Temperature dependence of the diffusion coefficient of poly(propylene oxide) in the undiluted state

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The temperature dependence of the diffusion of fluorescent-dye-labelled poly(propylene oxide) (PPO) through unlabelled PPO has been investigated for a range of molecular weights of labelled and unlabelled polymer. The technique employed was fluorescence redistribution after pattern photobleaching (FRAPP). It was found that all the diffusion data could be reduced to a single smooth curve as a function of temperature, and that this curve was well represented by the WLF (Williams–Landel–Ferry) equation using parameters determined from rheological measurements on the same PPO fractions. This agreement was independent of the molecular weights of both labelled and unlabelled PPO. At higher temperatures, both the rheological and diffusion data were well fitted by Arrhenius expressions with apparent activation energies of $E_V = 43$ kJ mol^{-1} and $E_{D/T} = 40$ kJ mol^{-1}, respectively. The slightly higher value of E_V compared to $E_{D/T}$ is qualitatively consistent with Doi–Edwards theory.

(Keywords: diffusion coefficient; poly(propylene oxide); fluorescence redistribution; reptation)

INTRODUCTION

Over the last decade the investigation of polymer diffusion has been particularly intense[1]. Much of the activity in this area has been stimulated by the need for precise experimental data to test the modern molecular theories[2–6] which attempt to describe the motion of polymer molecules. Reptation theory[7] has proved to be conspicuous in its success at predicting the scaling behaviour of the molecular weight dependence of the diffusion of a polymer chain through a highly entangled polymer melt. That the diffusion coefficient D is dependent upon the molecular weight M of the diffusion species as $D \propto M^{-2}$ is now widely accepted[8–12]. In addition, Klein[13] has demonstrated the independence of D upon the molecular weight P of the matrix, when $P \gg M$. Furthermore, Graessley[14] has derived from Doi-Edwards theory[4–6] an expression which predicts the absolute magnitude of the diffusion coefficients, and the results are in good agreement with experimentally determined values when reptation is the principal mechanism for diffusion. However, it has been demonstrated recently[15] that constraint release makes a significant contribution towards the mechanism for self-diffusion ($M = P$). Also, it has been shown[15–17] that there is a regime, $M_c < P < M$ (where M_c is the critical molecular weight for entanglement), in which the constraint release mechanism dominates over reptation.

More recently, attention has focused on the relationship between polymer diffusion and the various viscoelastic processes. While the fundamental modes of molecular relaxation for diffusion and shear flow are thought to be the same, it has been questioned[18] whether or not the molecular interactions via entanglement coupling are different. One means by which the relationship between the dynamic modes responsible for flow and transport properties may be probed is by a study of their temperature coefficients. Such an investigation of the temperature dependence of the diffusion coefficient and the zero shear viscosity η_0 has been undertaken by Nemoto *et al.*[19] These authors measured the self-diffusion coefficient D_s of a sample of polyisoprene ($M = 35\,000$) as a function of temperature. They found that the temperature dependence of D_s/T was represented extremely well by the Williams–Landel–Ferry (WLF) equation[20] using parameters determined from shear creep measurements. However, some doubt remained as to whether or not this excellent agreement was fortuitous, since the polyisoprene samples used in the diffusion and shear creep measurements had differing microstructures. Antonietti *et al.*[21] investigated the temperature dependence of D for polystyrene, and found that the dependence of D, rather than D/T, could be described by the WLF equation. However, the parameters used to fit the diffusion data varied with molecular weight of the diffusing species. This is probably a consequence of their choice to fit D, rather than D/T, since it is the temperature coefficient of D/T which is predicted by Doi–Edwards theory[4–6] to be very close to that of η_0.

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In the present investigation we have measured, as a function of temperature, the diffusion coefficients of several samples ($M_{n,l}$ = 2400 to 92 300) of fluorescent-dye-labelled poly(propylene oxide) (PPO), diffusing through a range of molecular weights ($M_{w,s}$ = 2000 to 32 000) of unlabelled PPO. The subscripts l and s refer to labelled polymer and polymeric solvent, respectively. The combinations of the various molecular weights of the dye-labelled and solvent PPO enable us to make measurements spanning the regimes in which each of the diffusion mechanisms defined by Daoud and de Gennes[22] are believed to be dominant. These mechanisms are Stokes–Einstein, constraint release and reptation. The temperature dependence of the diffusion coefficients is interpreted by comparison with shear viscosity measurements performed over a wide temperature range (−80 to +80°C) on the unlabelled solvent PPO samples.

EXPERIMENTAL

Diffusion of the fluorescent-dye-labelled PPO through unlabelled PPO was monitored as a function of temperature in the range 20–100°C by means of fluorescence redistribution after pattern photobleaching (FRAPP). Details of the FRAPP technique are described elsewhere[17,23–27], as are the procedures for the synthesis of the dye-labelled PPO[17,28], which had one chromophore approximately at the centre of each chain.

Rheological measurements on the unlabelled PPO were performed by Drs Bin Chung and Thomas Karis at IBM Research, San Jose. These measurements are to be described in full in a later publication.

