Self-diffusion, viscosity and spin–spin relaxation in liquid poly(propylene oxide) melts

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Self-diffusion, viscosity and spin–spin relaxation have been measured for a series of low molecular weight liquid poly(propylene oxide) melts. The data are discussed within the framework of theories commonly invoked for polymer dynamics including the Rouse chain and free volume effects. The average diffusion coefficients of a range of bimodal blends have also been measured and the results interpreted using the Rouse model.

(Keywords: poly(propylene oxide); melt; Rouse model)

INTRODUCTION

The self-diffusion coefficient D_s and viscosity η of macromolecules in solution and the melt have been theoretically predicted to follow power laws of the form[1-5]:

$$D_s = k_1 M^{\gamma}$$
$$\eta = k_2 M^{\beta} \qquad (1)$$

where k_1 and k_2 are constants and γ and β are exponents, whose value may depend on whether M, the molecular weight, is above or below a critical molecular weight M_c. The critical molecular weight is commonly defined as the molecular weight at which entanglements are first observed in the viscosity behaviour. This is seen as a dramatic change in β. Rouse theory[3] is based on the 'freely jointed bead-and-spring' model of a polymer chain and, below M_c, predicts $\gamma = -1$ and $\beta = +1$. Above M_c, reptation predicts $\gamma = -2$ and $\beta = +3$.

Experimentally, viscosity measurements for a range of polymers appear to fit well to the Rouse theory below M_c, but are best described by a $\beta = 3.4$ power law above M_c. It is generally accepted[6] that the higher-order motions of entangled linear polymer melts are Rouse-like within their entanglement tubes. Accordingly, the viscosity–molecular weight behaviour is predicted to follow a $M^{3.0}$ dependence. However, no contour length fluctuation effects are included in these simple treatments, and this factor is proposed to account for the discrepancy between the experimental and theoretical molecular weight dependences. This tends to confirm the validity of the Rouse approach and highlights its central role in the dynamics of entangled systems.

An interesting point arises from the literature in that most polymers, independent of their structure, appear to follow the same power laws; only the value of M_c varies, typically within the range 250–350 monomer units dependent on molecular structure[7]. This molecular weight behaviour suggests that transport properties in general are strongly dependent on the topological nature of the polymer chain. Specific intermolecular factors such as hydrogen bonding will only affect the absolute value of the viscosity and diffusion coefficient[8].

The diffusion coefficient–molecular weight exponents γ for a series of polymers over wide molecular weight ranges have been published and vary between $D_s \propto M^{-1}$ and $D_s \propto M^{-2}$. Radiotracer experiments on polystyrene melts have found greater exponents, $D_s \propto M^{-2.2}$ (ref. 9) and $D_s \propto M^{-2.7}$ (ref. 10), but correcting for the perturbing effect of the necessary chemical substitution revealed $D_s \propto M^{-2}$. For polyethylene and the alkanes[11], $D_s \propto M^{-2}$ has been observed both above and below M_c. Inclusion of free volume effects attempts to account for such factors as chain flexibility and the free volume associated with the greater mobility of the chain ends. With this correction, polystyrene[12] and polyisoprene[13] show both limiting cases with the transition from $D_s \propto M^{-1}$ to $D_s \propto M^{-2}$ occurring at the critical molecular weight. Poly(ethylene oxide) melts[14] show both limiting cases without the free volume correction. Polydimethylsiloxane, on the other hand[15], shows no transition from $D_s \propto M^{-1}$ to $D_s \propto M^{-2}$, even up to approximately $5M_c$.

Theoretical models for polymer diffusion are based predominantly on both the Rouse model and reptation. The suitability of the different approaches is limited by several factors. For Rouse motion to occur, it is assumed that any pair of segments have no motional correlation, i.e. move independently. This model is applicable, therefore, to flexible polymers such as

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polydimethylsiloxane, where there is a large degree of inherent free volume, and, to a lesser extent, polyisoprene. Reptation, on the other hand, requires that segmental motion is sufficiently constrained by neighbouring chains to be highly correlated and to occur in a curvilinear fashion, i.e. along a 'tube'. Stiff chains, such as polyethylene and the alkanes, which possess little or no free volume, would be expected to follow a closer adherence to the -2 power law predicted by reptation.

