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Diffusion in bimodal and polydisperse polymer systems: 1. Bimodal solutions of protonated and deuterated polymers

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In the first of two papers studying diffusion in bimodal and polydisperse polymer solutions, the self-diffusion coefficients of various protonated polymers in a series of bimodal solutions containing deuterated polymers have been measured. Utilizing the chemical specificity of the pulsed-field gradient nuclear magnetic resonance (p.f.g.n.m.r.) technique, it was possible to study the effects of both molecular weight and concentration of each component. A simple friction dependence was shown to account for the observed trends. The p.f.g.n.m.r. results are contrasted with mutual diffusion coefficient measurements, obtained from multi-tau photon correlation spectroscopy on similar bimodal systems.

(Keywords: diffusion; bimodal polymer solution; pulsed-field gradient n.m.r.)

INTRODUCTION

The diffusion of Brownian spheres in dilute and semi-dilute polymer solutions has been used to test the fundamental laws of polymer diffusion; diffusion of silica particles or polystyrene latices in water[1], aqueous solvent mixtures[2] and small molecules (glycerol) agreed well with the Stokes–Einstein equation after substituting the correct macroscopic viscosity. Cukier[3] developed a theory that relates the diffusion coefficient D of dilute Brownian spheres (radius R) in semi-dilute polymer solutions to the diffusion coefficient D_0 in pure solvent. The friction was represented by an equation of the form:

$$f = f_0(1 + \kappa R) \qquad (1)$$

Here κ is the screening constant, $\kappa = (\zeta_0 n_a/\eta)^{0.5}$, where n_a is the number concentration of Brownian spheres, ζ_0 is the monomeric friction coefficient, η is the viscosity of the continuous medium and f_0 is the friction at infinite dilution. Consequently, the reduced diffusion coefficient, $D/D_0 \propto R^{-1}$ and $n_a^{-0.5}$. For the region where κR is small, κR may be reduced to an effective concentration. Consequently, D/D_0 is ultimately represented by a power series in concentration. Results in agreement with this theory were found for the diffusion of carboxylate-modified polystyrene latex spheres in poly(acrylic acid)–water gels[4] and poly(L-lysine) solutions[5].

For polymeric systems at higher concentrations where coil overlap is present, a departure from this behaviour is observed. Reina *et al.*[6], in their study on particle diffusion in polyacrylamide solutions and gels, found a transition from purely Stokes–Einstein translational motion to diffusion associated with the complex cooperative relaxation of the gel network. The transition occurred close to the overlap concentration c^* of the gel.

Brown and Pu[7], studying probe polymer and probe particle diffusion in polyisobutylene solutions, found similar behaviour. In particular, two regions were observed. First, when the molecular weight of the probe polymer is greater than that of the secondary polymer (often called the *matrix* polymer), the diffusion over a wide concentration regime encompassing c^* was identical to an analogous system comprised of equivalently sized silica spheres, i.e. the presence of the matrix component merely affected the viscosity. Similarly, the diffusion of probe polystyrene coils in poly(methyl methacrylate) solutions was also shown to follow the Stokes–Einstein mechanism. In both cases, the diffusion of the probe could be modelled as a hard sphere. Secondly, when the matrix molecular weight is greater than the molecular weight of the probe and the radius of gyration of the probe is greater than the correlation length of the matrix, the probe diffusion was independent of the matrix concentration but strongly dependent on the molecular weight of the matrix, i.e. the complex gel motions dominated the probe motion.

In dilute solutions, therefore, a wide variety of data suggest that diffusion of probe moieties—polymer coils and particles—can be represented by the Stokes–Einstein equation subject to the correct macroscopic viscosity. At higher concentrations, coil overlap introduces a cooperative nature to the diffusion. Along similar lines, simple model polymer systems comprising deuterated and protonated monodisperse polystyrene fractions have been studied. The self-diffusion coefficient of the protonated polymer has been studied as a function of concentration and molecular weight of both

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*To whom correspondence should be addressed at: Department of Chemistry, University of Wales College of Cardiff, PO Box 912, Cardiff CF1 3TB, UK components. The trends observed in this study have been extended to mixtures of two monodisperse protonated polymers and, ultimately, polydisperse polymers.

THEORETICAL ANALYSIS

A simple representation of the mobility of an isolated polymer molecule may be obtained by treating it as an effective sphere by assuming that the solvent inside the polymer molecule is unperturbed during diffusion[8]. Thus, from Stokes' law:

$$D_S \propto \mu^{+1} \propto (R_h)^{-1} \tag{2}$$

where μ is the mobility and R_h is the hydrodynamic radius. The radius of gyration R_g is simply related to the hydrodynamic radius by a molecular-weight-independent constant[9], thereby giving the simple relationship:

$$D_S \propto M^{-\alpha} \tag{3}$$

where $\alpha = 0.5$ for a theta solvent and $\alpha = 0.6$ for a good solvent. These exponents are frequently observed: for polystyrene in benzene[10,11], $D_S \propto M^{-0.55}$; for polystyrene in toluene[12], $D_S \propto M^{-0.57}$; and $D_S \propto M^{-0.58}$ for polystyrene in carbon tetrachloride[13].

