Self and mutual diffusion measurements in dilute and semi-dilute polystyrene solutions

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(*Received* 22 *September* 1982)

Self diffusion coefficients have been obtained for polystyrene ($\bar{M}_w = 37\,000$) solutions in toluene (D_8) and cyclohexane (D_{12}) by the pulsed field gradient n.m.r. technique at 303 K. Mutual diffusion coefficients have been obtained by photon correlation spectroscopy (p.c.s.). In a poor solvent (cyclohexane) both techniques show a similar trend of a monotonic decrease in the diffusion coefficient with increasing concentration of polymer. However, in a good solvent (toluene) n.m.r. shows a monotonic decrease in the diffusion coefficient whereas p.c.s. shows an increase. The results are discussed in terms of self and mutual diffusion processes.

Keywords Polystyrene; diffusion; nuclear magnetic resonance; photon correlation spectroscopy; semi-dilute solutions

INTRODUCTION

Several experimental techniques exist for measuring the diffusion process of polymers in solution. These include photon correlation spectroscopy[1] (p.c.s.), neutron scattering[2] (NS) and pulsed field gradient nuclear magnetic resonance[3] (n.m.r.). In comparing these various techniques it is essential to take into account the various scales of time and length involved. In scattering experiments (p.c.s. and NS) the spectral variable is $\mathbf{Q}$, the wave vector and for neutrons $1/\mathbf{Q} \sim$ chemical bond lengths whereas for p.c.s. $1/\mathbf{Q} \sim$ size of the whole molecule in solution. In particular for p.c.s., if $\mathbf{Q}R_G > 1$ (R_G radius of gyration) then both internal motion and translational diffusion can be measured whereas if $\mathbf{Q}R_G < 1$ then only translational diffusion is detected. In the latter case p.c.s. essentially measures the mutual diffusion coefficient (D_m).

In a dilute solution a virial expansion of the mutual diffusion coefficient (D_m) and the mutual friction coefficient f_m can be made[4]:

$$D_m(c) = \frac{kT}{f_m(c)}(1 - V_2c)(1 + 2A_2\bar{M}_nc + 3A_3\bar{M}_nc^2 + \ldots.) \quad (1)$$

A_2 is the second virial coefficient, V_2 is the partial specific volume of the polymer. $\bar{M}_n$ is the number average molecular weight. $f_m(c)$ can also be expanded as:

$$f_m(c) = f_0(1 + K_f^m c) \quad (2)$$

where the subscript '0' refers to infinite dilution.

By combining equations (1) and (2), and neglecting terms $0(c^2)$:

$$D_m(c) = D_0(1 + (2A_2\bar{M}_n - K_f^m - V_2)c) \quad (3)$$

where $D_0 = \frac{kT}{f_0}$

In a good solvent A_2 is positive and if $2A_2\bar{M}_n > K_f^m + V_2$ then $D_m(c)$ increases with increasing concentration, whereas in a poor solvent (A_2 negative) the opposite trend is expected.

The field gradient n.m.r. technique measures diffusion over a fixed timescale by correlation of the coordinates of a given nucleus at time t, with the coordinates of the same nucleus at $t + \Delta$, summed over all nuclei in the sample. By definition this is the self diffusion process. Δ is limited by T_2, the spin–spin relaxation time, and is typically ~ 0.1 s. For a value of D_s of 10^{-11} m^2 s^{-1} the diffusion path length is $\sim 10^{-6}$ m, which is more than two orders of magnitude greater than R_G for polystyrene (PS), $\bar{M}_w = 37\,000$. Under these conditions the translation self diffusion (D_s) of the whole coil is the only contribution to the n.m.r. diffusion coefficient and there is no contribution from internal motion as previously suggested[3]. However, for high molecular weight entangled polymers if $R_G{}^2 \sim D_s\Delta$ then contributions from internal motion must be considered[3]. For self diffusion:

$$D_s(c) = \frac{kT}{f_s(c)} = \frac{D_0}{(1 + K_f^s c)} \quad (4)$$

In dilute solution ($K_f^s c < 1$)

$$d_s(c) \approx D_0(1 - K_f^s c) \quad (5)$$

and in more concentrated solution ($K_f^s c > 1$)

