Diffusion and nuclear magnetic relaxation in concentrated polystyrene solutions

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Nuclear magnetic relaxation times (T_1 and T_2) and diffusion coefficients (D) of polystyrene solutions in d_8 toluene have been measured as a function of molecular weight. The polymer T_1, T_2 and D values decrease monotonically with increasing molecular weight. T_1 and D reach limiting values at high molecular weights. The results are interpreted in terms of chain entanglements and the time scale of the experimental method.

INTRODUCTION

Some limited insight into the diffusion of macromolecules in concentrated solutions (30–40% by wt) may be gained by examination of dilute solution theories[1,2] and theories of the melt[3–5].

In a dilute solution the diffusion process is determined by the balance between thermodynamic and hydrodynamic interactions. In a good solvent the polymer chains are expanded well beyond their random flight dimensions and the diffusion coefficient increases with increasing concentration up to the semi-dilute region, where chain overlap begins. Beyond this concentration the hydrodynamic forces dominate and D decreases with further increase in concentration, despite the fact that the chain dimensions are still decreasing in this region.

Quantitatively, this can be expressed in terms of a virial expansion of the diffusion coefficient, in terms of concentration (c), assuming a linear dependence of the friction coefficient, f, on c :

$$D(c) = D\ (c = 0)\ [1 + (2A_2M - K_f - V)c + (0)c^2 + \cdots] \tag{1}$$

where $D(c = 0) = kT/f(c = 0)$.

In a good solvent the second virial coefficient, A_2, is positive and depends on molecular weight in the range $M^{0.05}$ to $M^{0.25}$ [6]. K_f is a hydrodynamic term and in a good solvent may depend on a high power of molecular weight, in a similar way to intrinsic viscosity[7]. V is a volume restriction term. At high concentrations this expansion may no longer be valid, but in the region of interest here (30–40% wt) the relative balance of the A_2 and K_f terms will determine the sign of $(\partial D/\partial c)$.

Diffusion in the concentrated region may also be discussed in terms of melt theories with certain added assumptions. Below M_c, the critical molecular weight for the occurrence of entanglements[8], the Rouse theory[3] predicts:

$$D \propto M^{-n} \quad \text{where } n = 1. \tag{2}$$

Above M_c in the melt, several different theoretical approaches[3–5,9] predict values of n from 2 to 3.4 corresponding to the large exponents found experimentally from viscosity measurements. In concentrated solution the number of interchain frictional contacts are reduced and the increase in free volume leads to increased segmental motion.

EXPERIMENTAL TECHNIQUES

Proton spin–lattice (T_1) and spin–spin (T_2) relaxation times were measured at 31 MHz for a series of polystyrene solutions in d_8 toluene using the 180°-τ-90° [10] and the Meiboom and Gill[11] pulse sequences.

Diffusion coefficients were measured using a pulsed field gradient technique[12,13]. In a laboratory magnetic field $B^0(z)$, there are always residual inhomogeneities, resulting in a distribution of precessional frequencies of the nuclear moments about $B^0(z)$. At thermal equilibrium the only observable component of the macroscopic magnetic moment M^0 is $M^0(z)$. A short radio-frequency pulse of appropriate frequency applied orthogonally to z can rotate $M^0(z)$ through any desired angle, resulting in a measurable component of M^0 in the xy plane. The instantaneous decay of the signal generated by this xy component – termed the Bloch decay – is caused by any process which allows the individual nuclear spins to lose phase coherence with one another, but is generally dominated by magnetic field inhomogeneities. The return of $M(z)$ to its thermal equilibrium value – the spin lattice relaxation process – involves a loss of spin energy to the surroundings and is characterized by the first order rate constant T_1.

The mechanism of the Bloch decay is partly reversible, since some processes, such as field inhomogeneities are time independent, and spin echoes of this signal can be generated by further excitation of the spin system over a time $\sim 5T_2$. The pulse sequence 90°-τ-180° $(2\tau - 180°)_n$ [14] generates a series of spin echoes whose amplitudes as a function of time measure the decay of the transverse magnetization M_{xy}. This decay is characterized by the first order rate constant T_2.