In the limit of the dilute regime, the self-diffusion coefficient is sensitive to the unperturbed hydrodynamic radius of the isolated chain[14]. At finite concentrations but still in the dilute region, the interactions between polymer molecules raise the friction experienced by the polymer above the solvent-dominated limit. The friction term is generally expressed as a power series in concentration[15]:

$$f(c) = f_0(1 + k_f c + k_f' c^2) \tag{4}$$

where the friction in the limit of infinite dilution, $f_0 = 6\pi\eta R_h$, and k_f and k_f' are molecular-weight-dependent coefficients. Consequently, the diffusion coefficient may be represented as:

$$D_S = D_0/(1 + k_f c + k_f' c^2) \tag{5}$$

where D_0 is the self-diffusion coefficient at infinite dilution. In dilute solutions, this is often approximated to:

$$D_S = D_0(1 - k_f c) \tag{6}$$

The linearity of the concentration behaviour has been observed in a variety of systems. Specifically for polystyrene, Callaghan and Pinder[16] and Sutherland[17] found linear behaviour up to concentrations close to the critical overlap concentration c^*. The Sutherland data, although discussed in terms of a linear concentration behaviour, are more accurately represented by a power series and, consequently, a second-order power series has therefore been adopted in this analysis.

The friction–concentration behaviour has been modelled by Pyun and Fixman[18] and by Yamakawa[19]. These models, based on the Kirkwood–Riseman approach, take into account both intermolecular and intramolecular hydrodynamic interactions by calculating the perturbation of the solvent velocity generated in the vicinity of one molecule caused by the presence of another molecule. 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 by pulsed-field gradient nuclear magnetic resonance (p.f.g.n.m.r.) experiments for a variety of polystyrene solutions: for example, $k_f \propto M^{+0.5}$ for polystyrene in cyclohexane[20–23]; and $k_f \propto M^{+0.8}$ for polystyrene in tetrahydrofuran[22,23]. In this paper we discuss how these theories have been utilized in the interpretation of the diffusion in polydisperse and bimodal polymer solutions.

The experimental study of polydispersity effects on the dynamics of polymer systems has only been considered qualitatively. The interpretation of p.f.g.n.m.r. diffusion results from polymers with $M_w/M_n < 1.3$ pose little problem[24]. For polydispersities greater than this, considerable departure from monodisperse behaviour is observed. Bernard and Noolandi[25,26] showed that, if a physical quantity $Q(M)$ is governed by a scaling law of the form $Q(M) \propto M^{\beta}$, then the averaged value $\langle Q(M) \rangle$ should scale with some calibrated standard molecular weight M_0 according to:

$$\langle Q(M) \rangle = g(P, \beta) M_0^{\beta} \tag{7}$$

where $g(P, \beta)$ is a numerical prefactor dependent on the polydispersity. Callaghan and Pinder[16] stated that, for a p.f.g.n.m.r. experiment, the measured signal A_δ (normalized by the intensity A_0 when $G = 0$) is the result from the summation of the net spin echoes generated by each active nucleus present:

$$\frac{A_\delta}{A_0} = \frac{\sum_i M_i \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D_S(M_i)] n_i}{\sum_i M_i n_i} \tag{8}$$

The difficulty with this approach is to deconvolute the resultant sum of exponentials, and in practice distribution functions were fitted to the data. A far more elegant method has been proposed by Morris and Johnson[27] based on a two-dimensional experiment. The second dimension is introduced via a Laplace transform of the attenuation function and the resultant 2D spectrum consists of the normal spectrum correlated with the diffusion coefficient distribution. This approach is not problem free however.

In order to obviate these problems, the present approach was adopted. By studying the diffusion of a narrow-fraction protonated polymer in a solution containing a deuterated polymer, the observed proton n.m.r. behaviour is still that of a monodisperse polymer, the deuterated polymer being invisible. The effect of polydispersity on the diffusion of the 'probe' or 'labelled' polymer (in this case the *protonated* polymer) has been systematically studied in a range of bimodal solutions by varying the molecular weight and concentration of the *deuterated* polymer[28].

EXPERIMENTAL

Sample description

The polystyrene samples were obtained from Polymer Labs (Shropshire, UK) and have polydispersities $M_w/M_n \leq 1.08$. Carbon tetrachloride (analytical grade) was obtained from BDH and used with no further purification. All samples were prepared in clean, weighed 5 mm n.m.r. tubes—the required amount of solvent was added to dry polymer. The measurements were performed after three days to allow for full dissolution and equilibration.

For all the p.f.g.n.m.r. experiments discussed, the samples were prepared with equal *masses* of protonated and deuterated polymer and their quoted polymer concentration is the *total* polymer concentration; e.g. a 5% w/w solution would contain 2.5 g of protonated polymer, 2.5 g of deuterated polymer and 95 g of solvent. The systems have the general nomenclature where M_w^{prot} 28 000 corresponds to a protonated polymer of molecular weight 28 000 and M_w^{deut} 10 500 to a deuterated polymer of molecular weight 10 500. A consequence of this fact is that, for the higher-molecular-weight species, although at the same *weight concentration* w_p as the lower-molecular-weight species, the *number concentration* n_p is less, i.e. $n_p = w_p/M_w$.

