purchased from Computer Graphics Service in Lansing, NY. The program performs complex iterative fits to RBS data given the specific parameters of the experimental configuration and the physical and chemical properties of the species in the sample.

Figure 6 shows the effect of changing the quantity of RDP in the limited-supply boundary condition. Only the phosphorus peak is plotted with the axes labelled in terms of depth and volume fraction RDP. Each sample was held for 1 h at 140°C. One of the samples had twice as much RDP present initially on the sample surface. This was accomplished by simply picking up two RDP/Ultem supply films from a water bath as described above.

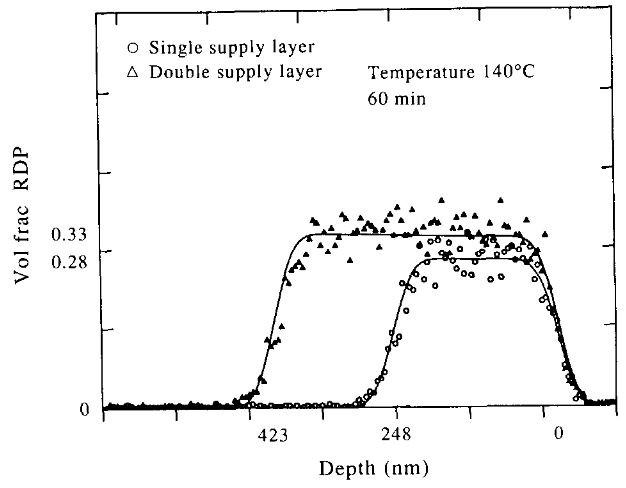

Figure 6 RBS data for single and double supply layer samples held for 60 min at 140°C

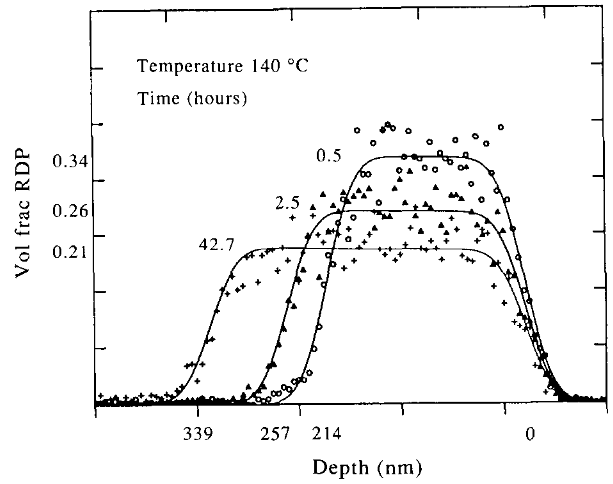

Figure 8 RBS data for samples held at 140°C for 0.5, 2.5 and 42.7 h

The penetration depth of RDP in the sample with twice the supply of RDP present is almost but not quite twice that of the sample with the single supply layer. A somewhat higher volume fraction of RDP in the plasticized zone in the double supply layer sample is therefore also observed. This indicates that diffusional resistance in the swollen layer is an important component of diffusion front propagation at this time and temperature.

Figure 7 shows the RBS data for a series of samples that were held for 20 h at temperatures ranging from 120 to 180°C. In each sample, a sharp diffusion front exists between an unswollen Ultem layer and a homogeneous swollen layer with a constant concentration of RDP. The depth of penetration of the front into the initially pure Ultem layer increases as the temperature increases. Each sample had approximately the same limited supply of RDP, and thus, by the conservation of mass, the further the penetration the lower the volume fraction of RDP in the swollen layer.