Another method to probe the dynamics of polymer melts is spin–spin relaxation. The isotropic segmental mobility may be intimately related to a correlation time describing the timescale of a particular molecular arrangement. Magnetic dipoles interact over a short distance scale (≈ 1 nm) and 'relax' from an initially ordered state. This relaxation is dependent on the local isotropic mobility of the polymer chains, as well as the overall chain translation. Significant changes occur in the spin–spin relaxation behaviour when the mobility becomes restricted or anisotropic, which has been shown to be due to the onset of molecular entanglements[16]. Polyethylene and polystyrene have been extensively studied. For polyethylene, three molecular weight dependent regions may be distinguished. The critical molecular weight characterizes the transition to a stronger dependence on molecular weight associated with the onset of molecular entanglements. The molecular weight dependence then becomes less pronounced at a greater, undefined molecular weight. For polystyrene, only two regions are observed, but in this instance, the transition is to a less steep dependence.

In this paper, results are reported on a series of paucidisperse ($M_w/M_n = 1.2$) poly(propylene oxide) melts using the pulsed field-gradient nuclear magnetic resonance (p.f.g.n.m.r.) technique[17–19]. The need for narrow fraction polymers has been discussed at length[20–22] and typically a polydispersity M_w/M_n of greater than 1.3 means that an average diffusion coefficient or spin–spin relaxation time is measured, which may be biased by either very low or very high molecular weight components. Nuclear magnetic resonance has been used successfully to measure diffusion[23] in a variety of polymeric systems, not only in solution but also in the melt. Intermediary to the flexibilities of the polyethylene and polydimethylsiloxane chains are those of polystyrene and poly(ethylene oxide). Comparisons of the general diffusional behaviour of a range of polymers — polyethylene (PE), poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), polytetrahydrofuran (PTHF), polyisoprene (PI), polystyrene (PS), polydimethylsiloxane (PDMS) — will be made and these observations discussed in terms of a simple argument based on chain flexibility. Conclusions drawn from these comparisons are further reinforced by the behaviour exhibited by bimodal blends.

EXPERIMENTAL

The measurements were performed on a JEOL FX100 high-resolution nuclear magnetic resonance spectrometer operating at 100 MHz (protons) modified to carry out self-diffusion measurements, using the pulsed field-gradient technique[17,18]. The spectrometer has been upgraded by the addition of a Surrey Medical Imaging Systems console, which replaces both the r.f. and computational components. The current amplifier used to generate the field gradients was calibrated with a sample of known diffusivity (water), giving field gradients G between 1.5 and 8.0 G cm^{-1}. The data were acquired with the same diffusion time parameters; the separation Δ of the field gradient pulses was set at 150 ms and the width δ of the field gradient pulses varied between 5 and 90 ms. A glass filament containing D_2O was used as an internal lock reference for greater stability. The spin echoes, after Fourier transformation, were integrated (A_δ), and could be fitted to equation (2), which assumes isotropic Brownian diffusion:

$$A_\delta = A_0 \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D_s] \qquad (2)$$

where γ is the magnetogyric ratio and A_0 is the integrated intensity of the spin echo when $G=0$. It is assumed in these experiments that any background gradients may be neglected since an attenuation function for water acquired over two orders of magnitude of signal intensity showed no deviation from the behaviour proposed by equation (2).

The spin–spin relaxation time measurements were performed using a low-resolution CPMG[24] sequence where only the height of the spin echoes is sampled. In all cases, the data could be fitted to a single-exponential decay to an accuracy of 5%.

RESULTS AND DISCUSSION

Single-component melts

Figure 1 shows the bulk viscosity of poly(propylene oxide) (PPO) as a function of molecular weight, measured with a simple Ostwald viscometer. The viscosity behaviour gives a value for $\beta = 0.96$ (± 0.08), in very good agreement with the Rouse model. The spin–spin relaxation time measurements for the same samples are shown in *Figure 2*, and also follow a power law. Similar behaviour has been observed for other non-entangled melts[12,25–27] and the results are summarized in *Table 1*. There is no physical significance to this purely empirical power law, but the same functional form does seem to account for a range of experimental observations.

