Diffusion studies in polymer melts by ion beam depth profiling of hydrogen

Peter F. Green, Peter J. Mills and Edward J. Kramer
Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, NY 14853, USA
(Received 3 September 1985)

Forward recoil spectrometry (FRES) is used to measure the volume fraction *versus* depth profiles of undeuterated polystyrene (PS) chains of molecular weight M that have diffused into a high molecular weight deuterated PS matrix. The tracer diffusion coefficient D^*_{PS} is extracted from these profiles. The D^*_{PS} is found to be identical with $D^*_{d\text{-}PS}$, the tracer diffusion coefficient of deuterated PS (d-PS) of the same molecular weight, as well as with D^*_{PS} measured by other techniques

(Keywords: diffusion; melts; hydrogen; forward recoil spectrometry; ion beam)

INTRODUCTION

Owing to the very slow translational diffusion rates of macromolecules in the melt, where the tracer diffusion coefficients may range from 10^{-8} to $10^{-18}\,cm^2\,s^{-1}$, experimental techniques with excellent depth resolution are required if diffusion measurements are to be made in reasonable times. Holographic grating techniques (forced Rayleigh scattering and fluorescence redistribution after pattern photobleaching)[1-7], small-angle neutron scattering (SANS) measurements[8], radiotracer methods[9,10], n.m.r. techniques[11-14], Rutherford backscattering spectrometry (RBS) measurements of inert marker movements[15,16], electron microprobe energy dispersive X-ray composition analysis[17,18] and infra-red microdensitometry[19-22] are techniques presently being used to perform such studies.

Forward recoil spectrometry (FRES) is an alternative ion beam analysis technique which can be used to measure diffusion[23]. It is particularly attractive because of its excellent depth resolution (80 nm) and high sensitivity (approximately 0.1 atomic per cent ^1H or ^2H). Previously[24,25] we demonstrated how the tracer diffusion coefficient, D^*, of deuterated polystyrene (d-PS) chains of molecular weight M can be obtained after diffusing a thin surface film of d-PS into an ordinary PS matrix by measuring the deuterium concentration depth profile using FRES.

While it seems reasonable that $D^*_{d\text{-}PS} = D^*_{PS}$ for chains of the same molecular weight, since any isotope effects should be small, no direct experimental verification of this assumption has been made. In this paper we provide verification by measuring the diffusion of PS into a high molecular weight d-PS matrix and compare the results of the FRES techniques with results on PS from other techniques in the literature.

FUNDAMENTALS OF ION BEAM ANALYSIS

In the FRES experiment, a schematic of which is shown in *Figure 1*, a monoenergetic beam of $^4He^{++}$ ions of energy E_0 is directed toward a sample at an angle of incidence of α with respect to the sample surface. The subsequent collision of the beam with the target nuclei may result in the ejection of those nuclei with energy E_2 at an angle θ with respect to the incident beam. Since energy and momentum are conserved in the collision (the collision is elastic), the energy E_2 is proportional to the energy E_1 of the incident beam just before impact, viz.

$$E_2 = KE_1 \tag{1}$$

where K is the kinematic factor for scattering which is given by

$$K = [4m_{He}m_t/(m_{He} + m_t)^2]\cos^2\theta \tag{2}$$

Here m_t and m_{He} are the masses of the target nuclei and $^4He^{++}$ projectiles respectively. At $\theta = 30°$ this factor is 0.479 and 0.667 for hydrogen and deuterium nuclei, respectively. The energy of the recoiling particles is measured using a silicon surface barrier detector which is located at an angle of $\theta = 30°$. When a particle is detected, a current pulse proportional to the particle energy is produced. The magnitude of this signal is measured and registered as a 'count' in the appropriate channel of a multichannel analyser.

The number of nuclei that recoil from a particular depth within the sample will depend on the area density of nuclei at that depth. The resulting counts (number of nuclei) *versus* energy curve is normalized to form the FRES spectrum $Y(E)$ by dividing $n(E)$, the number of counts at a given energy, by the charge Q collected on the sample (proportional to the number of incident $^4He^{++}$ ions), the solid angle Ω subtended by the detector and the energy width ε of a given channel, viz.

$$Y(E) = n(E)/Q\varepsilon\Omega \tag{3}$$

A Mylar foil of thickness 10.6 μm is placed in front of the detector to stop the forward scattered $^4He^{++}$

