The critical overlap concentration measured by pulsed field gradient nuclear magnetic resonance techniques

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The absence of any critical effects around c^* in the diffusional behaviour of a range of molecular weights of narrow fraction polystyrene in tetrachloromethane has been re-examined. Analysis of the molecular weight dependent concentration coefficients k_f of the concentration dependence shows sharp transitions between the dilute and semi-dilute behaviour. Spin–spin relaxation time measurements have also been performed and yield a value for c^*. These values and other calculated and measured values are discussed in terms of the spectrum of motions present in a polymer system.

(Keywords: critical overlap concentration; diffusional behaviour; pulsed field gradient n.m.r.)

INTRODUCTION

A fundamental transition in the physical properties of polymer solutions occurs between dilute systems where the coils are isolated and more concentrated states where the coils interpenetrate. In these more concentrated systems, entanglement coupling may also be present. The viscosity behaviour and osmotic pressure behaviour across these concentration and molecular weight boundaries have been studied in detail[1,2], but the diffusion behaviour is less well understood[3]. Typically, measurement of diffusion coefficients suggests the absence of any critical effects. In this paper, results are reported that support this premise, but upon further examination strong critical effects may be elicited.

The self-diffusion coefficient of a polymer molecule in solution (or the melt) gives a direct measure of its thermally driven translational motion. This diffusion coefficient is dependent on the temperature, molecular weight and concentration of the system as well as the complex dynamics of the polymer solution which exist over the timescale of the experiment. In the study of the dynamics of these systems, five different regimes can be considered[4] in which the molecular motion will be a function of molecular weight and concentration: (i) dilute; (ii) semi-dilute, non-entangled; (iii) semi-dilute, entangled; (iv) concentrated, non-entangled; and (v) concentrated, entangled.

In bulk polymers, the criterion for entanglements to occur is whether the molecular weight exceeds some critical value, defined as the 'critical molecular weight for entanglement', M_c, which characterizes the minimum size a chain must be before entanglement coupling is present. The situation is more complex in the presence of solvent, where the effect of concentration must also be considered. For example, the polymer chains may exceed the critical molecular weight but be so dilute that very few entanglements are possible and those that do occur are relatively short-lived. Hence, in this system entangled behaviour may not be exhibited.

At infinite dilution, the self-diffusion coefficient of a polymer molecule is given by the Stokes–Einstein expression[5]

$$D_0 = k_b T / 6\pi\eta_0 R_h \qquad (1)$$

where η_0 is the solvent viscosity. R_h is the hydrodynamic radius of the macromolecule and is a description of the time-averaged conformation of the polymer. An estimate of the friction, calculated from the reciprocal of the diffusion coefficient $f_0 = (6\pi\eta_0 R_h)^{-1}$, may be obtained by an appropriate summation over all monomers assuming a monomer friction coefficient ζ_0. Non-free draining arguments[6–8] lead to the following relationship between the hydrodynamic radius and the molecular weight M of the chain

$$R_h \propto M^{\nu} \qquad (2)$$

where ν is the Flory index, and thus for a good solvent $D_s \propto M^{-0.6}$.

At finite concentrations but still in the dilute regime, the occasional interactions between polymer molecules raise the friction above the limiting value. Under such conditions, a power series in concentration can be used to describe the friction[9,10]

$$f = f_0(1 + k_f c + k_f' c^2) \qquad (3)$$

Above c^*, the dynamics of polymer solutions are complex and the entanglement concept may be used to differentiate the two commonly invoked models. The Rouse model for non-entangled solutions (and melts), based on the 'bead and spring' model for a polymer chain, states that the velocity of each bead is a linear function of an applied force exerted by the nearest-neighbour beads. The origin of the bead mobility, or more accurately its reciprocal, the bead friction, is in the damping of the

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chain motion due to hydrodynamic drag from the solvent. Hence, the mobility of the whole chain is a summation over all monomers and thus $D_s \propto M^{-1}$. In more concentrated solutions where entanglement coupling is present, the bead mobility will be reduced by the impingement of other polymer chains, termed 'uncrossability effects'.