The behaviour of the spin–spin relaxation function will be discussed in terms of the Brereton model[16] for the polydimethylsiloxane (PDMS) and polyethylene (PE) data. The model assumes a hierarchy of polymer

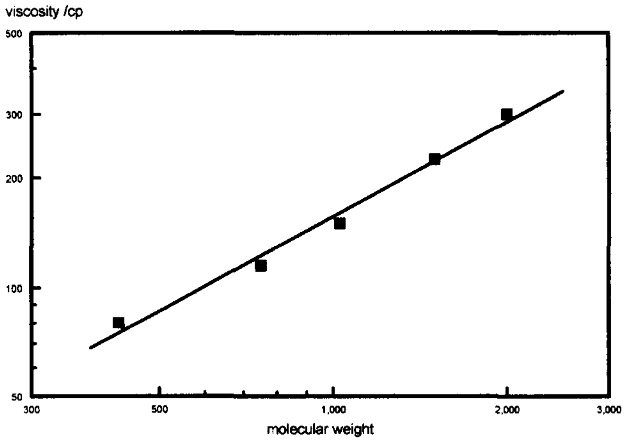

Figure 1 Molecular weight behaviour of the bulk viscosity of PPO melts

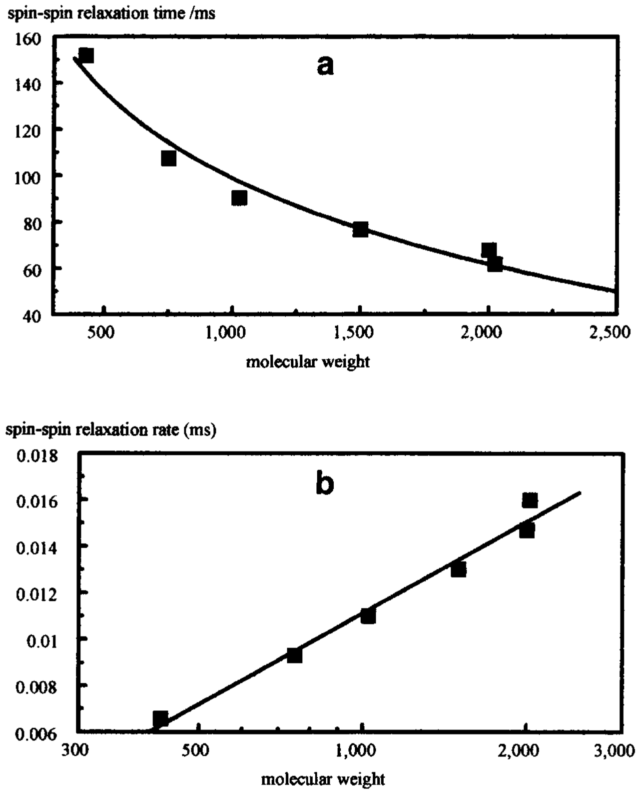

Figure 2 Molecular weight behaviour of the spin–spin relaxation time: (a) simple power law; (b) Brereton model

Table 1

Polymer melt	Power law exhibited
PPO	$T_2 \propto M_n^{-0.53}$
PE	$T_2 \propto M_n^{-0.53}$
PS	$T_2 \propto M_n^{-0.54}$
PDMS	$T_2 \propto M_n^{-0.57}$
PEO	$T_2 \propto M_n^{-0.53}$

Table 2

Polymer	Above M_c	Below M_c
PE	n/a	$\alpha = 0.89$, $\beta = -4.94$
PDMS	$\alpha = 14.7$, $\beta = -149.0$	$\alpha = 0.90$, $\beta = -3.5$
PPO	n/a	$\alpha = 5.7$, $\beta = -28.2$

dynamics comprising segmental motion and entanglement coupling. This model is actually a mathematical treatment of two correlation functions describing motion operating over two very different distance and time scales. An explicit expression relating T_2 to molecular weight is not derived, but the data may be represented as:

$$1/T_2 = \alpha \ln M_w + \beta$$

The values obtained for the polydimethylsiloxane and polyethylene data are given in *Table 2*. Since this model is semi-empirical, no significance can be attached to the values of α and β. The ratio β/α is very significant, though, and is related to the average number of segments, N_r, that comprise a Rouse unit.

Whilst no qualitative agreement is expected, the ostensibly good agreement between the polyethylene and polydimethylsiloxane melts may be contrasted to the diffusion results: polyethylene scales as $D_s \propto M^{-2}$ above and below M_c, whilst $D_c \propto M^{-1}$ is observed for polydimethylsiloxane above and below M_c. From the unentangled data shown in *Table 2*, it may be seen that N_r decreases with increasing flexibility ($N_{r,PE} = 5.6$, $N_{r,PPO} = 4.9$, $N_{r,PDMS} = 3.9$), i.e. the length scale of each subunit exhibiting isotropic motion increases with increasing stiffness of the chain.