0032-3861/86/071063-04$03.00

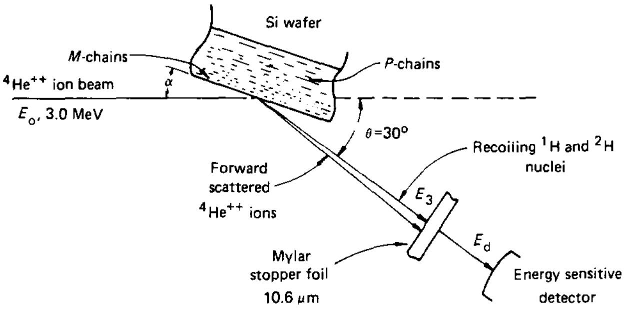

Figure 1 Geometry of forward recoil spectrometery experiment

projectiles and heavier nuclei. The recoiling particles, which are less massive and thus travel at higher velocities, pass through the filter with a modest loss in energy (several hundred keV).

It follows from the above discussion that the energy of a detected particle is

$$E_d = E_3 - \delta E_s \tag{4}$$

where E_3 is the energy which a recoiling nuclei has after leaving the sample surface and δE_s is the energy which it loses while passing through the stopper foil. As an example one can consider the case where both hydrogen and deuterium are on the surface of the sample. Since $E_3 = E_2 = KE_0$, then

$$E_d = KE_0 - \delta E_s \tag{5}$$

Alternatively, if the particle is located at a depth x beneath the sample surface then

$$E_3 = [E_0 - S_1 x/\sin(\alpha)]K - S_2 x/\sin(\theta - \alpha) \tag{6}$$

where S_1 and S_2 are the energy loss rates ($\mathrm{d}E/\mathrm{d}x$ for a very thin layer) for the incident ^{4}He^{++} ion and the recoiling hydrogen and deuterium nuclei, respectively. The term $S_1 x/\sin(\alpha)$ is the energy that the ^{4}He^{++} loses after travelling to a distance x below the surface. The term $S_2 x/\sin(\theta - \alpha)$ is the energy that the recoiling particle loses on its way out of the sample. It follows that

$$E_d = KE_0 - [S]x - \delta E_s \tag{7}$$

where $[S] = KS_1/\sin(\alpha) + S_2/\sin(\theta - \alpha)$ is the energy loss factor.

The energy loss functions of ^{1}H and ^{2}H in the stopper foil are experimentally determined by measuring the energies at which they recoil from the polymer film as a function of E_0. The energy scale is then converted to a depth scale by using a table of stopping cross sections[25] to find S_1 and S_2. Finally, one obtains the profile of volume fraction *versus* depth, shown in *Figure 3b*, by dividing the spectrum height of hydrogen with that of a thick film of PS; this procedure is permissible since the energy loss rates of ^{4}He^{++}, ^{1}H and ^{2}H are the same in d-PS as in PS.

EXPERIMENTAL PROCEDURE

Sample preparation

The sample consists of a bilayer of PS on d-PS supported by a polished silicon wafer. The layer of polystyrene that is directly in contact with the substrate is deuterated and will serve as a matrix for diffusion of undeuterated PS. It is approximately 0.6 μm thick and of molecular weight $P = 5.2 \times 10^5$ ($M_w/M_n < 1.1$; obtained from Polymer Laboratories). This film was produced by first spinning a solution of given viscosity onto a glass slide. It was then floated from the slide onto the surface of a bath of distilled water from where it was transferred to a wafer of polished silicon. The top layer of undeuterated PS, of molecular weight M ($M_w/M_n < 1.06$; obtained from Pressure Chemical Co.), was prepared in a similar manner but had a thickness of only approximately 15 nm. It was floated off the glass substrate onto the surface of a water bath from where it was picked up on top of the deuterated layer to produce the bilayer sample.

FRES measurement and analysis

A beam of doubly ionized helium ions of $E_0 = 3.0$ MeV impinges on the sample surface at an angle of incidence of $\alpha = 15°$. The particle detector is located at an angle of $\theta = 30°$ to record the energy, E_d, of the recoiled protons (^{1}H) and deuterons (^{2}H). *Figure 2a* shows the typical spectrum of yield versus energy of a sample before diffusion has occurred. Shown here are two well defined peaks; the lower energy peak consists of hydrogen from