The effects manifest themselves by suppressing the motion of each chain to a 'tube' formed by its neighbours. The simplest approach, formulated by de Gennes[11], is based on a Rouse motion of each chain along a tube. The mobility of each chain scales inversely with molecular weight, as does the curvilinear tube dimension. Consequently, the self-diffusion coefficient scales as the inverse square of the molecular weight. A more rigorous treatment has been given by Klein[12], which concludes that

$$D_s \propto M^{-2} c^{(\nu-2)/(3\nu-1)} \tag{4}$$

The point at which dilute behaviour, i.e. $D_s \propto M^{-0.6}$ and $f = f_0(1 + k_f c + k_f' c^2)$, breaks down should therefore be representative of c^*. For high molecular weight samples, this transition may be enhanced by the presence of entanglement coupling. Indeed for self-diffusion, an absence of any critical effects around c^* (and M_c) has been found in a variety of systems[13] and this anomaly is the subject of this paper.

EXPERIMENTAL

The measurements were performed on a JEOL FX100 high resolution nuclear magnetic resonance (n.m.r.) spectrometer, operating at 100 MHz (protons) and modified to carry out self-diffusion measurements using the pulsed field gradient technique[14]. The spectrometer was upgraded by the addition of a Surrey Medical Imaging Systems console which replaced both the radio frequency and computational components. The current amplifier used to generate the field gradients was based on the design by Stilbs[15]. The unit 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 of the field gradient pulses Δ was set at 150 ms and the width of the field gradient pulses δ varied between 5 and 90 ms. A glass filament containing D_2O was used as an internal lock reference for greater stability. The full spin echoes, after Fourier transformation, were integrated (A_δ) and could be fitted to equation (5), which assumes isotropic Brownian diffusion

$$A_\delta = A_0 \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D_s] \tag{5}$$

where γ is the magnetogyric ratio. The presence of any restricted diffusion was examined by studying the dependence of the diffusion coefficient on the diffusion time, Δ, but none was observed.

The spin–spin relaxation time measurements were performed using a high resolution CPMG[16] sequence; a spin echo was recorded and the intensity of the aliphatic peak measured after Fourier transformation. In all cases, the data could be fitted to a single exponential decay.

RESULTS AND DISCUSSION

The molecular weight behaviour and concentration behaviour of the viscosity of polystyrene solutions have been studied extensively[17]. However, the critical concentrations defining the boundaries between the dilute, semi-dilute and concentrated regimes are not precisely characterized. Not only do the critical effects depend on both the molecular weight and concentration of the system, but the range over which these effects manifest themselves also depends on these two parameters. The boundary between the dilute and semi-dilute regions will be discussed in the context of the results presented here.

The self-diffusion coefficients of narrow fraction polystyrenes in solutions of tetrachloromethane, a good solvent, have been measured as a function of both molecular weight and concentration. The results are discussed in terms of the established models for polymer diffusion in dilute solution as given earlier.

The effect of molecular weight

The experimental molecular weight dependence of the self-diffusion coefficient of polystyrene in tetrachloromethane at two concentrations, obtained using the pulsed field gradient n.m.r. technique, is shown in *Figure 1*, and may be represented by the following power law at 5% w/w concentration

$$D_s \propto M^{-0.63(\pm 0.05)}$$

and at infinite dilution by

$$D_0 \propto M^{-0.58(\pm 0.02)}$$

These exponents are in excellent agreement with the theoretical prediction of $D_s \propto M^{-0.6}$ for diffusion in a good solvent[18]. Similarly, the exponents are in excellent agreement with other moderately good and good solvent results: polystyrene in benzene[19,20] gives $D_0 \propto M^{-0.55}$ and polystyrene in toluene[21] gives $D_0 \propto M^{-0.57}$. The exponents observed in these results agree more closely with the theoretical prediction than those found previously for this system, but this is due probably to the greater molecular weight range used in this study. Weill and des Cloizeaux[22], whilst addressing the differences between the various observed static and dynamic exponents for the sizes of polymers in solution, suggested that a unique exponent only applies in the limit of inifinite molecular weight because excluded volume effects become more significant with increasing chain length.