In another series of samples, the temperature was held at 140°C and the diffusion time was varied from 0.5 to 42.7 h. The phosphorus peaks of the RBS data from these samples are plotted in terms of volume fraction RDP *versus* depth in *Figure 8*. The depth of penetration of the RDP diffusion front increases as the time of the experiment increases. However, the penetration depth clearly does not increase linearly with time. The front position changes from 214 nm to 257 nm for 0.5 to 2.5 h, and then only reaches a value of 339 nm after 42.7 h. A plot of the volume fraction RDP *versus* time for samples held from 0.5 h to 72 h at temperatures of 160 and 180°C is shown in *Figure 9*. For both temperatures, the volume fraction RDP, ϕ, in the plasticized zone decreases rapidly at short times and then decreases at a much slower rate at long times. The glass transition temperatures found in the separate d.s.c. experiments are plotted as a function of blend composition on the right axis of *Figure 9*. We note that the slope of the volume fraction RDP data as a function of time approaches zero as ϕ approaches a value such that the material in the plasticized zone has a glass transition temperature equal to the temperature of the experiment. Plotted in *Figure 10* are the values of ϕ in the plasticized layer after 2 and 72 h at 120, 140, 160 and 180°C. After 72 h at 180 and 160°C, the material in the plasticized zones have glass transition temperatures of approximately 180 and 160°C, respectively. The material in the plasticized zones after 72 h at 140 and 120°C have glass transition temperatures still well below 140 and 120°C, respectively.

A series of experiments were performed to explore the

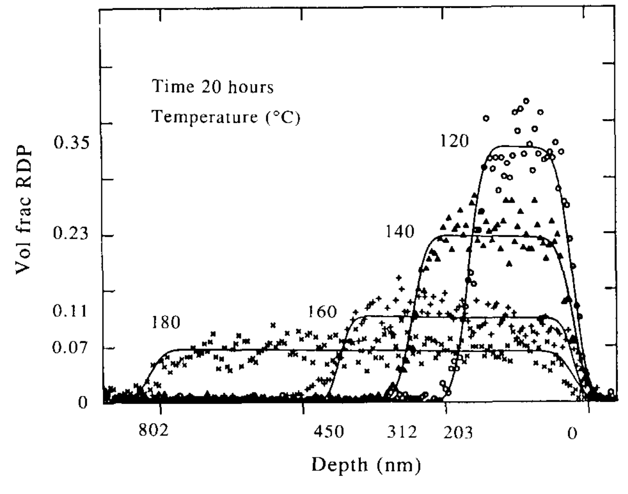

Figure 7 RBS data for samples held 20 h at 120, 140, 160 and 180°C

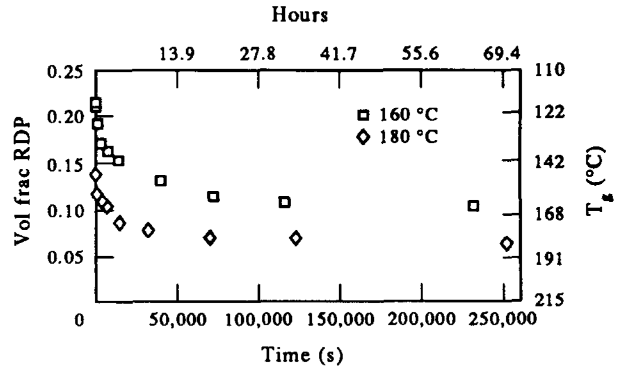

Figure 9 Plot of volume fraction *versus* time for samples held at 160 and 180°C. T_g as a function of volume fraction is shown on the right-hand axis