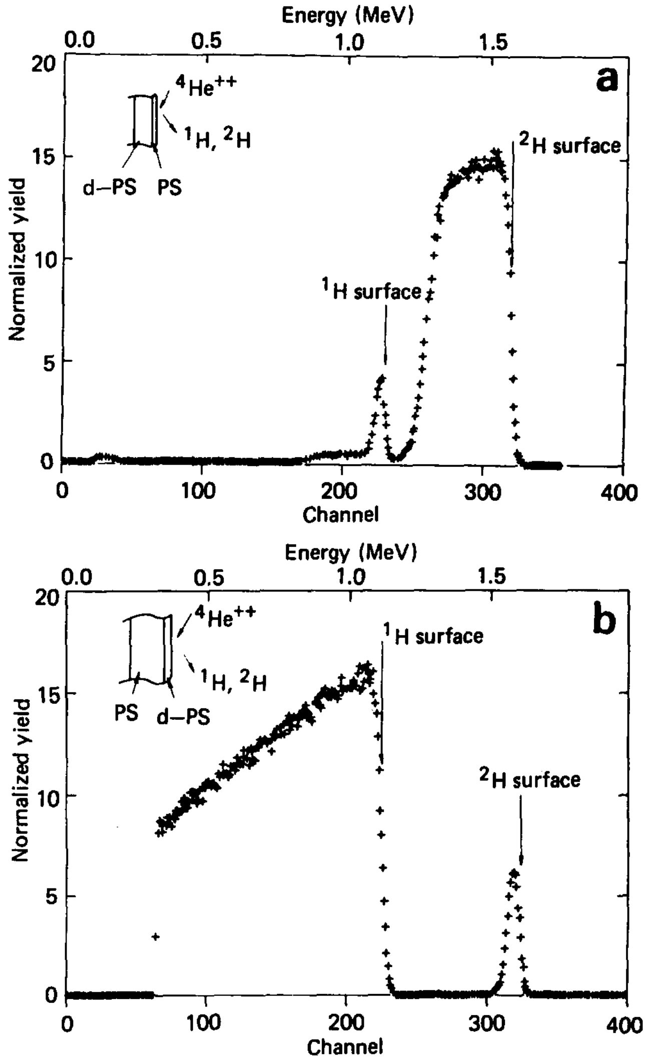

Figure 2 (a) FRES spectrum from a sample of a thin film of PS on a thicker d-PS film. The samples are shown schematically in the insert. (b) FRES spectrum from a sample of a thin film of d-PS on a thick PS film

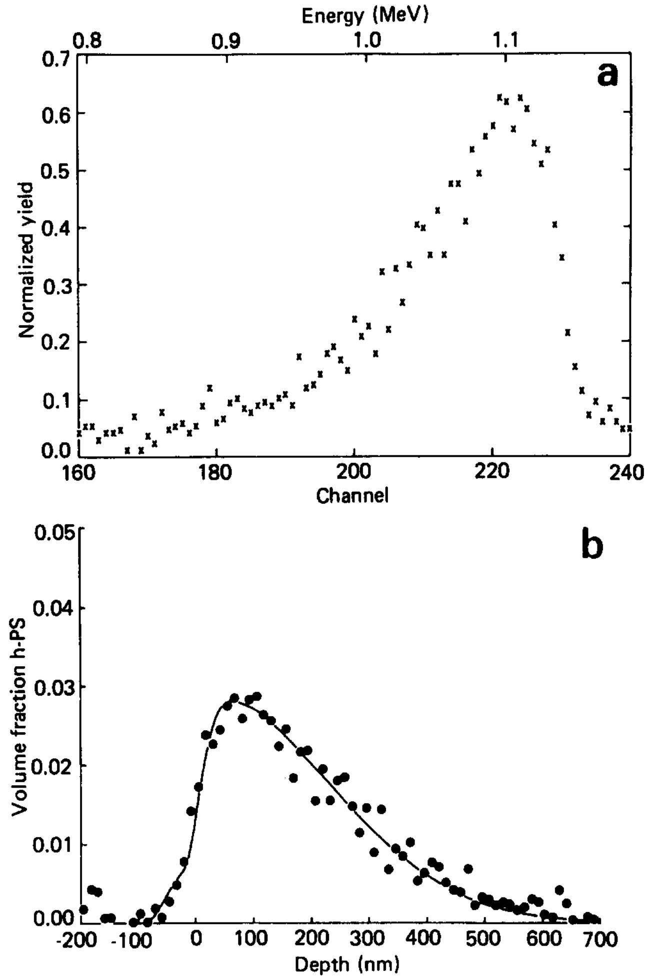

Figure 3 (a) FRES spectrum of a sample consisting of a thin film of PS ($M = 1.1 \times 10^5$) on d-PS ($P = 5.2 \times 10^5$) which was annealed for 240 s at a temperature of 171°C. (b) Volume fraction of PS derived from the FRES spectrum in (a). The solid line is a theoretical fit to the data using a D^* of 5.3×10^{-13} cm^2 s^{-1}