Most importantly, the adherence to the $D_s \propto M^{-0.6}$ power law over the entire molecular weight range studied

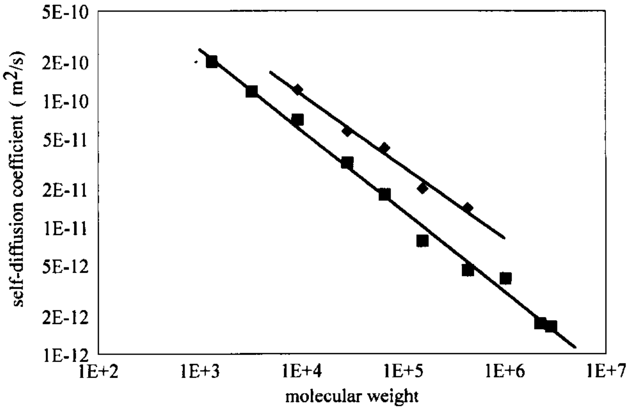

Figure 1 Self-diffusion coefficient *versus* molecular weight for polystyrene in tetrachloromethane: (■) 5% w/w concentration; (◆) infinite dilution

is somewhat surprising since, for the polymers of higher molecular weight, the concentration is well above the overlap concentration c^*. The values for c^* taken from ref. 10 and a simple calculation based on molecular volumes suggest that for a polymer of molecular weight approximately 250 000 c^* is 2% w/w (35 $\mathrm{kg\,m^{-3}}$). This concentration is somewhat lower than that shown by the viscosity concentration–molecular weight 'phase diagram' of ref. 4. Diffusion coefficient–molecular weight exponents between 0.5 and 0.7 have, however, been observed for polystyrene in toluene[23] up to concentrations of 50% w/w. The difficulty in unambiguously defining c^* is common and is compounded by the sensitivity of the various methods used to measure c^*.

Spin–spin relaxation time (T_2) measurements have also been performed on these polymer solutions and the results are shown in *Figure 2*. The spin–spin relaxation time has been shown to be more sensitive than the diffusion coefficient to the rotational and short-range dynamics of the system. The relaxation process characterized by the spin–spin relaxation time is dominated by the interaction of localized, fluctuating dipolar fields. These dipolar interactions may arise from the dipoles associated with the same molecule (intramolecular relaxation) or another molecule (intermolecular relaxation) that may be encountered through thermal motions. All molecular motions arising through conformational rearrangement, pendent group rotation and diffusion will provide a potential relaxation 'sink'. The spin–spin relaxation time data shown in *Figure 2* for the lower concentration (0.5% w/w) are independent of molecular weight. In such cases, the relaxation is a consequence of segmental motion, i.e. intramolecular relaxation. Similar behaviour has been observed for poly(ethylene oxide) in water and in hydrochloric acid[24] and for poly(dimethylsiloxane) in a variety of solvents[25].

At the higher concentration (5% w/w), two different molecular weight dependencies are observed. The relaxation times are much smaller than the dilute limit, indicating that the mobility of the molecules is reduced. The initial decrease in spin–spin relaxation time is related to the decrease in translational mobility and the subsequent, slower decrease is a measure of the reduction of segmental mobility. Expressed differently, the translational dynamics have been restricted by 'crowding' within the polymer solution, thus giving an estimate of c^*. It is evident that high frequency, low amplitude motions will have little effect on the viscosity of the system; the correlation time for segmental motion is typically of the order of 10^{-11} to 10^{-12} s[26], whilst the viscosity is measured over timescales of a few seconds. Consequently, spin–spin relaxation measurements give a lower estimate of c^*, whilst viscosity measurements give a somewhat higher estimate. From this molecular weight study, the critical overlap concentration has been exceeded for a 5% w/w solution of molecular weight greater than 10 000. This estimate reflects the relative sensitivity of the CPMG technique to measure the local segmental motion of the polymer chains. Another reason for this might be due to the frequency of motion that exists within the molecule. In order to provide an efficient mechanism for relaxation, the motions must occur at frequencies comparable to the resonance n.m.r. frequency ($\sim$100 MHz). Hence, motions of higher frequency will dominate this type of measurement.

