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Diffusion in bimodal and polydisperse polymer systems: 2. Fully protonated bimodal and polydisperse polymer solutions

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In the second of two papers studying diffusion in bimodal and polydisperse polymer solutions, the average self-diffusion coefficient of two polydisperse polystyrene samples has been measured as a function of concentration by the pulsed-field gradient nuclear magnetic resonance technique. Utilizing the concepts introduced in the previous paper, estimates of the molecular-weight distribution obtained from these self-diffusion coefficients show reasonable agreement with values obtained from gel permeation chromatography. Simple model systems reinforce the validity of this approach.

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

INTRODUCTION

Many of the characteristic physical properties of polymers depend on molecular weight. A knowledge of the molecular-weight distribution present in a given sample is, therefore, of fundamental importance, but no simple method for measuring this distribution *in situ* exists. The dynamics of polymers in solution depend on both molecular weight and concentration and inherently contain all the information about the molecular-weight distribution. This work is an attempt to address this point by probing the diffusion coefficient of polymers in model and real polydisperse systems. A detailed introduction to the approach adopted here was given in the previous paper and will not be repeated here.

Using calibrations performed on model bimodal and single-component solutions[1,2], the established theories for the discussion of dilute polymer solutions have been used to obtain various estimates of the molecular-weight distribution of two polydisperse samples. Addition of deuterated polymers (which are 'invisible' in this experiment) to these polydisperse polymer solutions perturbed the molecular-weight distribution and the results did indeed show this fact. Although this approach is largely qualitative, valuable information can be gained about the averaging processes that occur to the dynamics of polydisperse polymer solutions.

EXPERIMENTAL

Samples

As in the previous paper, the monodisperse, protonated and deuterated polystyrene samples were supplied by Polymer Labs (Shropshire, UK) whilst the polydisperse sample was specially synthesized. Carbon tetrachloride was obtained from BDH and used with no further purification. All samples were prepared in cleaned, weighed 5 mm n.m.r. tubes and allowed to equilibrate for three days before measurement. The samples were prepared at constant weight concentration and the quoted polymer concentration is therefore the *total* polymer concentration.

P.f.g.n.m.r. experiments

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 (p.f.g.) technique[3]. 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 unit used to generate the field gradients, based on the design by Stilbs[4], was calibrated with a sample of known diffusivity (water) giving field gradients G between 0.015 and $0.080\,\mathrm{T\,m^{-1}}$. 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 field stability. The data in the form of spin echoes were integrated after Fourier transformation and could be fitted to equation (1), which assumes isotropic Brownian diffusion:

$$A_\delta = A_0 \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D_S] \qquad (1)$$

where γ is the magnetogyric ratio and A_0 is the signal intensity when $\delta = 0$. Again 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.

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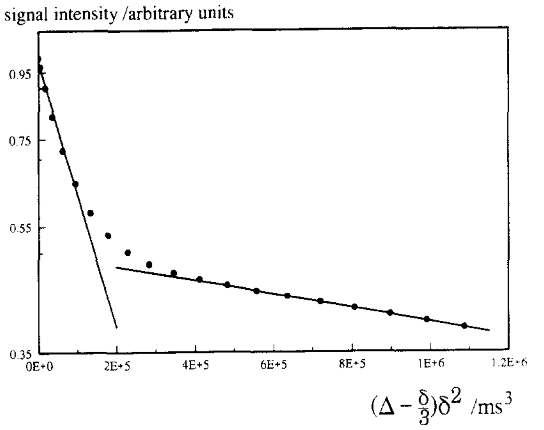

Figure 1 P.f.g.n.m.r. attenuation plot, signal intensity *versus* $\delta^2(\Delta-\delta/3)$, for the fully protonated system, M_w^{prot} 153 000–M_w^{prot} 1320, from which two self-diffusion coefficients may be extracted (full lines)