In the diffusion experiment[12] the magnetic field at the

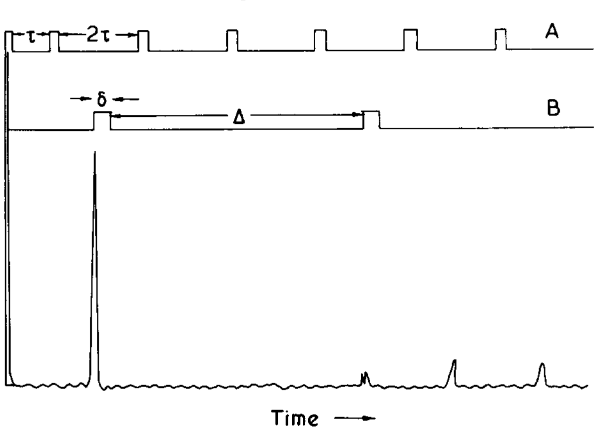

Figure 1 Meiboom and Gill sequence for measuring D. The spectrum shown (40% polystyrene solution, $\bar{M}_w = 4000$) has $\tau = 8$ msec, $\Delta = 48$ msec and $\delta = 0.1$ msec. A, is the r.f. pulse sequence 90°-τ-$(180^\circ - 2\tau)_n$; B, the field gradient sequence

nucleus is made time dependent by applying field gradient pulses (*FGP*) along z. A typical sequence, due to Packer *et al.*[13] is shown in *Figure 1*. The first *FGP* at 2τ virtually instantaneously dephases the xy magnetization by imposing a linear increase in precessional frequencies across the sample for a time δ. After an odd number of 180° pulses a second *FGP* at 8τ rephases the xy magnetization by a further linear increase in precessional frequencies. This change in frequency depends on the position of a nucleus in the field gradient. If this position is unchanged during the time Δ, the *FGP* separation, then the effects of the two *FGP* cancel. If the nucleus has changed its position then complete 're-focusing' is not achieved and the subsequent spin echo train is therefore attenuated. By assuming a diffusion model based on Brownian motion, Stejskal and Tanner[12] obtained the following relation for the attenuation:

$$\ln\left[\frac{M'_{xy}(t)}{M_{xy}(t)}\right] = -\gamma^2G^2\delta^2\Delta D \qquad (3)$$

where γ is the magnetogyric ratio, D the self diffusion coefficient and G the field gradient. This equation assumes $\Delta \gg \delta$.

D may be calculated by plotting ln (attenuation) against Δ—this reduces systematic errors due to the lack of pulse stabilization and also tests for restricted diffusion[14]. In this context, restricted diffusion refers to any process that leads to the termination of the random walks of a substantial number of nuclei. *Figure 2* shows the attenuation plot for a 40% polystyrene solution ($\bar{M}_w = 110\,000$). Within experimental error there is no evidence of restriction over the time Δ.

Apparatus

A 31 MHz spin echo spectrometer was used in conjunction with a Varian 12 in field stabilized magnet system. A 5 mm crossed coil probe was used with a recirculating gas flow temperature control system. Sample temperature regulation to better than 0.3K was achieved over the duration of the experiment. Field gradient pulses were developed in a quadrupolar coil[15] using a transistor current stabilized switch[16]. The field gradient (49 ± 0.5 mT/m/A in a 0.05 m diameter coil) was calibrated using the self diffusion coefficient of water[17].

The receiver system incorporated a linearized diode detector[18] together with special circuitry designed to minimize r.f. leakage. A Nicolet signal averaging computer and a single channel box-car integrator were used to accumulate spectra.

A range of narrow distribution polystyrene samples were obtained from Waters Associates and the Pressure Chemical Company ($\bar{M}_w/\bar{M}_n < 1.1$) and solutions were made up in d_8 toluene (99.9%). The samples were deoxygenated under vacuum and sealed over liquid nitrogen.

RESULTS AND DISCUSSION

In *Figure 3* the diffusion coefficient is plotted against molecular weight for two concentrated polymer solutions. D decreases both with increase in concentration and molecular weight. The concentration dependence follows that found by Rehage *et al.*[19]. The hydrodynamic contribution, K_f, is greater than the thermodynamic contributions $2A_2M$ (equation 1) leading to a negative value of $(\partial D/\partial c)$.