The apparent disagreement between the spin–spin relaxation data and the self-diffusion data may be rationalized by considering not only the frequency of motion but also the distance scale involved. Spin–spin relaxation is predominantly determined by the interaction of proximal dipoles whose fluctuating fields represent the local mobility of the polymer chain. Self-diffusion, on the other hand, is concerned with distance scales very much greater than the size of the polymer coil and, as such, is less sensitive to the complex segmental dynamics. In these experiments, the distance scale is approximately 2 μm (assuming $D_s \approx 10^{-11}\ \mathrm{m^2\,s^{-1}}$ and $\Delta = 0.15$ s). Assuming that this figure represents the average coil–coil separation, it corresponds to an approximate concentration of about 2% w/w. This value compares favourably to the value for c^* (2% w/w for M_w 250 000) obtained from ref. 10. Diffusing over this distance scale, the polymer chains will encounter many more polymer chains and a reduction in their translational mobility should be expected. Therefore an absence of any critical effects around c^* is surprising.

The effect of concentration

A far more consistent picture may be obtained from a complete investigation of the concentration dependence of the self-diffusion coefficient. *Figure 3* shows the concentration behaviour for five different molecular weight samples. Expressing the friction term as a power

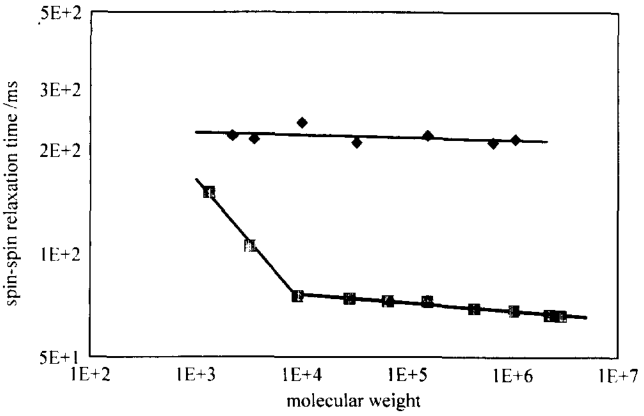

Figure 2 Spin–spin relaxation times *versus* molecular weight for polystyrene in tetrachloromethane: (■) 5% w/w; (◆) 0.5% w/w

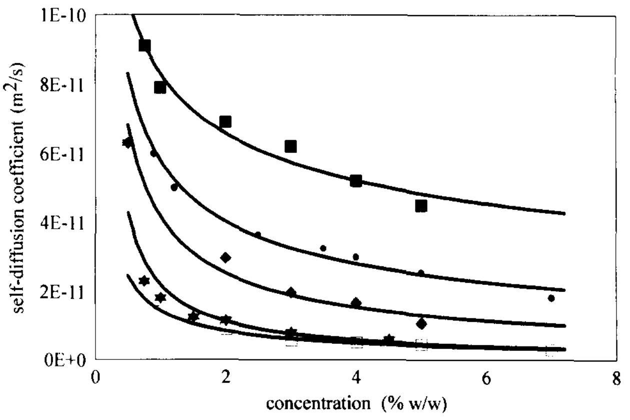

Figure 3 Self-diffusion coefficient *versus* concentration for five different molecular weights: (■) 9200; (●) 28 500; (◆) 66 000; (★) 156 000; (□) 435 500

series in concentration as described earlier, permits the diffusion coefficient to be represented as

$$D_s = D_0/(1 + k_f c + k_f' c^2) \qquad (6)$$

which in the dilute solution limit simplifies to

$$D_s = D_0(1 - k_f c) \qquad (7)$$

The linearity of the concentration behaviour of the diffusion coefficient has been observed in a variety of systems. Specifically for polystyrene, Callaghan and Pinder[10] and Sutherland[27] found linear behaviour up to concentrations close to c^*. The Sutherland data, although discussed in terms of a linear concentration behaviour, are more accurately represented by a power series. The friction–concentration behaviour for two molecular weights from this study is shown in *Figure 4*. The unsuitability of a linear concentration dependence is borne out by the sample of higher molecular weight. However, the sample of lower molecular weight does, within experimental error, follow a linear dependence. A second-order power law has therefore been adopted throughout this analysis; the solid lines represent the fits from equation (3). The infinite dilution friction f_0 obtained through this analysis is shown in *Figure 5*, and scales as $f_0 \propto M^{0.57(\pm 0.02)}$. This is in excellent agreement with the Kirkwood–Riseman approximation[28]. The interpolated value for polystyrene with $M_w = 37\,000$ in tetrachloromethane, $f_0 = 4.0\ (\pm 0.2) \times 10^{-11}\ \mathrm{kg\,s^{-1}}$, agrees very well with that found for the polystyrene–toluene[27] system ($f_0 = 4.8\ (\pm 0.4) \times 10^{-11}\ \mathrm{kg\,s^{-1}}$). Photon correlation spectroscopy studies have been performed on the same solutions[29]. The mutual friction at infinite dilution, analysed in an identical manner, follows a similar dependence: $f_0 \propto M^{0.53(\pm 0.07)}$. Within experimental error, the infinite dilution frictions from the two types of measurement follow the same molecular weight dependence.