RESULTS AND DISCUSSION

Diffusion in fully protonated bimodal solutions

Some insight into the complex nature of polydisperse p.f.g.n.m.r. attenuation functions may be gained by considering the attenuation plot from the equi-mass (M_w^{prot} 153 000–M_w^{prot} 1320) bimodal system shown in *Figure 1*. This fully protonated system has been studied as a function of concentration. Two regions are apparent in all the attenuation functions: a rapidly decaying signal representing the lower-molecular-weight fraction and the slowly decaying signal representing the higher-molecular-weight fraction. Analysis of these decays using a double diffusion non-linear least-squares regression method yields two diffusion coefficients. Within this analysis, the two-component nature of the attenuation function is maintained, i.e. the fitting routine assumes two components each with an initial height and a diffusion coefficient and a single baseline (a five-parameter fit). The diffusion coefficient–concentration behaviour of these two components, termed 'fast' and 'slow', is shown in *Figure 2*.

Reiterating the approach detailed in the previous paper, the friction opposing the motion of a polymer molecule is generally expressed as a power series in concentration[1,2]:

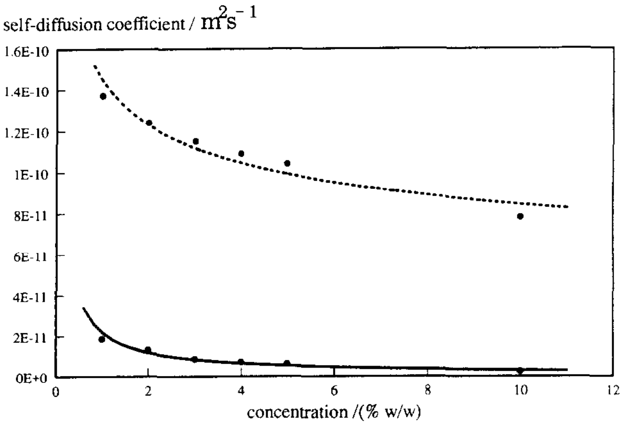

Figure 2 Self-diffusion–concentration behaviour of the 'fast' (····) and 'slow' (——) components extracted from a series of bimodal attenuation plots including that of *Figure 1*

Table 1 Friction power-series parameters for the diffusion concentration dependence for a bimodal polymer system and two calibrants

System	f_0 ($\times 10^{11}$ kg s^{-1})	k_f (m^3 kg^{-1})	k_f' (m^6 kg^{-2})
M_w^{prot} 1320	0.80	0.005	0
M_w^{prot} 153 000	8.00	0.10	0.02
M_w^{prot} 1320–M_w^{prot} 153 000			
'fast'	1.4	0.006	0
'slow'	8.4	0.08	0.05
typical errors	±0.50	±0.003	±0.01

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

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:

$$D_S = D_0/(1 + k_f c + k_f' c^2) \tag{3}$$

where D_0 is the self-diffusion coefficient at infinite dilution. Applying this friction power-series analysis usually invoked for the concentration behaviour yielded the values shown in *Table 1*.

As may be seen, the slow-component values are in reasonable agreement with those obtained from the single-component M_w 153 000 calibrant. Hence, the slow component is attributable to the M_w 153 000 component species. The fast diffusion is due therefore to the M_w 1320 component. The f_0 value in the table for the fast component is somewhat greater, but still within experimental error.

The friction coefficient–concentration behaviour for this fully protonated bimodal system follows the trends exhibited by the protonated–deuterated bimodal solutions studied previously[2]. Representing the behaviour as a power series, the values of k_f of both components in the blend are comparable to that in the single-component solution, suggesting that over this concentration range the polymer molecules diffuse independently; based on simple molecular-volume arguments, c^* was found to be approximately 7% w/w for PS M_w 150 000[1].

The effect of molecular weight was studied in fully protonated bimodal solutions by measuring the diffusion of a series of protonated polymers as a function of molecular weight in bimodal solutions also containing a protonated polymer of fixed molecular weight (M_w 153 000) as the second component. It should be stressed that, unlike the protonated–deuterated blends, both components are now *visible* and the diffusion coefficient of the *labelled* polymer is extracted from the double diffusion coefficient nature of the attenuation function. The molecular-weight dependence of the *labelled* species in 5% w/w total polymer concentration solutions is shown in *Figure 3* along with the corresponding value for a single-component solution of that molecular weight; the diffusion coefficient–molecular weight exponent of −0.5 (±0.1) observed is typical of diffusion in a theta solvent. This may be contrasted to an exponent of −0.63 (±0.05) in the single-component systems. The change in the exponent represents the significant perturbation of the solvency conditions, although the error associated