the PS top layer; the higher energy peak consists of deuterium from the d-PS bottom layer. That background ledge beneath the hydrogen peak is due to a small amount of ^{1}H in the d-PS film. The energies of the ^{1}H and ^{2}H recoiling from the surface are marked on the diagram. Since the energy of deuterium from the surface is higher than hydrogen one must avoid making the d-PS matrix film too thick so that the deuterium recoiling from deep in the d-PS film does not overlap in energy with the hydrogen recoiling from the thin PS film on the surface. For this reason the d-PS film is always thinner than 0.7 μm. In previous experiments the tracer diffusion coefficient of d-PS in a matrix of PS was measured by depth profiling deuterium. In this case the underlying film can be made thicker than several micrometers and precise control of its thickness is unnecessary. The FRES spectrum of such a film sandwich, with d-PS on thick PS, is shown for comparison in *Figure 2b*.

The peaks and edges of the spectrum are broadened due to the finite resolution of the instrument, approximately 40 keV. This energy resolution limit corresponds to a depth resolution $\Delta x = 80$ nm. For our values of α and θ the energy, and thus depth, resolution[27,28] is controlled primarily by the detector resolution and the straggling of the recoiling nuclei through the Mylar foil.

RESULTS AND DISCUSSION

Each sample is analysed after it is allowed to diffuse for a specified period of time at 171°C. *Figure 3a* shows the FRES spectrum of a sample consisting of a layer (15 nm thick) of PS ($M = 1.0 \times 10^5$) on a 0.65 μm thick layer of d-PS ($P = 5.2 \times 10^5$). The sample was allowed to diffuse for 240 s. The volume fraction depth profile of PS (h-PS) in the d-PS matrix is found by the procedure outlined above and is shown in *Figure 3b*.

Before attempting to extract the tracer diffusion coefficient from the volume fraction *versus* depth profile of a sample that has been allowed to diffuse, the background ledge beneath the hydrogen peak must be subtracted, as follows: the peak heights of the front surface of the profiles of the thick d-PS layers from both the standard sample (e.g. *Figure 2a*) and the diffused sample should be normalized to the same value. The height of the ledge in the profile of the standard film is measured and its value subtracted from the spectrum of the sample that has diffused.

The solid line shown in *Figure 3b* is a theoretical fit to the diffusion profile. Since the experimental profile $\phi_E(x)$ is a convolution of the true volume fraction profile $\phi_t(x)$ with the experimental resolution function, which is a Gaussian, the theoretical line is constructed by convoluting the calculated profile $\phi_c(x)$ with the instrumental resolution function. This calculated profile is[29]

$$\phi_c(x) = 1/2\{\mathrm{erf}[(h+x)/(4D^*t)^{1/2}] + \mathrm{erf}[(h-x)/(4D^*t)^{1/2}]\} \qquad (8)$$

Here D^* is the tracer diffusion coefficient of the species of molecular weight M, t is the diffusion time and h is the thickness of the original top PS film. The value of h can be obtained by integrating $\phi_c(x)$.

A value for $D^* = 5.3 \times 10^{-13}$ cm^2 s^{-1} is obtained from the fit shown in *Figure 3b* and is plotted together with values for other M-chains in *Figure 4*. The values of the tracer diffusion coefficients, D^*_{PS}, for various diffusing chain lengths that were extracted from PS volume fraction profiles (hydrogen profiling) are plotted as open squares. The solid triangles that point to the left (◀) represent those $D^*_{\text{d-PS}}$ obtained from FRES volume fraction profiles of d-PS at 171°C and the others (▶) are those which were scaled from measurements at 174°C using the WLF equation with constants that were found to describe the temperature dependence of diffusion for PS[30,31]. The circles represent D^* for PS obtained by Antonietti and coworkers at 172°C using a holographic grating technique[32]. Values of D^* obtained from the results of RBS studies of inert marker movements at 174°C that were scaled to 171°C using the WLF equation are shown as crosses. Shown as a broken line are the results of the n.m.r. PS diffusion experiments of Fleischer[13], performed at 225°C but scaled to 171°C. The solid line has slope -2.