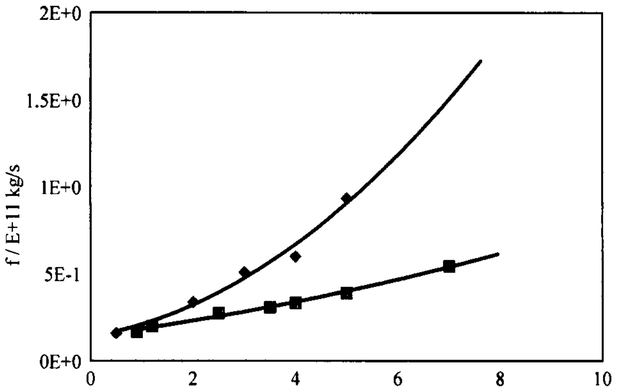

Figure 4 Friction *versus* concentration for two molecular weights: (◆) 66 000; (■) 28 500. The solid lines represent fits from equation (3)

The friction coefficient–concentration behaviour itself has been modelled by Pyun and Fixman[30] and by Yamakawa[31]. The friction coefficient may be regarded as the sensitivity of the concentration dependence of the diffusion coefficient to the molecular weight of the polymer, i.e. high molecular weight polymers show a more pronounced dependence on concentration than low molecular weight polymers. The models are based on the Kirkwood–Riseman approach, taking into account both intermolecular and intramolecular hydrodynamic interactions. The perturbation of the solvent velocity generated in the vicinity of one molecule, which is caused by the presence of another molecule, is calculated. Thus, the effective, localized hydrodynamics are obtained.

Both models predict $k_f \propto M^{0.5}$ for theta solvents and $k_f \propto M^{0.8}$ for good solvents. This scaling behaviour of the concentration independent k_f term has also been observed for a variety of polystyrene solutions. The behaviour of the k_f term from these data is shown in *Figure 6*. The low molecular weight behaviour shows the trend expected for a moderately good solvent, i.e. $k_f \propto M^{0.7(\pm 0.03)}$. However, above $M_w = 300\,000$, this simple dependence breaks down, the friction being much more sensitive to concentration and molecular weight.

The failure of the dilute solution theories over these concentration ranges therefore suggests that these systems are above c^*. Therefore the approach of de Gennes[11], where the diffusion is formulated through blobs, is more suitable

$$D_s \propto M^{-2} c^{(\nu-2)/(3\nu-1)} \qquad (8)$$

Consequently, for good solvents ($\nu = 0.6$) $D_s \propto c^{-1.75}$, whilst for theta solvents ($\nu = 0.5$) $D_s \propto c^{-3.0}$. The concentration behaviour generally exhibited is a smooth transition between these exponents; the conditions where the asymptotic value of -3.0 is reached being dependent on the molecular weight and hence concentration of the system[3]. The concentration behaviour of the diffusion coefficient for the two high molecular weight samples in

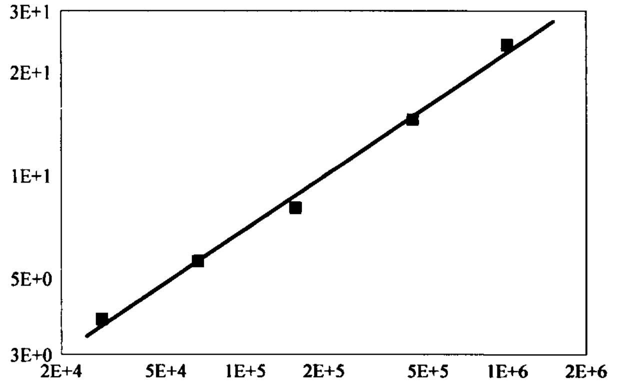

Figure 5 Infinite dilution friction from pulsed field gradient n.m.r. data *versus* molecular weight