RESULTS

Measurements of the shear storage modulus G' and the shear loss modulus G'' of the unlabelled PPO samples were made over a range of frequencies. The temperature range for these rheological studies was between −80 and +80°C. Time–temperature shifting was used to superimpose the curves of G' against frequency for all temperatures and molecular weights; the same procedure was carried out for G''. It was found that all of the shift factors a_T for both of these moduli fell on a single smooth curve. These values of a_T are plotted in *Figure 1* with a reference temperature of 273 K. The curve through these points represents a fit of the form:

$$\log a_T = -\frac{4.46(T-273)}{111.5+(T-273)}$$

and 4.46 and 111.5 correspond to the values of the WLF parameters c_1 and c_2, respectively. These values of c_1 and c_2 compare favourably with the values of 3.93 and 99 calculated from the dielectric data of Williams[29,30].

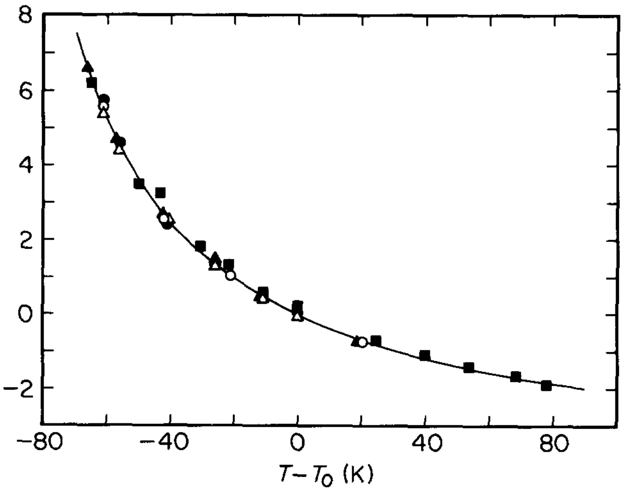

Figure 1 Shift factor a_T plotted against the temperarture difference $T-T_0$ for a reference temperature T_0 = 273 K. Molecular weights of the poly(propylene oxide) samples were: $M_{w,s}$ = 2000 (●); $M_{w,s}$ = 4200 (△); $M_{w,s}$ = 12 400 (▲); $M_{w,s}$ = 21 000 (○); $M_{w,s}$ = 32 000 (■)

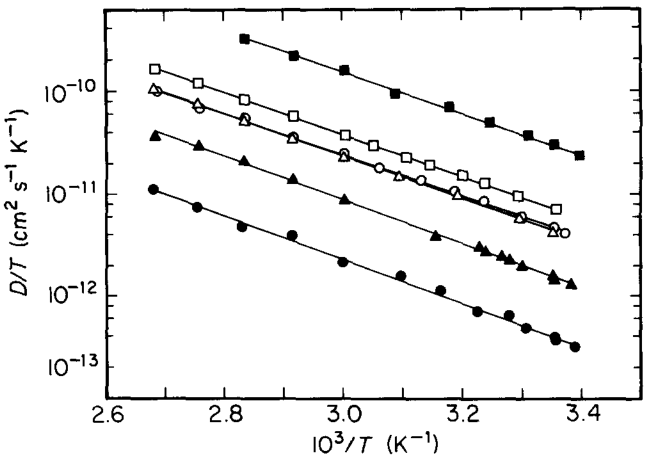

Figure 2 Arrhenius plots of D/T. Molecular weights of the labelled polymer and solvent polymer in each sample, and the apparent activation energies (kJ mol^{-1}) were: $M_{n,l}$ = 2400, $M_{w,s}$ = 32 000, $E_{D/T}$ = 39.5 (■); $M_{n,l}$ = 16 800, $M_{w,s}$ = 4200, $E_{D/T}$ = 39.5 (□); $M_{n,l}$ = 92 300, $M_{w,s}$ = 2000, $E_{D/T}$ = 38.6 (○); $M_{n,l}$ = 11 000, $M_{w,s}$ = 12 400, $E_{D/T}$ = 39.9 (△); $M_{n,l}$ = 16 800, $M_{w,s}$ = 32 000, $E_{D/T}$ = 41.2 (▲); $M_{n,l}$ = 33 600, $M_{w,s}$ = 32 000, $E_{D/T}$ = 41.6 (●). The full lines represent least-squares fits to each of these sets of data

Figure 2 is a plot of D/T against $1/T$ for different molecular weights of fluorescent-dye-labelled PPO diffusing in the various unlabelled PPO samples. These diffusion coefficients span in excess of three orders of magnitude. The mechanism for the diffusion of the labelled PPO is not expected to be the same for all the samples studied. For example, the mechanism of diffusion corresponding to the data represented by the open circles ($M_{n,l}$ = 92 300 in $M_{w,s}$ = 2000) is almost certainly Stokes–Einstein, whereas the filled circles ($M_{n,l}$ = 33 600 in $M_{w,s}$ = 32 000) correspond to self-diffusion (approximately), for which the diffusion mechanism is probably a combination of reptation and constraint release[15,17]. However, all the plots in *Figure 2* have approximately equal gradients giving an activation energy $E_{D/T} = 40 \pm 0.8$ kJ mol^{-1}.