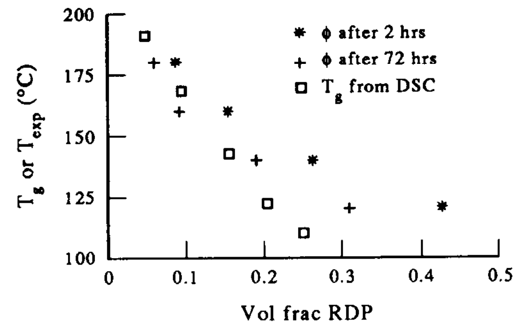

Figure 10 Plot of T_g and ϕ after 2 and 72 h as a function of volume fraction

effect of matrix properties on the propagation of the diffusion front. A two-step process was used; one supply layer was allowed to diffuse for 9 h at 180°C in all of the samples, and then a second supply layer was applied and allowed to diffuse for various time periods at 120°C. RBS data and fits for two of these samples are shown in *Figure 11*. A two-step concentration profile is created; penetration to a depth of approximately 700 nm with a volume fraction RDP in the plasticized zone equal to 0.08 occurs at 180°C, and the superimposed second front at higher volume fractions RDP is formed at 120°C. In this process, the front that propagates at 120°C does so in a material that is a 0.08 volume fraction blend of RDP in Ultem. In *Figure 12* a plot of ϕ as a function of log time at 120°C in pure Ultem is compared to the results of the full series of two-step experiments. Both sets of data exhibit two regimes of diffusion behaviour where there is a noticeable change of slope in the semilog plot. At long times, the two sets of data eventually coincide and the effect of different matrix properties is minimal. At short times, however, the two sets of data show an apparent shift in time, and the slopes differ.

As described in the 'Experimental' section, several samples were subjected to externally applied stresses while diffusion proceeded at 120°C. Results of these experiments are summarized in *Table 1*. Despite the application of radial and tangential stresses in the plane of the sample as high as 40 MPa in tension or compression, there is no significant, observable effect on the limited-supply diffusion of RDP in Ultem after either 1 h or 72 h.

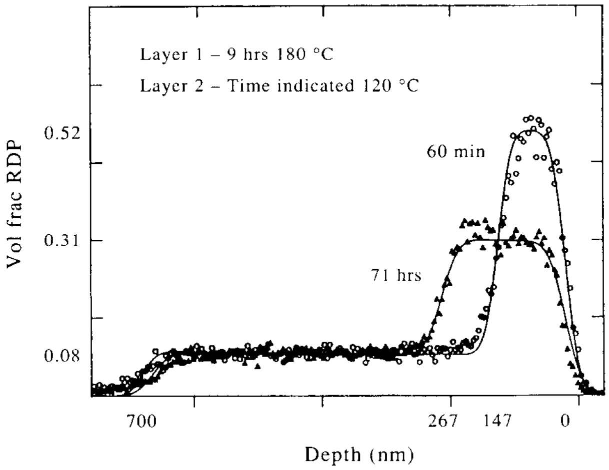

Figure 11 RBS data from two-step diffusion experiments for samples held for 60 min and 71 h at 120°C during the second step

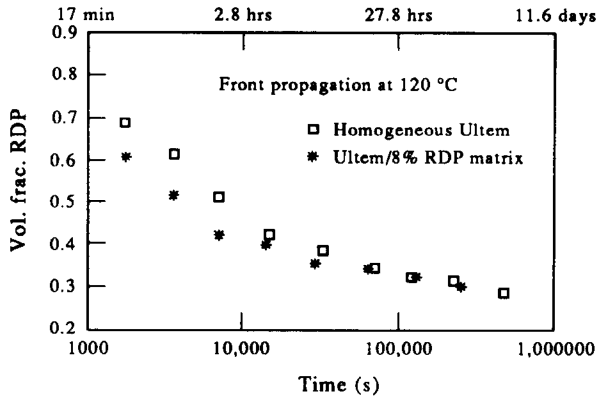

Figure 12 Plot of volume fraction *versus* log time for front propagation at 120°C in pure Ultem, and Ultem with 0.08 volume fraction RDP in the second step of the two-step experiments

DISCUSSION

In order to compare the results of this investigation to previous work regarding non-Fickian diffusion in plasticizer–glassy polymer systems, we must find the means to compare diffusion with a limited-supply boundary condition to diffusion with an infinite-reservoir boundary condition. The differences that arise because of the boundary conditions are readily apparent. With the limited-supply boundary condition, the propagation of the diffusion front is clearly not linear with time (*Figures 8* and *9*); also the volume fraction RDP, ϕ, in the plasticized zone necessarily decreases with time and penetration depth. Therefore the properties of the material behind the diffusion front change with time and penetration depth, continuously changing the local driving forces that advance the diffusion front. In contrast, in an infinite-reservoir boundary condition, a fully developed diffusion front propagates under a constant driving force with a constant velocity and ϕ does not vary with time and penetration depth. The properties of the material behind the diffusion front are constant. However, ϕ can be varied in the infinite-reservoir experiments by changing the activity of the plasticizer in the reservoir[9,25]. The front velocity v as a function of ϕ has been determined both experimentally