The results of the n.m.r. experiment are a factor of approximately 2.6 higher than the other results. The disagreement between these data and the rest may result from the fact that the n.m.r. data are the results of self-diffusion measurements ($M = P$) using molecular weights of $M < M_c$[33]. The other D^* quoted are obtained by studying the diffusion of chains into high molecular weight matrices; these values of D^* are not expected to be

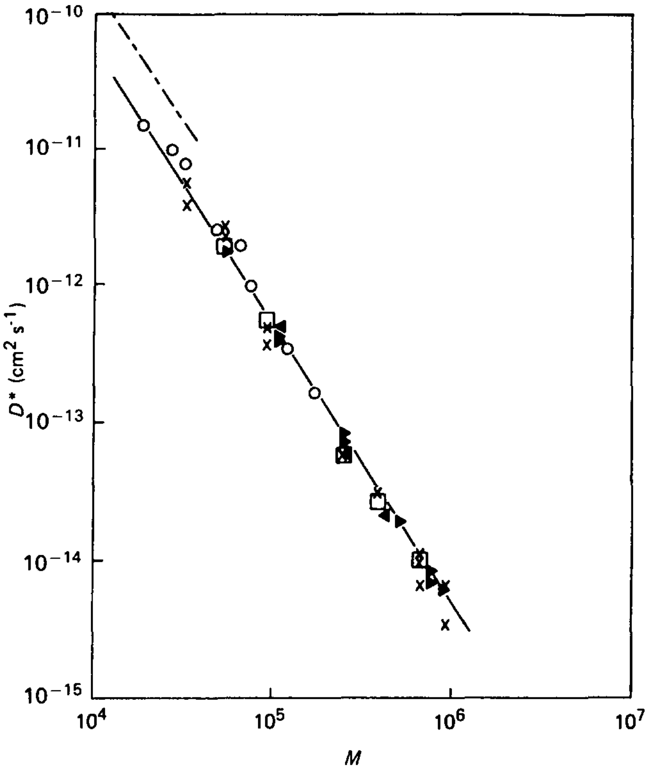

Figure 4 Plot of the tracer diffusion coefficient D^* of polystyrene as a function of diffusing chain molecular weight M from various techniques: hydrogen profiling after diffusion at 171°C using FRES [PS diffusion] (□); deuterium profiling (171°C) using FRES [d-PS diffusion] (◀); deuterium profiling by FRES (scaled to 171°C from 174°C) (▶); holographic grating technique at 172°C (○) (ref. 32); RBS measurements of marker motion (scaled to 171°C from 174°C) (×) (ref. 16) and n.m.r. data [self-diffusion] (scaled from 225°C) (— — — —) (ref. 13)

affected by the simultaneous diffusion of the matrix chains[25].

The most important result however is that the various other methods (hydrogen profiling via FRES, marker displacement measurements via RBS and forced Rayleigh scattering (the holographic grating technique)) are in excellent agreement. This agreement allows us to draw several more conclusions:

(1) The tracer diffusion coefficients D^* of deuterated PS and hydrogenated PS are identical within experimental uncertainty (*ca.* ±20%). Thus hydrogen profiling or deuterium profiling via FRES can be used interchangeably to obtain D^* values. The choice of method can be dictated by the availability of suitable tracer and matrix molecules. In some cases this fact will allow us to measure the diffusion of PS molecules of special topologies, e.g. rings, which have not been synthesized in deuterated versions.

(2) The good agreement with the forced Rayleigh scattering data of Antonietti *et al.*[4,32] implies that the fluorescent label molecules used by this group do not seriously affect (at these M and at this temperature) the diffusion of PS.

(3) The good agreement of the RBS marker measurements[16] with those of the other three methods implies that the theory developed to derive D^* from the marker displacement is valid.

ACKNOWLEDGEMENTS

The financial support of this research by the NSF-DMR Polymers Program under Grant DMR-8303174 is gratefully acknowledged. P. F. Green received partial support in the form of a Public Health Service Predoctoral Fellowship. We also benefited from the use of the facilities of the Cornell Materials Science Center which is funded by the DMR-MRL program of NSF. We especially thank J. W. Mayer for his enthusiastic encouragement and helpful discussions and C. J. Palmstrøm for his assistance.