For the photon correlation spectroscopy (p.c.s.) studies, only protonated polymers were used and the requirement of fixed weight concentration was relaxed. The concentrations of each system will be given in the figure legends.

P.f.g.n.m.r. studies

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[29]. The spectrometer has been upgraded by the addition of a Surrey Medical Imaging Systems console, which replaces both the r.f. and computational parts. The current amplifier used to generate the field gradients was based on the design by Stilbs[30]. The unit was calibrated with a sample of known diffusivity (water) giving field gradients G between 0.015 and 0.080 T m^{-1}. The data were all 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 field stability. The data in the form of spin echoes were integrated after Fourier transformation and could be fitted to equation (9), which assumes isotropic Brownian diffusion:

$$A_\delta = A_0 \exp(-2\Delta/T_2) \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D_S] \quad (9)$$

where γ is the magnetogyric ratio and T_2 is the spin–spin relaxation time. Any background gradients are assumed to be negligible since an attenuation plot for water showed no deviation from linearity over two decades of signal intensity.

Multi-tau p.c.s. studies

The light scattering experiments were performed on a Malvern 4700 variable-angle multi-tau spectrometer interfaced to a K7032 computing correlator. The light source was an argon-ion laser operating at 488 nm (5 W) in a vertically polarized mode. The 256-channel correlator was run in its fully expanded arrangement of 32 channels each operating at eight ratiometrically spaced sample times, i.e. the multi-tau arrangement. Analysis of the single-component scattering functions used the method of cumulants; the initial slope gives the z-average of the distribution and the degree of curvature gives the polydispersity. For the bimodal samples, the fitting of a model distribution is not necessarily going to give accurate information about the sample. For dealing with such cases, the instrument contains an analysis fitting algorithm which tries to fit an essentially model-free distribution to the data. This is done by finding the best combination of a number of stored correlation functions that best fits the data. Constraints are imposed so that the calculated distribution is realistic. This function is further deconvoluted by attempting to account for the fact that different-sized components scatter different amounts of light. This latter point will be discussed in the following section.

RESULTS AND DISCUSSION

The inclusion of a second polymer into a polymer solution may affect the solution properties in a number of ways. Apart from a frictional interaction, a thermodynamic interaction may arise due to (a) the compatibility between the two polymers or (b) the respective solvent quality for each polymer. Utilizing the chemical specificity of the p.f.g.n.m.r. technique, the diffusion of protonated polymers in bimodal solutions containing deuterated polymers provides a non-invasive 'handle' with which to investigate the dynamics of the system, without seriously complicating the experimental measurement. This approach is very different to the 'probe' studies commonly employed to measure dynamics, since it is tacitly assumed in those studies that inclusion of the probe does not perturb the system. Similarly, the effect of mutual compatibility may be minimized by studying isotopic mixtures where differences in, for example, the Flory–Huggins parameter is less than 10^{-3}.

The approach adopted in the discussion below is to consider the friction opposing the motion of a given protonated polymer.

The effect of concentration

The variation of the diffusion coefficient of three protonated polymers in a range of protonated–deuterated polystyrene solutions is shown in *Figures 1, 2* and *3*. The diffusion coefficient of the protonated polymer decreases with increasing concentration and molecular weight of deuterated polymer for all the systems. In a single-component solution of a narrow-fraction molecular-weight polymer, the friction opposing the diffusion is

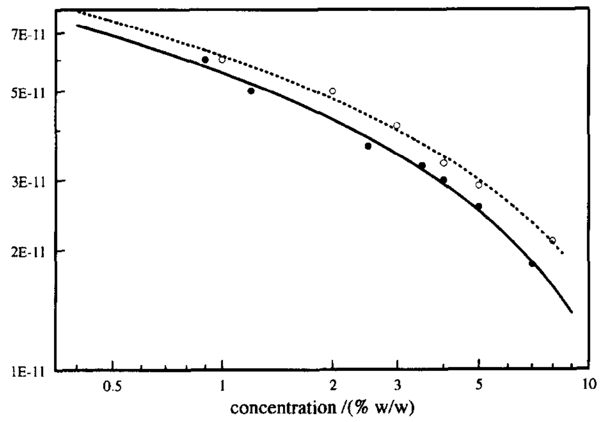

Figure 1 Self-diffusion coefficient of protonated PS M_w 28 000 as a function of total concentration (% w/w) in a single-component solution (——) and in a 50:50 by weight bimodal solution containing deuterated PS M_w 10 000 (· · · ·). The curves represent the fits from equation (3) yielding the parameters given in *Table 1*

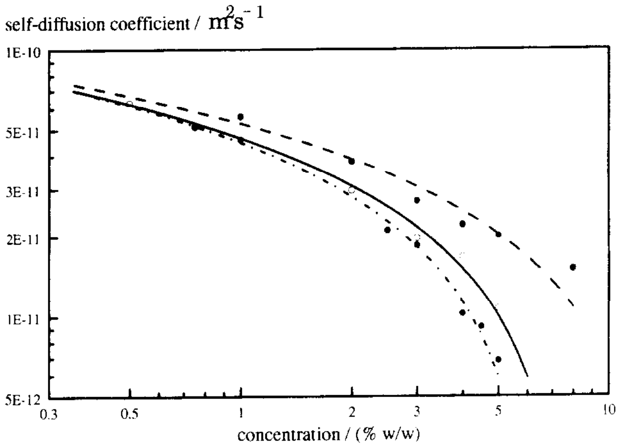

Figure 2 Self-diffusion coefficient of protonated PS M_w 66000 as a function of total concentration (% w/w) in a single-component solution (——) and in 50:50 by weight bimodal solutions containing deuterated PS M_w 200000 (– · – · –) or deuterated PS M_w 10000 (– – –). The curves represent the fits from equation (3) yielding the parameters given in *Table 1*