Table 1 Results from samples subjected to an external stress

Run number	Time (h)	Stress[a] (MPa)	Volume fraction RDP
1	72	0	0.33, 0.34
		32.3 (C)	0.34
		19.8 (T)	0.28
2	72	0	0.27
		43.1 (C)	0.29
		26.7 (T)	0.27, 0.26
3	72	0	0.28
		12.7 (C)	0.27
		37.6 (T)	0.26
4	1	0	0.36, 0.35
		5.1 (T)	0.34
		9.9 (T)	0.38
		25.3 (T)	0.35

[a] T = tension, C = compression

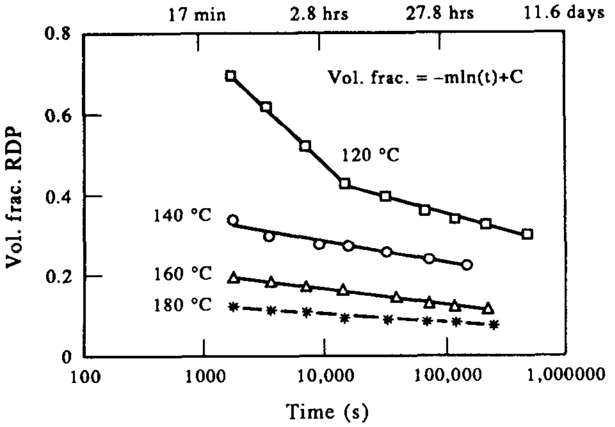

Figure 13 Plot of volume fraction *versus* log time for samples held at 120, 140, 160 and 180°C with fits to the data of the equation $\phi = -m\ln(t) + C$

and theoretically[9]. These results from the literature are compared to results in this study with the limited-supply boundary condition by calculating an instantaneous front velocity as a function of ϕ in the RDP/Ultem system as described below.

Figure 13 is a plot of the volume fraction RDP *versus* log time in the plasticized zone at all the temperatures studied. The solid lines represent the best least-squares fit of the equation:

$$\phi = -m\ln(t) + C \qquad (2)$$

where t is the time in seconds, and m and C are constants. Equation (2) has been applied to the 120°C data with different values of m and C to account for the two distinct regimes of behaviour for volume fractions above and below approximately 0.43. The values of m and C for the different data sets are tabulated in *Table 2*. Although equation (2) fits the experimental data quite well, we do not place any particular physical significance on the parameters.

Instantaneous front velocities are calculated as a function of ϕ in the following way. The conservation of mass requires that:

$$\phi z = S \qquad (3)$$

where z is the penetration depth, and S is a constant. From the experimental data at 120°C and 140°C, S is determined to be 72 ± 9 nm. At 160°C and 180°C, experimentally determined values of S systematically decrease from this same value of 72 nm to approximately 50 nm at times greater than 4 h. It is possible that there is a small evaporation rate at the higher temperatures, or that RDP diffuses into the Ultem beyond the front at volume fractions that are too low to quantify. For the purpose of the calculations, we use $S = 72$ nm for all of the data. The instantaneous front velocity is given by:

$$v = \frac{dz}{dt} = -\frac{z^2}{S}\frac{d\phi}{dt} \qquad (4)$$

Combining equations (2) and (4):