Whereas the polyethylene spin–spin relaxation data exhibit two molecular weight dependent regimes with the critical molecular weight characterizing a transition to a steeper dependence, the spin–spin relaxation data for polystyrene melts show a break at the critical molecular weight in this instance from a strong molecular weight dependence to a weaker one. Consequently, it seems that spin–spin relaxation measurements are more sensitive to shorter-range motions than diffusion measurements. Unlike the other two examples, poly(propylene oxide) does not have a 'symmetrical' backbone; polydimethylsiloxane has two pendent methyl groups per monomer whereas polyethylene is just a methylene chain. Consequently, in those polymers, the dipolar relaxation is the result of several different interactions. The correlation times associated with each group are significant also — pendent group rotation is typically more rapid than backbone rotation. These two types of motion may be coupled by spin diffusion and, hence, only a single relaxation time is exhibited. The rotation of pendent groups will necessarily affect the backbone mobility and the differences between pendent methyl and pendent phenyl groups have a direct effect on the overall chain mobility.

The diffusion results are shown in *Figure 3*. Fitting the slopes of the diffusion plot to equation (2) gives $\gamma = -0.95$ (± 0.04). The concept of chain flexibility will be illustrated by comparing a range of polymers: polyethylene, poly(ethylene oxide), poly(propylene oxide), polystyrene, polydimethylsiloxane, polytetrahydrofuran and polyisoprene. The increase in number of backbone carbon units may be illustrated by comparing poly(ethylene oxide) with polytetrahydrofuran. The effect of pendent group on chain stiffness may be enlightened by comparing polyethylene with polystyrene, and poly(ethylene oxide) with poly(propylene oxide). This simplistic view may be rationalized by the observed diffusional behaviour of the two extremes of chain flexibility: the stiffest — polyethylene — follows the reptation theory whilst the most flexible — polydimethylsiloxane — follows the

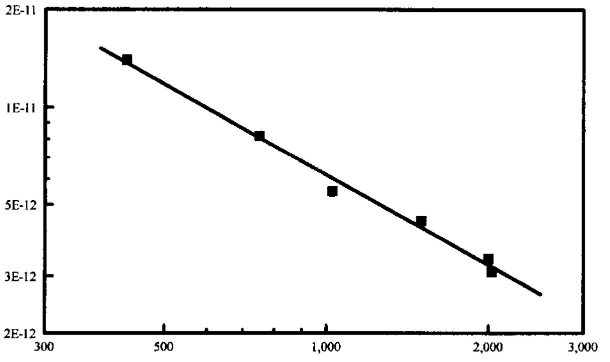

Figure 3 Molecular weight behaviour of the self-diffusion coefficient in single-component PPO melts

Rouse model, both over wide molecular weight ranges encompassing M_c.

Increasing the number of backbone carbon units, i.e. poly(ethylene oxide) and polytetrahydrofuran, modifies the molecular weight behaviour of the diffusion coefficient: poly(ethylene oxide) shows $D_s \propto M^{-1}$ below M_c without the free volume correction and $D_s \propto M^{-2}$ above M_c, whilst polytetrahydrofuran only shows $D_s \propto M^{-2}$ over the somewhat limited molecular weight range studied, which did encompass M_c. The stiffer chain dampens the isotropic motion required for Rouse behaviour and the reptation exponent is exhibited, i.e. the motion more closely resembles that of polyethylene as the number of backbone carbon units (between the flexible oxygen linkages) per monomer group increases.

Although the polyethylene results may be obscured by inherent crystallinity, similar trends arising from the effects of pendent groups may be extracted by comparing polyethylene with polystyrene, and poly(ethylene oxide) with poly(propylene oxide). Polyethylene anomalously shows $D_s \propto M^{-2}$ over the entire molecular weight range, whilst polystyrene shows a transition from $D_s \propto M^{-1}$ to $D_s \propto M^{-2}$ at the critical molecular weight with the free volume correction. Poly(ethylene oxide) shows $D_s \propto M^{-1}$ below M_c, as does poly(propylene oxide), without the free volume correction. In both cases, the larger pendent groups will give rise to a stiffer chain due to steric factors, but the effect is much weaker than that arising through the increase in the number of backbone carbon atoms. Similarly, the larger pendent groups will necessarily increase the tube size and may result in a lower level of constraint within that tube. This will counter the effect of the stiffer chain by weakening the reptative component to the overall motion.