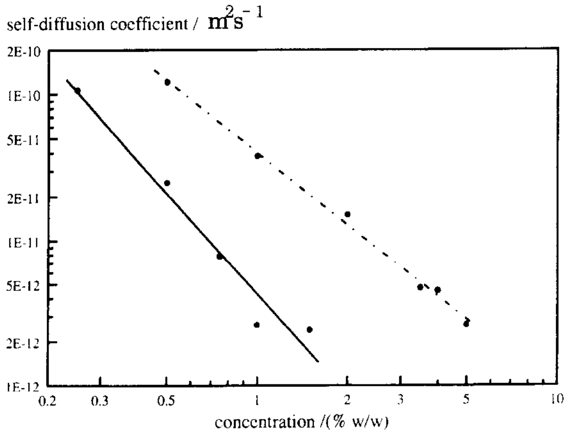

Figure 3 Self-diffusion coefficient of protonated PS M_w 1030000 as a function of total concentration (% w/w) in a single-component solution (——) and in 50:50 by weight bimodal solution containing deuterated PS M_w 200000 (– · – · –). The curves represent the fits from equation (3) yielding the parameters given in *Table 1*

due to interactions with other polymer molecules and the solvent. In the case of a bimodal solution, the friction from polymer–polymer interactions will also arise through collisions between different molecular-weight polymers. The change in the concentration–friction coefficients k_f will therefore be related, in some manner, to the two molecular weights.

Analysing the bimodal solutions in terms of the power series yielded the values shown in *Table 1* and the curves shown in the figures. The corresponding single-component solution values are shown for comparison.

At infinite dilution (of both species), the polymer molecules are well separated and thus are expected to behave independently. The good agreement between the infinite-dilution values f_0 of the bimodal system obtained from the protonated polymer diffusion and the corresponding single-component system represent independent behaviour, i.e. the diffusion of the protonated polymers, in the dilute limit, is unperturbed by the presence of the deuterated polymer.

Table 1 Parameters characterizing the power-series fits to the bimodal self-diffusion data

System	f_0 ($\times 10^{11}$ kg s^{-1})	k_f (m^3 kg^{-1})	k_f' (m^6 kg^{-2})
M_w^{prot} 28000	4.00	0.03	0.00
M_w^{prot} 66000	5.60	0.05	0.00
M_w^{prot} 1030000	23.6	2.50	0.60
M_w^{prot} 28000–M_w^{deut} 10500	3.60	0.02	0.00
M_w^{prot} 66000–M_w^{deut} 10500	5.20	0.03	0.00
M_w^{prot} 66000–M_w^{deut} 203000	5.60	0.08	0.05
M_w^{prot} 1030000–M_w^{deut} 203000	21.2	0.37	0.14

The infinite-dilution friction f_0 obtained from the single-component solutions through this analysis scales as $f_0 \propto M^{0.57(\pm 0.02)}$, in excellent agreement with the Kirkwood–Riseman approximation[31] and other experimental data[32]. Single-tau photon correlation spectroscopy studies have been performed on the same solutions and the mutual friction at infinite dilution, analysed in an identical manner, follows a similar dependence: $f_0 \propto M^{0.53(\pm 0.07)}$.

In a bimodal solution, the friction term will be dependent to some extent on both the size and number of each component present. Representative of this feature are the relative magnitudes of the k_f and k_f' terms describing the molecular-weight-dependent friction behaviour of the protonated polymer. Increasing the molecular weight of the polymer in a single-component solution increases the concentration sensitivity of the diffusion, i.e. k_f increases. The k_f value is, for example, 50 times greater for the 1030000 molecular-weight polymer than it is for the 66000 one—given only a factor of 15 in molecular weight. Identical behaviour is observed in the bimodal systems. Not only do the k_f terms increase with molecular weight of each component, but the change in the k_f term increases with a greater difference in the two molecular weights of the two components. As may be seen in *Figures 1*, *2* and *3*, this approach accurately represents the concentration dependence of a protonated polymer in a solution containing deuterated polymers and will be applied in the second paper to polydisperse samples[28].

The single-component behaviour of the k_f term from these data has been published elsewhere[13] and the low-molecular-weight behaviour shows the trend expected for a moderately good solvent: $k_f \propto M^{+0.7(\pm 0.03)}$. However, above $M_w = 300000$, this simple power law breaks down, the friction being much more sensitive to concentration. The failure of the dilute-solution theories has been attributed to the onset of polymer coil overlap, i.e. semi-dilute behaviour. Consequently, the self-diffusion coefficient vs. concentration behaviour of the M_w 1030000 solution has been shown to follow an entangled scaling law, and it is therefore possible that analysis in terms of a concentration power law such as equations (4), (5) or (6) is invalid for the high-molecular-weight systems. This may explain the ostensibly different concentration behaviour of the higher-molecular-weight solutions; *Figure 3* is linear whereas *Figures 1* and *2* are not, although this may be due, in part, to the range over which the power series operates. Moreover, the fits to the data are very good. The higher term, $k_f' c^2$, is a significant factor in the higher-molecular-weight system and is taken to represent the greater polymer–polymer interactions present in entangled solutions.