$$D_s(c) \approx \frac{D_0}{K_f^s c} \quad (6)$$

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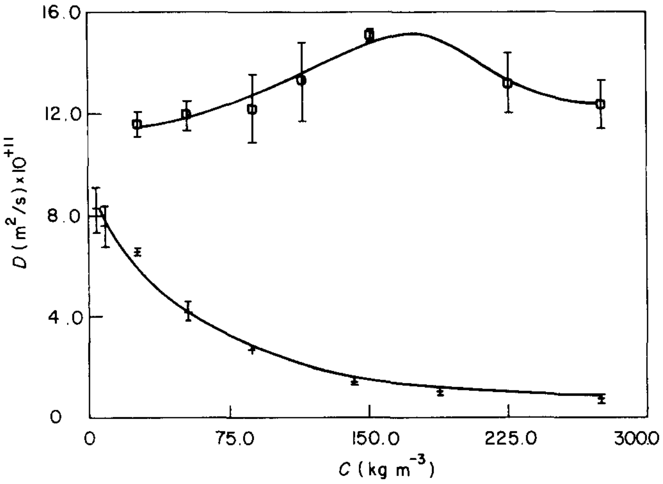

Figure 1 Self (+) and mutual (□) diffusion coefficients for polystyrene in toluene as a function of concentration

By extrapolation both p.c.s. and n.m.r. should give the same value for D_0 using equations (3) and (5).

In this paper diffusion coefficients have been obtained for PS(37 000) solutions in toluene (D_8) and cyclohexane (D_{12}) in the concentration range 0–30 wt% using the pulsed field gradient n.m.r. technique. P.c.s. results have also been obtained for the toluene solutions.

EXPERIMENTAL

Materials

The n.m.r. results were obtained on a home-made computer controlled[5] pulsed spectrometer operating at 60 MHz. Field gradient pulses were developed in a quadrupolar coil using a current controlled transistorized switch[6]. The Carr–Purcell–Meiboon–Gill modification[7] of the pulsed field gradient experiment was used exclusively. Typical values for the field pulse separation (Δ), width (δ) and the 180°$_y$ pulse separation (τ) were 0.12 s, 0.2–0.8 ms and 10 ms respectively. In experiments where Δ was also varied no evidence of restricted diffusion was evident. The field gradient (G) was calibrated using distilled water at 303 K[8], giving a value of 3.5 T m^{-1}. All spectra were recorded off resonance and analysed using the relation for the spin–echo attenuation (R).

$$\ln(R) = -\gamma^2 G^2 \delta^2 \Delta D_s$$

γ is the magneto-gyric ratio. The n.m.r. diffusion coefficients have been corrected for the differences in viscosity of the deuterated and protonated solvents.

The photon correlation spectrometer was supplied by Malvern Instruments and incorporated a multi-bit correlator and a PDP11 computer system. A Krypton ion laser with a mode stabilized etalon operating at 647.1 nm was supplied by Coherent Radiation. The values of D_m were calculated assuming a Lorenztian lineshape for the Doppler broadened laser line. Both the pure solvent and the solutions were filtered using a 0.05 μm Millipore filter.

The PS(37 000) was a narrow fraction ($\bar{M}_w/\bar{M}_n = 1.03$) obtained from Waters Associates. The deuterated solvents were supplied by C.E.A. (France).