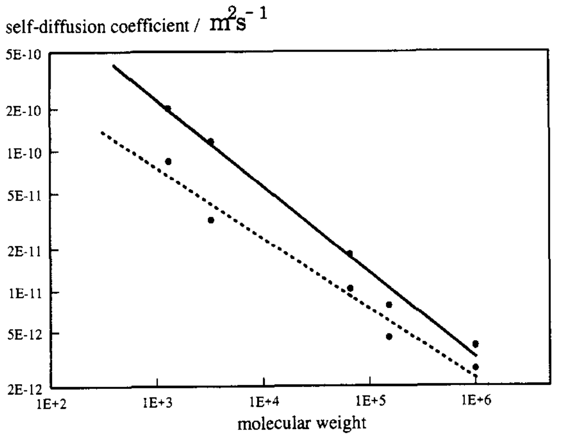

Figure 3 Self-diffusion coefficient–molecular weight behaviour of the 'labelled' (····) component extracted from the bimodal attenuation plots. Also shown for comparison is the single-component solution value (——)

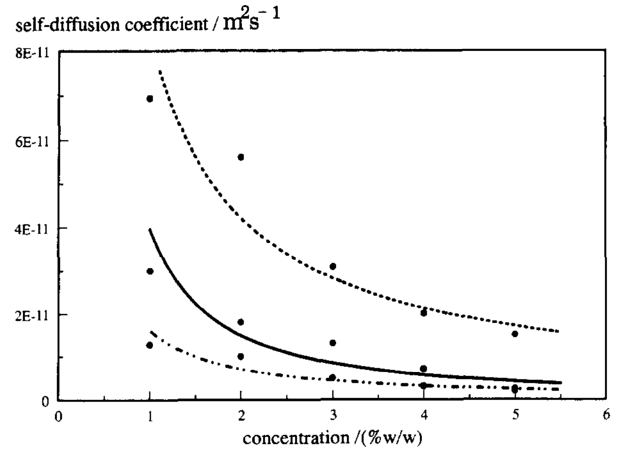

Figure 5 Self-diffusion coefficient–concentration behaviour for the 'fast' (····), 'medium' (——) and 'slow' (–··–··–) components for polydisperse polymer A, $M_w/M_n = 2.80$

with this approach is somewhat greater. This reinforces the problem of studying polydisperse samples and highlights the subtlety of the protonated–deuterated blend approach.

Summary of the fully protonated bimodal solution studies

The diffusion of probes in dilute polymer solutions—whether the probes are polymer molecules or Brownian spheres—follows the Stokes–Einstein equation; two parameters are required, the size of the sphere and the correct macroscopic viscosity. In semi-dilute solutions, the diffusion of low-molecular-weight polymers and Brownian spheres also follows the Stokes–Einstein equation. The diffusion of higher-molecular-weight polymers in semi-dilute solutions is complicated by such factors as coil overlap and network formation. Similar behaviour has been observed in this study. The diffusion of low-molecular-weight protonated polymers in bimodal solutions of both fully protonated and part deuterated blends, over a wide concentration range, has been shown to follow dilute-solution behaviour. The diffusion of the higher-molecular-weight analogous bimodal solutions has been discussed in terms of semi-dilute behaviour[1].

The self-diffusion coefficient of a low-molecular-weight polydisperse polymer might therefore be expected to be the summation of the mobilities of each component diffusing through a viscous medium comprised of the remaining fractions. This supposition will be tested by studying the diffusion of polydisperse polymers.

Diffusion in polydisperse samples

The raw attenuation plots for a polydisperse sample are shown in *Figure 4*. As may be seen, the deviation from single-component behaviour represents the problem of studying polydisperse samples—which region of the attenuation function represents the bulk of the sample. This factor is exploited in the 2D DOSY experiment[5] where the normal high-resolution spectrum is correlated with the diffusion coefficient distribution.