Semi-dilute entangled scaling behaviour predicts[33] $D_S \propto c^{(\nu-2)/(3\nu-1)}$ and the concentration behaviour of the (M_w^{prot} 1030 000–M_w^{deut} 203 000) system, $D_S \propto c_{total}^{-2.5}$, is again evidence of an entangled semi-dilute solution, giving $\nu = 0.53$. The single-component data exhibit $D_S \propto c^{-2.25}$ and give $\nu = 0.55$. This subtle solvency effect is discussed in greater detail later. Interestingly, the values of the self-diffusion coefficient when extrapolated to infinite dilution show good agreement with the dilute-solution values, stressing the underlying complexity of the transition from dilute to semi-dilute entangled behaviour.

Very-dilute-solution behaviour studied by multi-tau p.c.s.

Complementary to the observed infinite-dilution behaviour extracted from the p.f.g.n.m.r. diffusion data are the diffusion coefficient distributions shown in *Figures 4*, *5* and *6* obtained from photon correlation spectroscopy. These curves represent a measure of the molecular-weight distribution. Since p.c.s. offers little chemical specificity, fully protonated bimodal systems were studied. *Figure 4* shows the diffusion coefficient distribution for two systems, the single-component solution M_w 1030 000 at 0.25% w/w concentration and the bimodal solution (M_w^{prot} 1030 000–M_w^{prot} 153 000) at 0.5% w/w total polymer concentration, i.e. 0.25% w/w concentration of each component. As is evident, the distribution function is identical in both cases. From this, two important points may be drawn. First, at these low concentrations, inclusion of the M_w 153 000 polymer has not perturbed the diffusion of the M_w 1030 000 polymer—in agreement with the deductions from the constant f_0 terms obtained from the concentration dependence of the self-diffusion coefficient in the bimodal solutions. Secondly, the technique is very sensitive to the size of the scatterers. The normalized intensity of scattered laser light at an angle θ, wavelength λ, a distance r from the scatterer follows[34]:

$$\frac{I_\theta}{I_0} \propto \frac{8\pi^4}{r^2}\frac{R^6}{\lambda^4} \qquad (10)$$

Thus, if there are two types of polymer molecules present whose molecular weights differ by a factor of 10, and assuming $R \propto M_w^{0.5}$, then $I_a/I_b \approx 1000$; hence, the M_w 153 000 component was not detected. This factor represents a serious limitation to the applications of the technique in bimodal and very polydisperse solutions. Similar conclusions have been drawn from other studies[35–43].

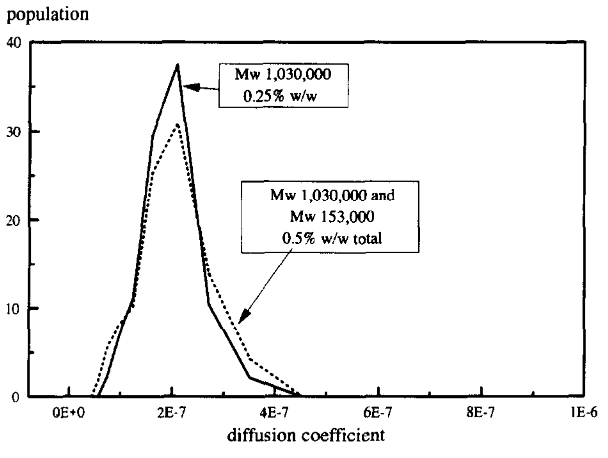

Figure 4 Diffusion coefficient distributions measured by multi-tau photon correlation spectroscopy: bimodal solution of PS M_w 1030 000–PS M_w 153 000 (· · · ·) at a total polymer concentration of 0.5% w/w. Also shown for comparison is the PS M_w 1030 000 single-component solution (——)

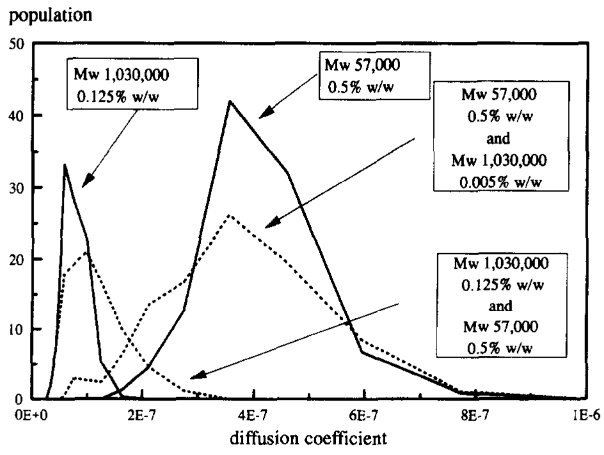

Figure 5 Diffusion coefficient distributions measured by multi-tau photon correlation spectroscopy: (i) bimodal solution of PS M_w 1030 000–PS M_w 57 000 at polymer concentrations of 0.125% w/w and 0.5% w/w respectively (· · · ·); (ii) bimodal solution of PS M_w 1030 000–PS M_w 57 000 at polymer concentrations of 0.005% w/w and 0.5% w/w respectively (· · · ·). Also shown for comparison are the single-component solutions, PS M_w 57 000 (0.5% w/w) (——) and PS M_w 1030 000 (0.125% w/w) (——)