REFERENCES

1 Shiah, T. Y-J. and Morawetz, H. *Macromolecules* 1984, **17**, 792
2 Wesson, J. A., Noh, I., Kitano, T. and Yu, H. *Macromolecules* 1984, **17**, 782
3 Léger, L., Hervet, H. and Rondelez, F. *Macromolecules* 1981, **14**, 1732
4 Antonietti, M., Coutandin, J., Grutter, R. and Sillescu, H. *Macromolecules* 1984, **17**, 798
5 Smith, B. A., Samulski, E. T., Yu, L. P. and Winnik, M. A. *Phys. Rev. Lett.* 1984, **52**, 45
6 Smith, B. A. *Macromolecules* 1982, **15**, 469
7 Phol, D., Schwartz, S. E. and Irniger, U. *Phys. Rev. Lett.* 1973, **31**, 32
8 Bartels, C. R., Graessley, W. W. and Crist, B. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 495
9 Bueche, F. J. *J. Chem. Phys.* 1968, **48**, 1410
10 Kumugai, Y., Watanabe, K., Miyasaki, T. and Hata, J. *Chem. Eng. Jpn.* 1979, **12**, 1
11 Tanner, J. E. *Macromolecules* 1971, **4**, 748
12 Kimmich, R. and Bachus, R. *Colloid Polym. Sci.* 1982, **260**, 911
13 Fleischer, G. *Polym. Bull.* 1983, **9**, 152
14 Zupancic, L., Lahajnar, G., Blinc, R., Reneker, D. H. and VanderHart, D. L. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 387
15 Kramer, E. J., Green, P. F. and Palmstrøm, C. J. *Polymer* 1984, **25**, 473
16 Green, P. F., Palmstrøm, C. J., Mayer, J. W. and Kramer, E. J. *Macromolecules* 1985, **18**, 501
17 Price, F. T., Gilmore, P. T., Thomas, E. L. and Lawrence, R. L. *J. Polym. Sci., Polym. Symp. Edn.* 1978, **63**, 33
18 Gilmore, P. T., Falabella, R. and Lawrence, R. L. *Macromolecules* 1980, **13**, 880
19 Klein, J. *Nature* 1978, **274**, 143
20 Klein, J. and Briscoe, B. C. *Proc. Roy. Soc. London A* 1979, **365**, 53
21 Klein, J. *Philos. Mag.* 1981, **43**, 771
22 Klein, J., Fletcher, D. and Fetters, L. J. *Nature* 1983, **304**, 526
23 This technique is identical to that developed by Doyle and Peercy to profile ^{1}H and ^{2}H in metals; see Doyle, B. L. and Peercy, P. S. *Appl. Phys. Lett.* 1979, **34**, 811
24 Mills, P. J., Green, P. F., Palmstrøm, C. J., Mayer, J. W. and Kramer, E. J. *Appl. Phys. Lett.* 1984, **45**, 958
25 Green, P. F., Mills, P. J., Palmstrøm, C. J., Mayer, J. W. and Kramer, E. J. *Phys. Rev. Lett.* 1984, **53**, 2145
26 Ziegler, J. F. 'The Stopping Ranges of Ions in Matter', Pergamon, New York, 1977, Vol. 4; Anderson, H. H. and Ziegler, J. F. *ibid.* Vol. 3
27 Turos, A. and Meyer, O. *Nucl. Instrum. Methods* 1984, **232**, 92
28 Ecuyer, L., Brassard, C. and Cardinal, C. *Nucl. Instrum. Methods* 1978, **149**, 271
29 Crank, J. 'The Mathematics of Diffusion', 2nd Edn., Oxford University Press, Oxford, UK, 1975, p. 15
30 Our recent results indicate that the temperature dependence of D^* is described by a Vogel equation ($\log D^*/T = A - B/(T - T_\infty)$) (or the equivalent WLF equation) up to about $T = 215$°C. The constants (B, T_∞) that produce the fit are the same ones that describe the temperature dependence of the viscosity of PS ($T_\infty = 49$°C, $B = 710$°C at a reference temperature of $T = 169.5$°C; Graessley, W. W. and Roovers, J. *Macromolecules* 1974, **5**, 954)
31 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., John Wiley, New York, 1980
32 Antonietti, M., Coutandin, J. and Sillescu, H. *Macromol. Chem., Rapid Commun.* 1984, **5**, 525
33 Antonietti, M., Coutandin, J. and Sillescu, H. submitted to *Macromolecules*