$$v(\phi) = \frac{Sm}{\phi^2 \exp[(C - \phi)/m]} \qquad (5)$$

A semilog plot of the calculated instantaneous front velocities as a function of the volume fraction of RDP in the plasticized layer is shown in *Figure 14*. The most interesting data set is for the experiments conducted at 120°C. At values of $\phi > 0.43$, v decreases slowly as ϕ decreases. Here the characteristic time for relaxation of the glassy Ultem is very much longer than the characteristic time for diffusion in the plasticized zone; that is $De \gg 1$, and this is the regime of case II diffusion. At values of $\phi < 0.43$, v decreases more rapidly as ϕ decreases. These values of v and ϕ occur at the longer experimental times when the material in the plasticized zone is approaching its rubber to glass transition. In this regime, the characteristic time for diffusion in the plasticized zone is the same order of magnitude as the characteristic relaxation time of the glassy Ultem. The De is of order 1 and the system shows anomalous diffusion behaviour. At all temperatures above 120°C, we capture only the anomalous diffusion behaviour because experiments in the case II regime require time periods that are too short for accurate temperature control in our experimental set-up. The instantaneous front velocities at temperatures above 120°C are also expected to increase less rapidly at higher values of ϕ. The plots are expected to have the same form as the plot for the data at 120°C. The shape of the semilog plot of v *versus* ϕ at 120°C is qualitatively the same shape as the semilog plot of the normalized front velocity *versus* ϕ published by Hui *et al.*[9] in their theoretical treatment of non-Fickian diffusion. The results from the RDP/Ultem system with a limited-supply boundary condition are therefore consistent with the existing theory of non-Fickian diffusion as it was developed for the infinite-reservoir boundary condition.

Table 2 Values of m and C for the various data sets

Temperature (°C)	m	C
120 ($\phi > 0.43$)	0.127	1.649
120 ($\phi < 0.43$)	0.039	0.794
140	0.025	0.502
160	0.019	0.33
180	0.012	0.212

Hui *et al.* defined ϕ_c as the composition where the diffusion coefficient, $D(\phi)$, undergoes a step change: $D(\phi < \phi_c)$ is equal to the diffusion coefficient in the glassy polymer, D_g, and $D(\phi > \phi_c)$ is equal to the diffusion coefficient in the plasticized rubbery polymer,

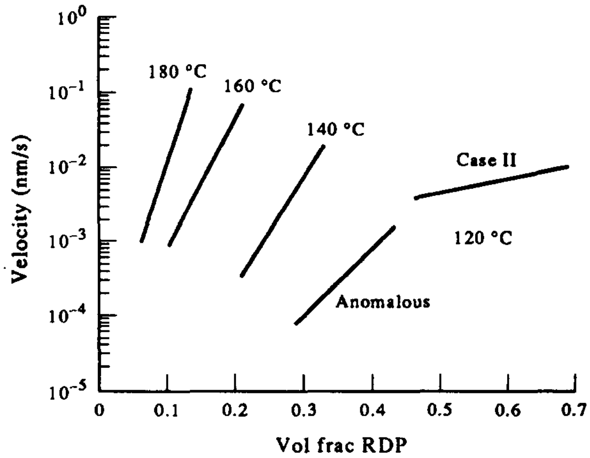

Figure 14 Semilog plot of instantaneous front velocity *versus* ϕ

$D_r (D_r \gg D_g)$. They do not state explicitly that ϕ_c corresponds to the material composition that has a glass transition temperature equal to the temperature of the diffusion experiment, even though this seems to be implied in their definition of $D(\phi)$. Gall *et al.*[8] argue that the onset of case II diffusion occurs when the glassy polymer begins to yield in response to the stress generated at the interface between plasticized material and unswollen material, not when the T_g of the plasticized material drops below the ambient temperature. They cite evidence from experiments with *N*-methylpyrrolidinone (NMP) diffusing into an aromatic polyimide in which the swollen material is not above its T_g (ref. 26). From the results of the present study (*Figures 9* and *10*), ϕ_c in the RDP/Ultem system is clearly identified as the composition at which a rubber to glass transition occurs at the temperature of the experiment. This supports the view that non-Fickian diffusion fronts form when the volume fraction of plasticizer reaches a value such that the plasticized zone is rubbery. The limited-supply boundary condition can then be viewed as an innovative experiment to determine ϕ_c; diffusion fronts are formed at values of $\phi > \phi_c$ and then ϕ decreases with time and penetration depth towards an asymptotic value ϕ_c. A novel aspect of the RDP/Ultem system is the non-volatile nature of the plasticizer and its high level of solubility in the glassy polymer. Good agreement was obtained when independent d.s.c. measurements of T_g in static cast blends were compared to values of ϕ_c determined in the diffusion measurements. Such comparisons were difficult or impossible to perform in previously studied systems in which the penetrants were volatile.