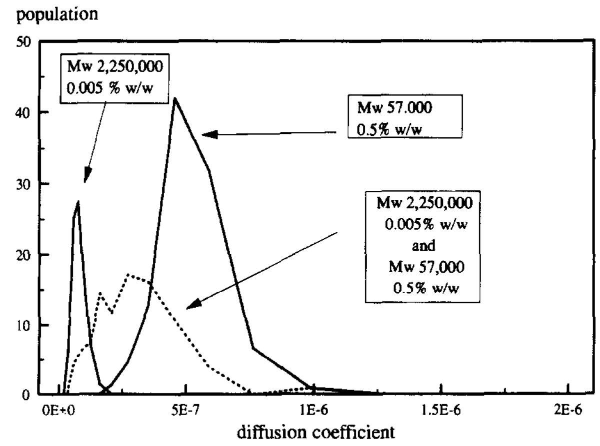

Figure 6 Diffusion coefficient distributions measured by multi-tau photon correlation spectroscopy: bimodal solution consisting of PS M_w 2250 000–PS M_w 57 000 at polymer concentrations of 0.005% w/w and 0.5% w/w respectively (· · · ·). Also shown for comparison are the single-component solutions for PS M_w 2250 000 (——) at 0.005% w/w concentration and PS M_w 57 000 (——) at 0.5% w/w concentration

By diluting the stronger scattering species, it may be possible to balance the scattering intensities. Although this will inherently modify the systems such that direct comparisons to the n.m.r. data are no longer valid, such an approach was indeed taken for the data shown in *Figure 5*. The full lines represent the two pure components (M_w 57 000 at 0.5% w/w and M_w 1030 000 at 0.125% w/w). Combinations of these two solutions, i.e. a number concentration ratio of 80, gives no strong indication of the scattering from the smaller species. At the other extreme, the mixture M_w 57 000 at 0.5% w/w and M_w 1030 000 at 0.005% w/w, i.e. a number concentration ratio of 2000, gave no strong indication of the high-molecular-weight species. This is broadly in agreement with the rough calculation following equation (10). Significantly though, the dominant scattering from the bimodal distribution closely follows the corresponding single-component species, suggesting, as in the previous figure, that no significant perturbation of the diffusion of each species occurs, even in the presence of a greater concentration of smaller molecules. The best attempt to balance the scattering intensities is displayed in *Figure 6*. The bimodal distribution function is, in this case, an average of the two single-component functions. However, since the dynamics are unperturbed in the previous bimodal systems shown in *Figures 4* and *5*, the averaging represents the problem of mathematically deconvoluting the complex correlation function. Finsey[42], for these sorts of reasons, reviewed the various methods for interpreting multimodal and polydisperse correlation functions. The only significant agreement between these PES, REPES, CONTIN, maximum-entropy and multi-tau analyses was whether or not the sample was unimodal.

The effect of molecular weight

The dependence of the self-diffusion coefficient of the protonated component (measured by p.f.g.n.m.r.) as a function of deuterated molecular weight at a low total polymer concentration, 0.5% w/w, is shown in *Figure 7*. Two regions are apparent. In the upper region, where the deuterated molecular weight is greater than the protonated molecular weight, the diffusion of the protonated polymer decreases with increasing molecular weight of the deuterated polymer. During diffusion, the protonated polymer must displace a polymer of greater size and this will inherently provide a greater friction to its motion; thus the diffusion coefficient will be less than in a single-component solution of equivalent concentration. By analogy, the single-component solution may be regarded as a bimodal solution consisting of two equal halves. Accordingly, these data should overlay the bimodal data and the low-molecular-weight data are therefore also included in *Figure 7* (starred). Neglecting all but those terms linear in concentration, the total friction f_{total} for a two-component mixture can be given by:

$$f_{\text{total}} = f_0^{\text{prot}} + f_0^{\text{deut}} + c(f_0^{\text{prot}} k_f^{\text{prot}} + f_0^{\text{deut}} k_f^{\text{deut}}) \quad (11)$$

where f_0 is the friction at infinite dilution and k_f is the friction coefficient, and the superscripts prot and deut refer to the protonated and deuterated components. For a given protonated (*probe*) polymer, since k_f increases with molecular weight, f_{total} *must* increase concomitantly, and hence the diffusion coefficient of the protonated polymer *must* decrease. This effect applies to both the protonated and deuterated polymers such that increasing the molecular weight of either component should result in a reduction in the protonated polymer diffusion coefficient. This effect will be more pronounced at higher concentrations and is evident in *Figure 8* where a much wider range of samples have been examined. However, inspection of the lower part of *Figure 7* shows that, for the high-molecular-weight protonated polymers in 0.5% w/w total concentration solution, the diffusion coefficient of the protonated polymer is largely independent of the deuterated molecular weight. Ostensibly, this result cannot be reconciled from a purely friction argument.