RESULTS AND DISCUSSION

Good solvent

The n.m.r. and p.c.s. results for the polystyrene/toluene system are shown in *Figure 1*. In dilute solution D_m increases with increasing concentration going through a maximum at 150 kg m^{-3}, whereas D_s decreases monotonically as expected. At low concentrations D_m and D_s converge towards a common value. In order to extrapolate these values to zero concentration to obtain D_0 we require the functional dependence of $D_{m,s}$ on c. This is most easily achieved by calculating the respective frictional coefficients f_m and f_s which are linear in concentration[9] as c tends to 0 (equation 2). *Figure 2* shows the variation of f_m and f_s with c. f_m extrapolates linearly to give a value for $D_0 = 12.6 \pm 3.8 \times 10^{-11}$ m^2 s^{-1}. The behaviour of f_s is more complex, showing a change of slope at 40 kg m^{-3} which is close to c^* (45 kg m^{-3}) calculated assuming the effective volume of the polymer coil is $\frac{4}{3}\pi R_G^3$. The intercept at $c = 0$ gives a value of D_0 of $8.57 \pm 0.9 \times 10^{-11}$ m^2 s^{-1}. Within experimental error the two estimates of D_0 are the same. A comparative value for D_0 (from p.c.s. at 294 K) can be obtained from the results of Pusey *et al.*[10] of 9.0×10^{-11} m^2 s^{-1}, showing closer agreement with the n.m.r. result. Hence it would appear that n.m.r. measurements give the correct values for D_s at least at low concentration. This is in marked contrast to the results of Pinder *et al.*[11] for polystyrene ($\bar{M}_w = 110 000$) in carbon tetrachloride and in chloroform where the difference between D_m and D_s as $c \rightarrow 0$ is significant, although more recent results in toluene[12] are in agreement with the present work.

The differences between f_m and f_s (*Figure 2*) are outside experimental error indicating that f_m values cannot be used directly to obtain D_s. This is not surprising as f_m is the result of particle velocity cross-correlations whereas f_s is due only to particle velocity self correlations[17].

At higher concentrations equation 6 shows that D_s should scale as $c^{-1.0}$, assuming a linear variation of f_s with c. A double logarithmic plot of D_s vs. c is given in *Figure 3*. Above a concentration of ~40 kg m^{-3} we find that $D \sim c^{-0.96}$ in good agreement with this simple theory. Scaling theory[13], however, predicts that $D \sim c^{-1.75}$ for polymers of high molecular weight. Clearly the discrepancy here is due to the low molecular weight of this

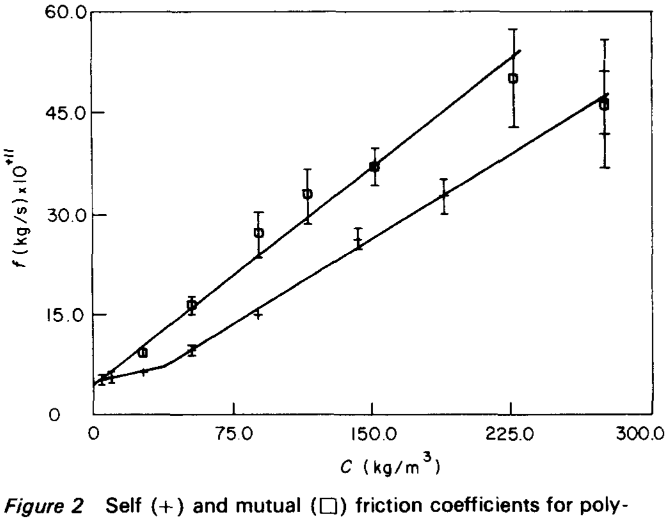

Figure 2 Self (+) and mutual (□) friction coefficients for polystyrene in toluene as a function of concentration

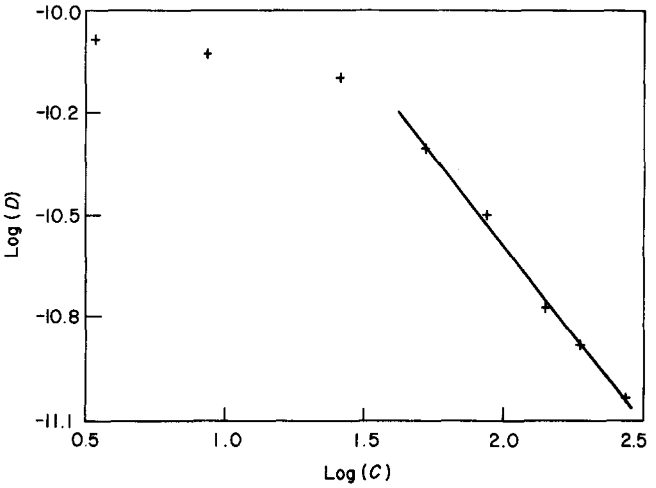

Figure 3 Double logarithmic plot of the self diffusion coefficients for polystyrene in toluene as a function of concentration