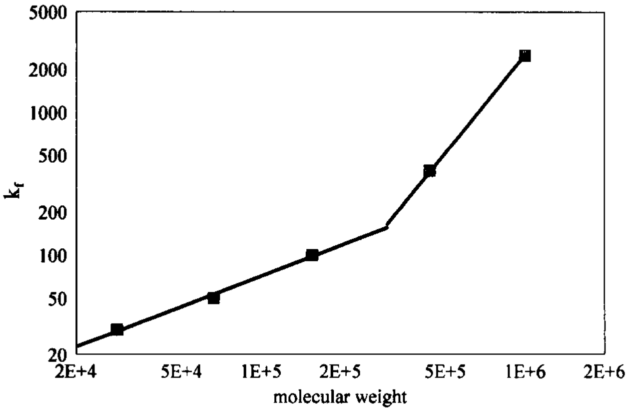

Figure 6 Friction coefficient *versus* molecular weight

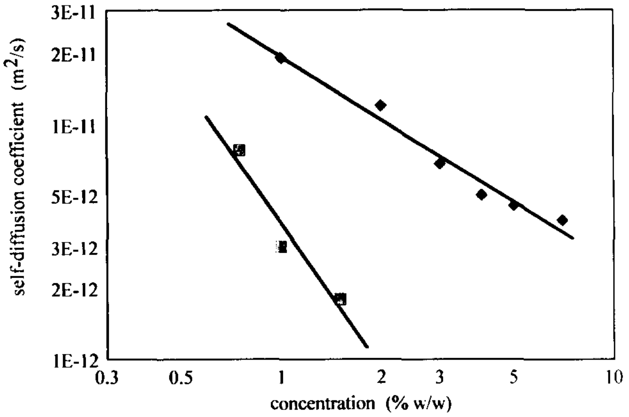

Figure 7 Self-diffusion coefficient *versus* concentration for higher-molecular-weight samples: (◆) 435 500; (■) 1 030 000

this study is shown in *Figure 7*; the scaling relationships exhibited are $D_s \propto c^{-0.91(\pm 0.04)}$ for the sample with $M_w = 435\,500$ and $D_s \propto c^{-2.25(\pm 0.10)}$ for the sample with $M_w = 1\,030\,000$. Whilst the higher molecular weight sample is well above c^*, the lower molecular weight sample is at too low a concentration to exhibit clearly the entangled behaviour scaling laws. Similarly, these experimental exponents are in fair agreement with theoretical exponents for the concentration behaviour and other experimental data[31-34]. This interpretation of the molecular weight dependent concentration coefficients obtained from the diffusion behaviour gives a value for c^* in agreement with that found by Callaghan and Pinder[10].

An alternative interpretation of these results has, however, been proposed[35] which suggests that a transition from a rod-like molecule (low molecular weight) to a random coil at higher molecular weight might result in a break in the molecular weight behaviour of the k_f term not dissimilar to that observed in this study. However, Cotton *et al.*[36] have shown that down to $M_w \approx 10\,000$ a random coil approach is valid, and hence any rod–coil transition should occur below this value. The observed transition at $M_w = 250\,000$ (*Figure 6*) is unlikely, therefore, to be due to a rod–coil transition.

CONCLUSIONS

The molecular weight dependence of the diffusion coefficient for a range of molecular weights was representative of good solvent, dilute solution behaviour. No effects of c^* were observed initially. The simple concentration dependence of the self-diffusion coefficient did not show any substantial deviation from dilute solution behaviour.

The concentration behaviour of the molecular weight dependent friction coefficients for the lower molecular weight species was again representative of good solvent, dilute solution conditions. However, the concentration behaviour for the higher molecular weight species was representative of good solvent, semi-dilute behaviour. This analysis did yield a value for c^* in agreement with simple calculations based on molecular volume and the value obtained from viscosity.

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