The molecular weight dependence is more complex as it is likely that K_f will depend on different powers of molecular weight above and below M_c. Since the exact

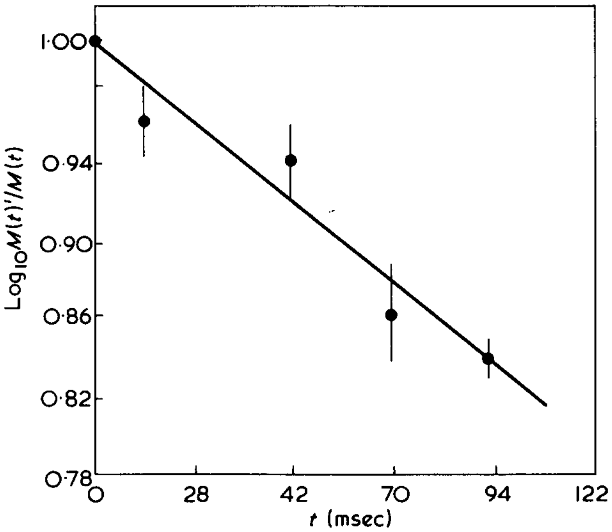

Figure 2 Attenuation plot using equation (3), for a 40% polystyrene solution $\bar{M}_w = 110\,000$

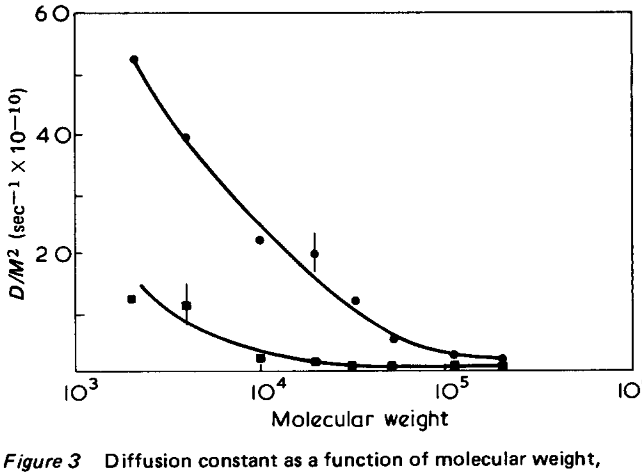

Figure 3 Diffusion constant as a function of molecular weight, for 30% (●) and 40% (■) solutions at 353K

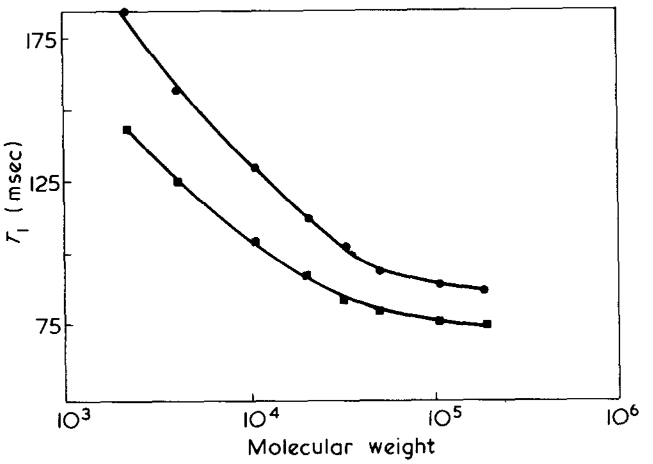

Figure 4 Spin–lattice relaxation time T_1, as a function of molecular weight, for 30% (●) and 40% (■) solutions at 353K