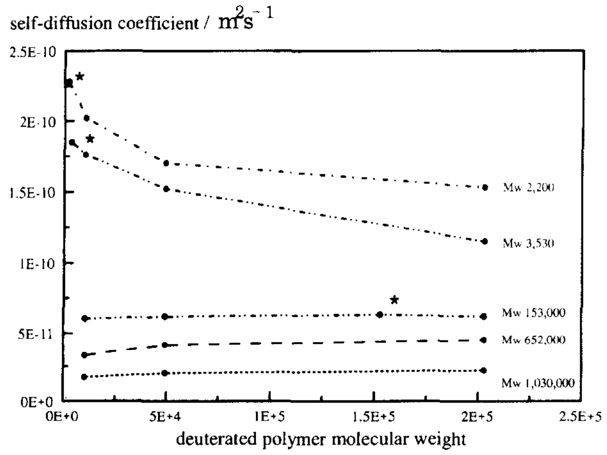

Figure 7 Self-diffusion coefficient of protonated polymers as a function of deuterated polymer molecular weight in bimodal solutions of 0.5% w/w total polymer concentration. Protonated polymer molecular weights are shown next to the curves. Selected-single component data are included for comparison (*)

The key to this apparent inconsistency lies in the complex balance of the terms in equation (11). It must be remembered that, for a good solvent, $k_f \propto M_w^{0.8}$ and $f_0 \propto M_w^{0.6}$, whereas for a theta solvent, $k_f \propto M_w^{0.5}$ and $f_0 \propto M_w^{0.5}$; so f_{total} *should* increase with increasing k_f^{deut} and f_0^{deut}, i.e. increasing deuterated polymer molecular weight. In an earlier paper[13], the behaviour of the k_f term for single-component polystyrene in tetrachloromethane was studied. The self-diffusion coefficient and, hence, $f(c)$ (equation (4)) was studied as a function of concentration for a series of molecular weights. Fitting the concentration dependence described by equation (4)

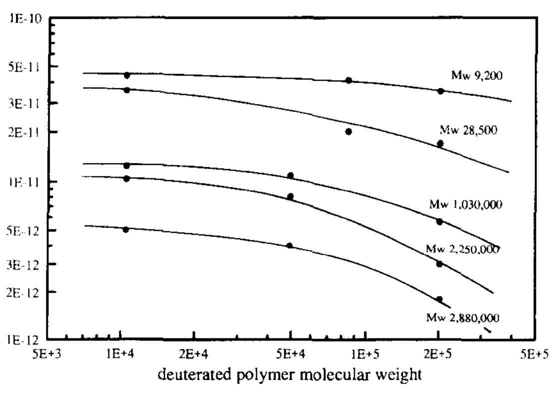

Figure 8 Self-diffusion coefficient of protonated polymers as a function of deuterated polymer molecular weight in bimodal solutions of 5.0% w/w total polymer concentration. Protonated polymer molecular weights are shown next to the curves

allowed the molecular-weight dependence of the k_f term to be extracted. Up to M_w 300 000, this behaviour closely followed the theoretical prediction, $k_f \propto M_w^{0.7(\pm 0.03)}$. Above M_w 300 000, the behaviour of the k_f term becomes much more molecular-weight sensitive. The interpretation attached to this observation is that, for the majority of the concentration region studied, the concentrations were such that c^* had been exceeded, i.e. there was considerable coil–coil interaction. The lower-concentration systems, however, need not necessarily be above c^* though.

Comparison with *Figure 7* shows that those protonated polymers where k_f is following the stronger molecular-weight dependence fall into the lower portion while those protonated polymers that follow the weaker molecular-weight dependence fall into the upper portion. A closer inspection of equation (11) with this in mind is now more informative. For the smaller protonated polymers (those following the weaker k_f vs. molecular weight dependence), the deuterated polymer is comparable to, or bigger than, the protonated one and thus $f_0^{\text{deut}} > f_0^{\text{prot}}$ and $k_f^{\text{deut}} > k_f^{\text{prot}}$. The total friction is sensitive to *all* the terms and hence the total friction increases with increasing deuterated molecular weight and the protonated polymer diffusion coefficient decreases. For those protonated polymers with molecular weight greater than the deuterated polymer molecular weight, where k_f is following the greater molecular-weight dependence, $f_0^{\text{prot}} > f_0^{\text{deut}}$ but $k_f^{\text{prot}} \gg k_f^{\text{deut}}$. For the lower concentration of *Figure 7*, the total friction is dominated by f_0^{prot} and k_f^{prot}—both of which are constant for a given protonated polymer. Hence, the total friction and the (protonated polymer) diffusion coefficient are much less sensitive to the deuterated polymer molecular weight. At the higher concentration of *Figure 8*, the concentration term is now an order of magnitude greater and, since f_0^{prot} is concentration independent, the deuterated polymer now has an effect. However, there would appear to be a slight increase in the diffusion coefficient with increasing deuterated polymer molecular weight in the lower part of *Figure 7* which is outside experimental error. The reason for this is unclear and is the subject of current study.