In order to examine how well the free volume effect, as embodied in the WLF equation, can account for the temperature dependence of diffusion, the reduced diffusion coefficient, $\log(D_0T/DT_0)$, where T_0 = 298 K, is plotted in *Figure 3*. The full curve in this figure represents the temperature shift factor:

$$\log a_T = -\frac{3.64(T-298)}{136.5+(T-298)}$$

where the WLF parameters are those determined from the rheological data and adjusted to a reference temperature T_0 = 298 K. As seen in *Figure 3*, all the diffusion data for the range of molecular weights of labelled and solvent PPO are well represented by free volume theory using WLF parameters determined from shear viscosity measurements.

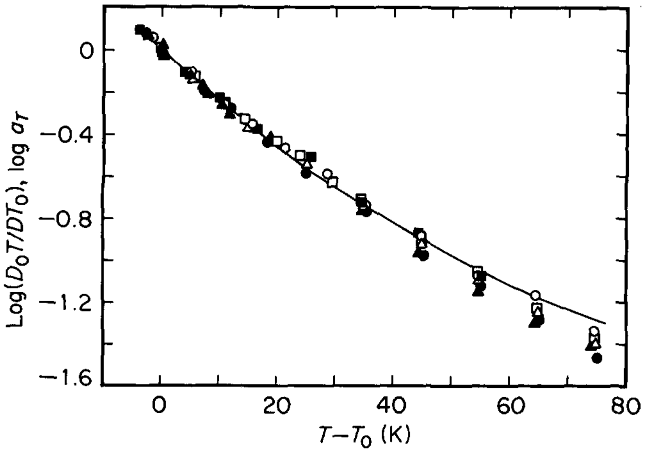

Figure 3 Logarithm of the reduced diffusion coefficient, $\log(D_0T/DT_0)$, plotted against the temperature difference $T-T_0$ for a reference temperature $T_0=298$ K. Molecular weights of the labelled polymer and solvent polymer in each sample were: $M_{n,l}=2400$, $M_{w,s}=32\,000$ (■); $M_{n,l}=16\,800$, $M_{w,s}=4200$ (□); $M_{n,l}=92\,300$, $M_{w,s}=2000$ (○); $M_{n,l}=11\,000$, $M_{w,s}=12\,400$ (△); $M_{n,l}=16\,800$, $M_{w,s}=32\,000$ (▲); $M_{n,l}=33\,600$, $M_{w,s}=32\,000$ (●). The full curve represents the temperature shift factor a_T determined from the rheological measurements on the unlabelled PPO samples (see text for equation for log a_T)

DISCUSSION

The glass transition temperature for PPO is $T_g \sim 190$ K[27,30] and varies little with molecular weight. Thus, the diffusion coefficients presented here have been measured in the temperature range of 100 to 200 K above T_g. The WLF equation might be expected not to be applicable in this temperature regime where the proportion of free volume is relatively high, and the dependence of D/T upon the inverse of temperature (*Figure 2*) is clearly Arrhenius. At these temperatures, in excess of 100 K above T_g, the temperature dependence of the relaxation processes is usually regarded as being governed by more specific features of the polymer; the reduced diffusion coefficients, however, have been seen (*Figure 3*) to be well correlated with the shift factors determined from shear flow measurements on the solvent PPO. In *Figure 3*, the slight deviation at high temperatures between the diffusion data and the full curve representing the shift factor may indicate the start of the breakdown of this free volume interpretation, although this deviation is within the scatter of the data. It is particularly noteworthy that the WLF equation is so successful in describing the temperature dependence of diffusion and shear flow using identical parameters irrespective of the dominant diffusion mechanism. This is indicative of the same molecular origin for the temperature dependence of diffusion and that of shear flow. These results are qualitatively consistent with those of Nemoto *et al.*[19]

The observation that the apparent activation energy for the diffusion process is approximately the same for all the regimes does not place these data at odds with reptation theory. Theory[4–6] predicts that the activation energy for diffusion $E_{D/T}=-R\,\mathrm{d}\ln(D/T)/\mathrm{d}T^{-1}$ should be approximately equal to that for shear flow $E_V=-R\,\mathrm{d}\ln(a_T)/\mathrm{d}T^{-1}$. Bartels *et al.*[12] have derived an expression for the difference between these two activation energies as a function of the volume expansion coefficient and the temperature dependence of the end-to-end distance. The magnitude of $E_{D/T}$ is predicted to be somewhat smaller than E_V. In the present study, E_V was determined by plotting semilogarithmically the values of a_T measured at the higher temperatures as a function of inverse temperature. (Values of a_T from the temperature range 20 to 80°C formed a good Arrhenius plot.) The resulting value of E_V was 43 kJ mol^{-1}. Since $E_{D/T}$ was found to be 40 kJ mol^{-1}, these results are in full agreement with models of diffusion of a polymer chain through a tube. The fact that this agreement holds even for the samples in which reptation is clearly not the diffusion mechanism simply serves to illustrate that $E_{D/T}$ is particularly insensitive to the mode of diffusion, at least for PPO.

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