The general picture that entangled polymers follow the reptation scaling law has become well established. The point at which entanglements first occur is poorly defined by diffusion results and does not necessarily coincide with the critical molecular weight as perceived by viscosity[4,28]. Arguments based on chain flexibility or stiffness and free volume do, qualitatively, explain the discrepancies. Unentangled systems have received less attention, but it appears that the dynamics of low molecular weight systems may be represented by a simple approach such as the Rouse model in which tube constraints are minimal.

Further insight into this model may be obtained from the average diffusion coefficient of a series of bimodal blends. A simple method to test the validity of the Rouse model is to consider blends of low molecular weight melts. If the chain dynamics may be properly represented by an average monomer mobility determined both by the 'labelled' chain flexibility and the flexibility of the neighbouring chains, the model should be as applicable to low molecular weight bimodal blends.

Bimodal blends

The raw attenuation plot for the 50/50 (wt%) bimodal blend (M_w 2000/M_w 450) is shown in *Figure 4*; only one characteristic diffusion process is present, contrasting the behaviour exhibited by a blend of two different molecular weight polymers in semidilute solution[22]. Identical behaviour was observed for all the blends studied. The average self-diffusion coefficient–weight composition dependence is shown in *Figure 5*. The limits of the data are the single-component melts, i.e. the single-component melts may be regarded as a bimodal melt of two equal halves. Two important points arise from these observations: (i) the blends are completely miscible; and (ii) the dynamics of the two components have been fully averaged to yield a single effective diffusion coefficient.

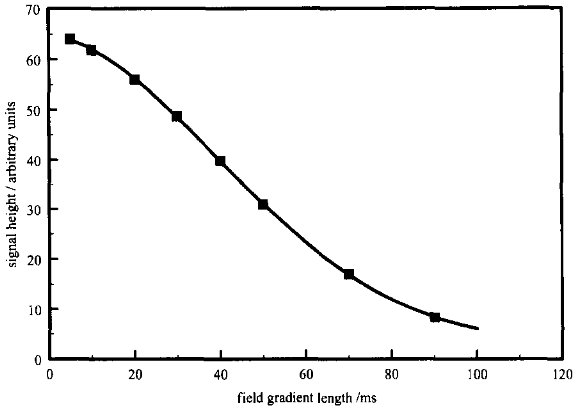

Figure 4 Raw attenuation plot for a 50/50 (wt%) blend of M_w 2000 and M_w 450; the full curve is the single-component fit

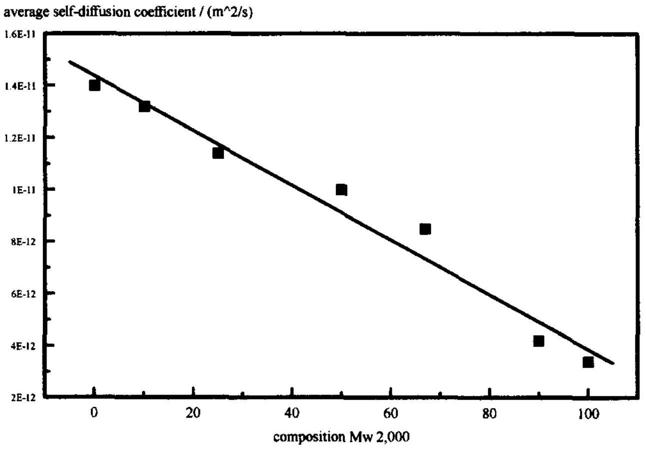

Figure 5 Average self-diffusion coefficient as a function of composition (%) for a blend of PPO melts of M_w 2000 and M_w 450

The linearity of the attenuation plot and the composition dependence represent microscopic averaging. The diffusion of the polymer molecules through the melt are determined by cooperative motions between neighbouring chains and is governed by how efficiently the motions are transmitted through the neighbouring media. The presence of small chains, which are inherently more flexible, will increase this efficiency and, therefore, enhance the diffusion. By the same argument, the diffusion of the smaller chains will be retarded by the bigger chains. Since the critical molecular weight for poly(propylene oxide) melts is 6000–7000[29], no contributions from entanglement coupling are likely to be present. The average diffusion coefficient might, therefore, be expected to follow a simple law of the form:

$$D_s = pD_s^a + (1-p)D_s^b \tag{3}$$

where p is the fraction of segments comprising a chain with self-diffusion coefficient D_s^a. For example, given that D_s^a (M_w 450) = $14.0 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$ and D_s^b (M_w 2000) = $3.4 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$, a 75/25 (wt%) blend would be expected to have an average diffusion coefficient $D_s = 11.35 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$. The measured diffusion coefficient, $D_s = 11.4 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$, very closely agrees.