The two-step diffusion experiments provide a unique means to explore the effect of matrix properties on non-Fickian diffusion behaviour and test some principles of the Thomas and Windle theory. The propagation of the diffusion front at 120°C in the pure Ultem is compared to propagation of the front at the same temperature in a matrix that is a blend of 0.08 volume fraction RDP in Ultem (*Figure 13*). In the Thomas and Windle theory[14], the mean normal stress ahead of the diffusion front is calculated with an osmotic pressure analogy. The osmotic pressure, P_{os}, is proportional to the difference in chemical potential between the actual penetrant concentration in any material element and the local equilibrium value in that element if the stress were relaxed to zero. The actual penetrant concentration profile exhibits a Fickian tail that extends into the glassy polymer ahead of the diffusion front, and the maximum in P_{os} occurs somewhere along the Fickian tail where the actual concentration is small, the local equilibrium concentration is high, and the ratio of the concentration values is the greatest. In the two-step diffusion experiment, 0.08 volume fraction RDP is already in the matrix. Since the actual concentration of plasticizer can never reach values below 0.08 volume fraction, the calculated osmotic pressure as a function of depth must be significantly affected both in shape and (reduced) magnitude. The velocity of the diffusion front in the two-step experiments differs from that observed in the experiments with pure Ultem (*Figure 15*), not only because of different matrix viscosity, but also because of a significantly different profile of the mean normal stress ahead of the front.

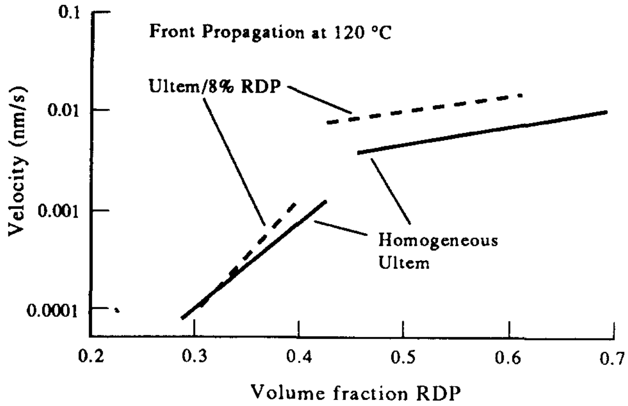

Figure 15 Semilog plot of instantaneous front velocities at 120°C in pure Ultem and Ultem with 0.08 volume fraction RDP in the second step of the two-step experiments

The effect of the altered matrix properties on front propagation at 120°C in the case II regime ($\phi > 0.43$) is essentially to shift the ϕ *versus* time data to shorter times (*Figure 12*). This implies that the induction time is shorter for propagation in the matrix with 0.08 volume fraction RDP. The material with 0.08 volume fraction RDP has a lower matrix viscosity, η_0, than pure Ultem. Thomas and Windle[14] predict that the induction time is a function of η_0 only, and decreases with decreasing η_0. A promising avenue of future research is to take advantage of the compatibility and thermal stability of the RDP/Ultem system and use measured front velocities in various two-step diffusion experiments to test the validity of non-Fickian diffusion models.