To investigate this behaviour further, one set of samples, those containing the M_w 1030 000 protonated polymer, were repeated in a theta solvent, d_{12}-cyclohexane at 40.0°C. These data are shown in *Figure 9*. Under theta conditions, the coils are collapsed. This may be illustrated by the single-component behaviour where $D_S^{\text{good}} < D_S^{\text{theta}}$, since $R_g^{\text{good}} > R_g^{\text{theta}}$. Similarly, the effects of coil–coil overlap will still occur but at higher concentrations (for a given molecular weight), i.e. the transition in the k_f behaviour to the greater molecular-weight dependence occurs at a higher molecular weight. Consequently, for the theta solvent data, the behaviour of the terms in equation (11) is akin to the upper region of *Figure 7*: $f_0^{\text{prot}} > f_0^{\text{deut}}$ and $k_f^{\text{prot}} > k_f^{\text{duet}}$. However, k_f^{prot} is not substantially greater than k_f^{deut}, so all the terms contribute to the total friction. Since $k_f \propto M_w^{0.5}$ in the theta solvent, the k_f contributions to equation (11) are smaller than in the good solvent. Not only are the contributions smaller, but the relative magnitudes are also smaller, i.e. $k_f^{\text{prot}}/k_f^{\text{deut}}$ is considerably smaller in the theta solvent compared to the good solvent. This has the added effect of effectively reducing the protonated polymer molecular weight, bringing it more into line with the upper region of *Figure 7*.

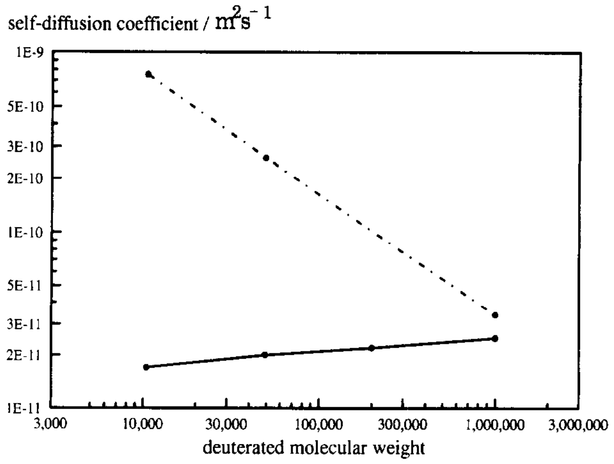

Figure 9 Self-diffusion coefficient of protonated polymer M_w 1030 000 as a function of deuterated polymer molecular weight in a good solvent, CCl_4 at 17°C (——), and a theta solvent, d_{12}-cyclohexane at 40°C (–·–·–)

CONCLUSIONS

The diffusion of protonated polymers in protonated–deuterated bimodal solutions has been shown to follow similar behaviour as for the single-component solutions. The infinite-dilution friction coefficients in the blends agree very closely with the infinite-dilution behaviour in the single-component solutions. On increasing dilution therefore, the polymers diffuse more independently. The limiting behaviour is that of an isolated coil. The concentration behaviour of the diffusion coefficient is analysed in terms of a power series that successfully accounts for the single-component solution. The molecular-weight behaviour of the friction–concentration coefficients k_f is again analogous to the single-component behaviour. Specifically, increasing the molecular-weight difference between the two components in the bimodal solutions increases the concentration sensitivity, i.e. the change in k_f. The magnitude of the k_f coefficient may be envisaged as the strength of frictional interaction between the polymer molecules. For high molecular weights, this interaction is strong and thus k_f is large—the diffusion is sensitive to the concentration. For lower molecular weights, the converse is true. For the M_w^{prot} 28 000 and M_w^{prot} 28 000–M_w^{deut} 10 500 systems, the change in k_f on addition of the deuterated polymer, Δk_f, is small (0.1); while for the M_w^{prot} 1030 000 and M_w^{prot} 1030 000–M_w^{deut} 203 000 systems, Δk_f is substantially greater (2.1).

The magnitude of the relative contributions of the f_0 and k_f terms to the total friction ascribes a complex behaviour to the measured protonated polymer diffusion coefficient. In dilute solution, the behaviour may be assumed to be that of dilute coils and the total friction given by a simple approach such as equation (11). However, for large protonated polymers in dilute solution, the delicate balance between the f_0 and k_f terms is upset because of a greater molecular-weight dependence of the k_f term. This results in an unexpected behaviour of the diffusion coefficient as a function of deuterated polymer molecular weight. This balance can be re-introduced by collapsing the coils in a theta solvent so that the greater molecular-weight dependence of the k_f term is removed and the expected trend recovered.

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Note added in proof

Since the writing of this paper, there have been a number of methodological improvements in spectrometer design which has had a significant impact on the ability to measure accurately, slow diffusion coefficients and widths of diffusion coefficient distributions. For more recent presentations of these factors, see the following references:

Griffiths, P. C. and Stilbs, P. Adsorption fractionation studies by size-resolved pulsed-gradient spin-echo-NMR. *Langmuir* 1995, **11**(3), 898
Söderman, O. and Stilbs, P. NMR studies of complex surfactant systems. *Prog. Nucl. Magn. Reson. Spectrosc.* 1994, **26**, 445