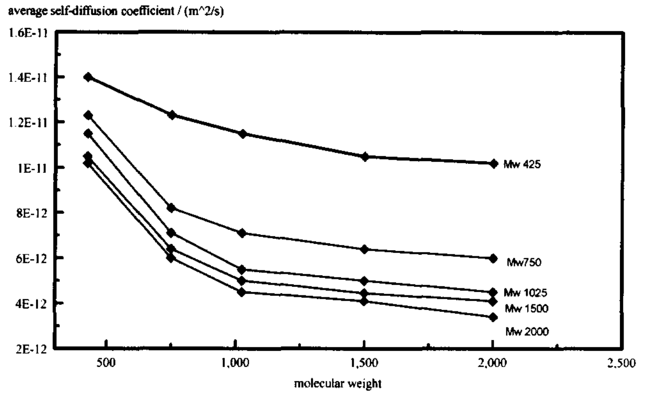

Figure 6 Average self-diffusion coefficient as a function of molecular weight for a series of PPO blends

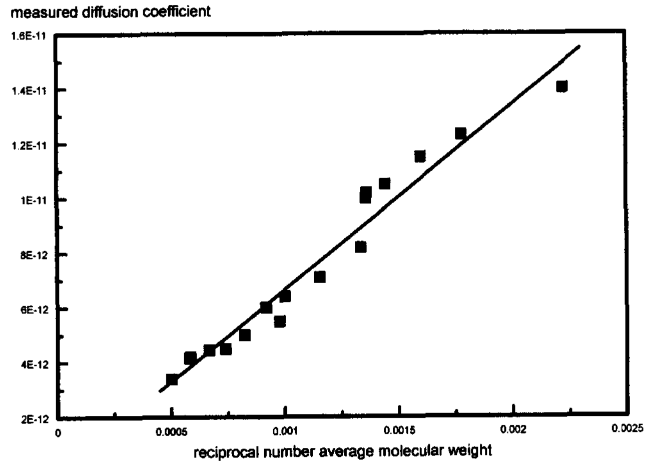

Figure 7 Average self-diffusion coefficient as a function of reciprocal number-average molecular weight

The effect of molecular weight is shown in *Figure 6*. In all cases, increasing the molecular weight of one component decreased the average diffusion coefficient. The agreement between predicted and measured values for the average diffusion coefficient for all the blends follows equation (3) within experimental error. This approach is comparable to that of Meerwall *et al.*[30], who formulated that the average diffusion coefficient is a summation of the component diffusivities, $D_s(M_i)$:

$$D_s = \sum_i D_s(M_i) = \sum_i D_s(M_{ref})(M_i/M_{ref})^{\alpha} \qquad (4)$$

where M_{ref} is a monodisperse standard whose self-diffusion coefficient is known. By setting $\alpha = 1$, i.e. $D_s \propto M^{-1}$, as in this example, a bimodal blend simplifies to the model given before:

$$D_s = pD_s^a + (1-p)D_s^b \qquad (5)$$

Meerwall *et al.* in their study of polydisperse paraffins found non-linear attenuation functions; the upward concavity in the plot increased with increasing polydispersity. However, the pure-component diffusivities had a molecular weight exponent of approximately −2, signifying that Rouse motion is not occurring. Inherently, the effects of polydispersity are likely to be stronger and significant departure from linearity expected. All the bimodal melt data are superimposed in *Figure 7*, where the measured diffusion coefficient has been plotted against the reciprocal number-average molecular weight, M_n^{-1}. The number-average molecular weights for the bimodal samples have been calculated using the general formula:

$$M_n = \sum_i n_i M_i \Big/ \sum_i n_i \qquad (6)$$

where n_i is the number of chains with molecular weight M_i. The slope is -1.0 (± 0.05), confirming the validity of the Rouse model to these systems.

CONCLUSION

For low molecular weight poly(propylene oxide) melts, both the viscosity and the diffusion follow the Rouse law. The spin–spin relaxation times reinforce a simple picture for the dynamics of low molecular weight polymer melts. The results presented here are compared to other polymer melts and show good qualitative agreement. Transition to a reptative-type motion is closely related to chain flexibility and, inherently, free volume. It is clear, therefore, that the reptation theory is only a basis with which to describe the dynamics of high molecular weight polymers. Studies of the average dynamics of simple blends support the occurrence of Rouse motion.

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