The results of the experiments where an external biaxial stress was applied in the plane of the sample, normal to the direction of the diffusion front velocity z, cannot be explained in the framework of the Thomas and Windle model. The mean normal tensile stress generated near the interface between the plasticized layer and the unswollen substrate is of order 50 to 100 MPa[9,13,14]. The largest externally applied biaxial stresses ($\sigma_{rr} = \sigma_{\theta\theta} = \sigma_{\text{biaxial}}, \sigma_{zz} = 0$) correspond to mean normal stresses ($2\sigma_{\text{biaxial}}/3$) of order 20 MPa, a significant fraction of the stress generated near the diffusion front. However, the superimposed mechanical stress had no detectable effect on the diffusion behaviour (see *Table 1*), even though Thomas and Windle consider the swelling rate in the interfacial region to be linearly proportional to the mean normal tensile stress (or osmotic pressure in their terminology). Owing to lateral constraints in the planar geometry of our experiment, the deformation or swelling of the polymer occurs only in the direction of penetration, z. Our results suggest that the swelling rate is influenced only by the component of stress in the penetration direction (σ_{zz}) rather than the mean normal stress. The magnitude of σ_{zz} was unaffected by the externally applied stress fields in our experiments and thus the diffusion behaviour did not change. An experiment that would verify this hypothesis would be to apply an external stress in the penetration direction and monitor changes in the diffusion behaviour.

The primary objective of our research was to obtain insight into the diffusion process that occurs in the toughening mechanism mentioned in the 'Introduction'. We note that Fickian diffusion at room temperature cannot account[3,7] for the required flux of polybutadiene into polystyrene to locally plasticize the material drawn into crazes[1,2]. We anticipated that the interplay of stress and plasticization in both the toughening mechanism and non-Fickian diffusion would be sufficient to account for the required flux of polybutadiene plasticizer. This scenario would be similar to the model of Brown[4] for environmental crazing in polymers. The required velocity of the diffusion front is about 10 nm s^{-1} based on a characteristic craze fibril diameter of 10 nm and a typical craze velocity of 10 nm s^{-1} measured at 70°C below the T_g of polystyrene[6]. Examination of *Figure 14* reveals that the front velocity at 145°C (70°C below the T_g of Ultem) is nowhere near 10 nm s^{-1}. In fact, even at 180°C, the front velocity does not appear likely to attain a value of 10 nm s^{-1}.

In view of the above, neither Fickian nor non-Fickian diffusion can explain toughening by localized plasticization. We are therefore forced to conclude that a more complex process is responsible for the toughening phenomenon observed in blends of PB in PS. The diffusion process and the deformation process of crazing must be highly interactive. Thus we propose that the act of plastic deformation of the PS locally creates a material with altered properties which enhances the diffusion of PB and accelerates the deformation. This observation is consistent with examples of deformation-enhanced diffusion found in the literature. Miller and Kramer[27] describe an increase of orders of magnitude in the diffusion rate of Freon 113 in crosslinked PS and poly(*p*-methylstyrene) in localized shear deformation zones, and Harmon *et al.*[28] show that deformed PMMA samples absorb methanol at much higher rates than undeformed samples. Tests are under way in our laboratory to document more completely this apparent relationship between active deformation and diffusion.

SUMMARY

Non-Fickian diffusion of RDP in Ultem was measured with RBS when the RDP was present in a limited supply initially on the surface of the Ultem. The volume fraction *versus* depth profiles of the plasticizer in the glassy polymer were essentially step functions and had sharp diffusion fronts less than 50 nm in width. The limited-supply boundary condition requires that, as the plasticizer front penetrates deeper into the glassy substrate, the volume fractions of RDP, ϕ, behind the front must decrease. At long time periods, ϕ approaches a value such that the material behind the front has a glass transition temperature equal to the temperature of the experiment. We identify this value of ϕ as the critical volume fraction of plasticizer, ϕ_c, as defined by Hui *et al.*[9,10], Lasky *et al.*[25] and Gall *et al.*[8]. Data taken at 120°C exhibit two regimes of non-Fickian diffusion behaviour, anomalous and case II. Only the anomalous regime was observed at 140, 160 and 180°C. The transition between regimes is interpreted in the framework of an inte-gral sorption Deborah number as defined by Wu and Peppas[13]. Calculations of the instantaneous front velocities, especially for the 120°C data, as a function of ϕ allow us to make a favourable comparison to the model of Hui *et al.*[9]. Unique two-step volume fraction profiles were produced by diffusion of a limited supply of RDP at 180°C followed by diffusion of a second limited supply of RDP at 120°C, and the effects of an altered matrix on front propagation at 120°C were considered. Externally applied biaxial tensile and compressive stresses in the plane of the sample of order 10 to 30 MPa had no measurable effect on diffusion normal to this plane at 120°C in experiments in the case II or the anomalous regime.