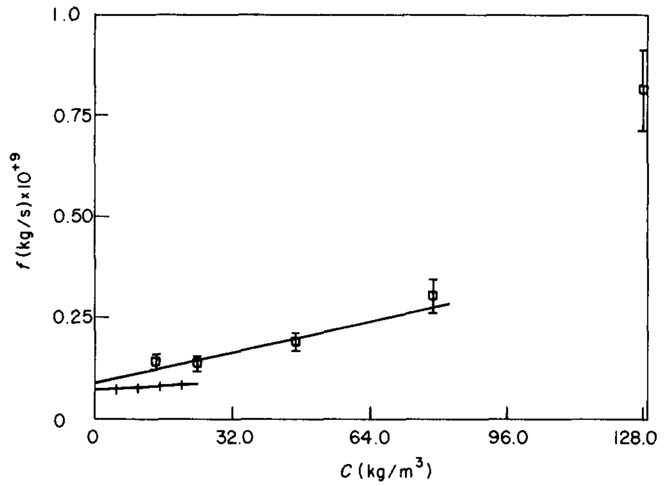

Figure 5 Self (□) and mutual (+) friction coefficients for polystyrene in cyclohexane as a function of concentration

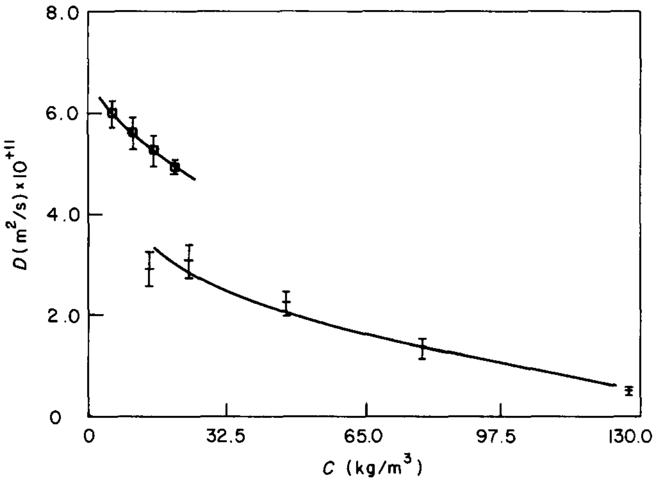

Figure 4 Self (+) and mutual (□) diffusion coefficients for polystyrene in cyclohexane as a function of concentration

sample. This is also evident in the static scaling[14] of R_G with $\bar{M}_w$ where an exponent of 0.52 is observed for polymers with $\bar{M}_w \sim 37\,000$ instead of the Flory value of 0.6.

Poor solvent

D_s and D_m values for PS(37 000) in cyclohexane are shown in *Figure 4*. The p.c.s. results have been taken from the paper by Pritchard and Caroline[15]. In a poor solvent both D_m and D_s decrease with increasing concentration as predicted (equations 3 and 5). *Figure 5* compares the variation of f_m and f_s. Although the values of f_m are rather inaccurate, f_m and f_s extrapolate to give values for D_0 of $6.4 \pm 0.02 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ and $4.3 \pm 2.0 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$, respectively.

The values for D_s for the poor solvent system are smaller than those for the good solvent reflecting the increased friction coefficient. The Kirkwood Riseman[16] theory gives the following expression for f_0

$$f_0 = \mathrm{P}\eta_0\langle R_G{}^2\rangle^{\frac{1}{2}}$$

where P is a constant, η_0 is the solvent viscosity. The major difference between these two systems is the solvent viscosity $\eta_0(\text{toluene}) < \eta_0(\text{cyclohexane})$ consistent with the observed values of D_0.

CONCLUSION

Self and mutual diffusion coefficients have been obtained for PS (37 000) in toluene, in the dilute and semi-dilute region, and have been shown to be consistent with modern theroies of polymer diffusion. The self diffusion of a polymer PS(37 000) in a poor solvent (cyclohexane) was investigated for the first time. The dependence of D_s on concentration was similar for both good and poor solvent systems, in contrast to D_m. The absolute values of the self diffusion coefficient in the poor solvent were smaller, indicating a greater frictional resistance to motion.

ACKNOWLEDGEMENT

S.E.R.C. is acknowledged for providing a research studentship (JMS) and for providing funds for the n.m.r. and p.c.s. equipment.

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