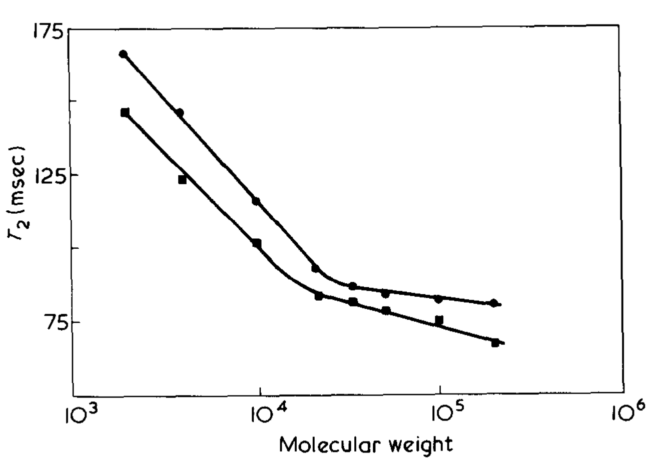

Figure 5 Spin–spin relaxation time T_2 as a function of molecular weight, for 30% (●) and 40% (■) solutions at 353K

nature of this dependence is unknown it is probably more instructive to consider these data in terms of melt theories.

Fitting the experimental data to equation (2) gave values of n (below M_c) of 0.53 ± 0.05 for the 30% solution and 0.7 ± 0.1 for the 40% solution. These values are smaller than those predicted theoretically for the melt. Above M_c, D becomes much less dependent on molecular weight at both concentrations. This contradicts the theoretical prediction of a strong molecular weight dependence. However, these equations are for the self diffusion of the centre of mass of the polymer. The magnetic resonance experiment essentially measures diffusion by a space time correlation of atomic coordinates. For rigid molecules this measures the centre of mass translation. However, in polymer solutions, superimposed on the centre of mass motion are the random positional fluctuations of the polymer segments. Over the time scale of these experiments ($\Delta \sim 10^{-1}$ sec) the segmental motion will contribute to the measured value of D. Allen *et al.*[20] have observed a similar phenomenon in neutron scattering experiments. Below M_c the measured value of D contains both translational and segmental contributions leading to a reduced dependence on molecular weight. Above M_c when the translational motion is severely restricted the major contribution to D is from segmental motion. It is interesting to note that Paul *et al.*[21] have observed a similar effect using a light scattering technique in the system polystyrene/cyclohexanone. The concentration dependence of D, above M_c, is to be expected because of the damping of the backbone motion by the increase in interchain contacts.

Figures 4 and *5* show the corresponding T_1 and T_2 data. Spin relaxation is determined by the intensity of the fluctuating local magnetic fields arising from the motions of the surrounding lattice,

$$1/T_1 \propto J(w_0) + J(2w_0)$$

where $J(w_0)$ and $J(2w_0)$ are the amplitudes of the spectral density function at the resonance frequency w_0 and at $2w_0$, respectively. T_1 is therefore sensitive to molecular processes that are very rapid on a time scale $\sim 10^{-7}$ sec. The spin–spin relaxation time T_2 also depends on the amplitude of the spectral density function around zero frequency, $J(0)$:

$$1/T_2 \propto J(0) + J(w_0) + J(2w_0)$$

Both T_1 and T_2 depend on the same fluctuating local magnetic field but draw upon different parts of its frequency spectrum.

In the spin-echo experiment an average of the relaxation times for all the protons in the sample is measured. The T_2 results (*Figure 5*) show a sharp break at $\sim M_c$, similar to that reported by McCall *et al.*[22] for bulk polyethylene. The concentration dependence is also interesting, showing that the critical break occurs at a lower molecular weight at the higher concentration. The values of M_c are 17 000 for the 40% solution and 26 000 for the 30% solution. *Figure 4* shows the results for T_1. Here the behaviour is very different: above M_c, T_1 shows a much weaker dependence on molecular weight and there is no clear break point. The dependence is also weaker at the higher concentration. This is understandable because the major contributions to T_1 $[J(w_0), J(2w_0)]$, arise from the motion of the backbone, between entanglements and the side group motion. Above M_c, at constant weight concentration, both these motions will be virtually independent of molecular weight.

In summary, these results show that both D and T_2 reflect the formation of an entangled network in concentrated polymer solutions. Above M_c, the polymer backbone motion determines the behaviour of D over the time scale of the n.m.r. experiments.

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