ACKNOWLEDGEMENTS

We thank Professor E. J. Kramer and his research group for many useful discussions, and for demonstrations of sample preparation and analysis techniques. Dr Roger Kambour of General Electric Co. helped us to identify the model polymer–plasticizer system. Alexis Black developed and implemented the polishing procedures for Ultem surfaces as part of the Undergraduate Research Opportunity Program at MIT. This research was supported by NSF/MRL, through the Center for Materials Science and Engineering at MIT under Grant No. DMR-90-22933.

REFERENCES

1 Gebizlioglu, O. S., Beckham, H. W., Argon, A. S., Cohen, R. E. and Brown, H. R. *Macromolecules* 1990, **23**, 3968

2 Argon, A. S., Cohen, R. E., Gebizlioglu, O. S., Brown, H. R. and Kramer, E. J. *Macromolecules* 1990, **23**, 3975

3 Nealey, P. F., Cohen, R. E and Argon, A. S. *Macromolecules* 1994, **27**, 4193

4 Brown, H. R. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 1273

5 Argon, A. S., Cohen, R. E. and Mower, T. M. *Mater. Sci. and Engng.* 1994, **A176**, 79

6 Spiegelberg, S. H., PhD Dissertation, MIT, 1993

7 Nealey, P. F., Cohen, R. E. and Argon, A. S. *Macromolecules* 1993, **26**, 1287

8 Gall, T. P., Lasky, R. C. and Kramer, E. J. *Polymer* 1990, **31**, 1491

9 Hui, C., Wu, K., Lasky, R. C. and Kramer, E. J. *J. Appl. Phys.* 1987, **61**, 5137

10 Hui, C., Wu, K., Lasky, R. C. and Kramer, E. J. *J. Appl. Phys.* 1987, **61**, 5129

11 Lasky, R. C., PhD Dissertation, Cornell University, 1986

12 Lustig, S. R., Caruthers, J. M. and Peppas, N. A. *Chem. Eng. Sci.* 1992, **47**, 3037

13 Wu, J. C. and Peppas, N. A. *J. Polym. Sci., Polym. Phys. Edn* 1993, **31**, 1503

14 Thomas, N. L. and Windle, A. H. *Polymer* 1982, **23**, 529

15 Durning, C. J. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 1831

16 Vrentas, J. S., Jarzebski, C. M. and Duda, J. L. *AIChE J.* 1975, **21**, 894

17 Kambour, R. P. *Polym. Commun.* 1983, **24**, 292

18 Roark, R. J. 'Formulas for Stress and Strain', 4th Edn, McGraw-Hill, New York, 1965

19 Chu, W. K., Mayer, J. W. and Nicolet, M. A. 'Backscattering Spectroscopy', Academic Press, New York, 1978

20 Feldman, L. C. and Mayer, J. W. 'Fundamentals of Surface and Thin Film Analysis', Elsevier Science, New York, 1986

21 Nealey, P. F., PhD Dissertation, MIT, 1994

22 Crank, J. 'The Mathematics of Diffusion', 2nd Edn, Oxford University Press, Oxford, 1975

23 Doolittle, L. R. *Nucl. Instrum. Meth. (B)* 1985, **9**, 344

24 Doolittle, L. R. *Nucl. Instrum. Meth. (B)* 1986, **15**, 227

25 Lasky, R. C., Kramer, E. J. and Hui, C. *Polymer* 1988, **29**, 673

26 Gattiglia, E. and Russel, T. P. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 2131

27 Miller, P. and Kramer, E. J. *J. Mater. Sci.* 1990, **25**, 1751

28 Harmon, J. P., Sanboh, L. and Li, J. C. M. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 3215