In photon correlation spectroscopy (p.c.s.) studies, the degree of curvature of a polydisperse correlation function is analysed by the method of cumulants to extract information on the sample distribution[6]. A similar approach is adopted here; the attenuation function may be broken down into three arbitrary

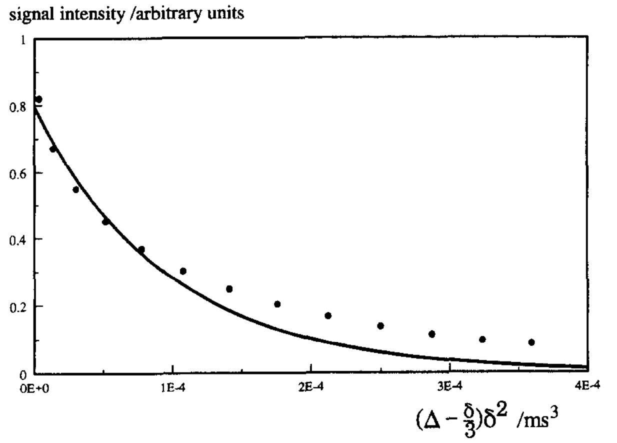

Figure 4 P.f.g.n.m.r. attenuation plot, signal intensity *versus* $\delta^2(\Delta-\delta/3)$, for a polydisperse polymer, $M_w/M_n = 2.8$. The full curve represents monodisperse behaviour

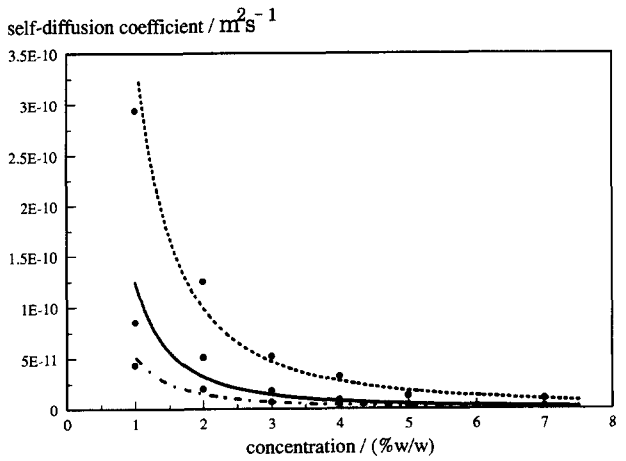

Figure 6 Self-diffusion coefficient–concentration behaviour for the 'fast' (····), 'medium' (——) and 'slow' (–·–·–) components for polydisperse polymer B, $M_w/M_n = 2.06$

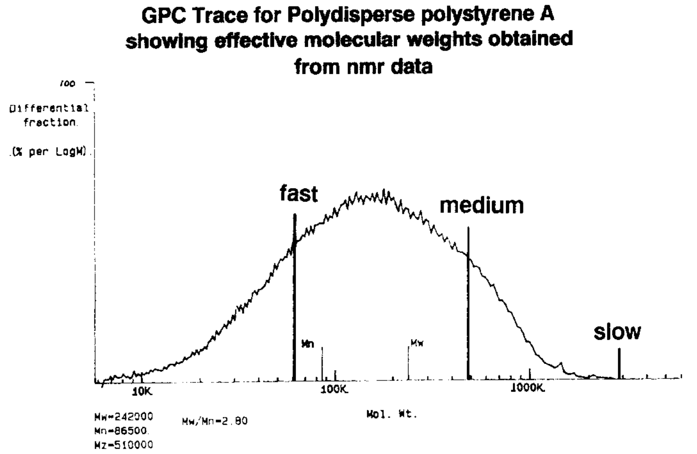

Figure 7 Gel permeation chromatography trace of the molecular-weight distribution of polydisperse polymer A, $M_w/M_n = 2.80$, showing the molecular-weight estimates of the 'fast', 'medium' and 'slow' components

portions termed the fast, medium and slow components. The fast component is obtained over the range $0 < \delta < 30$ ms. The medium component is obtained from the decay over the range $30 < \delta < 60$ ms, whilst for the slow decay $60 < \delta < 90$ ms. In the monodisperse protonated–deuterated blend, by observing the diffusion of only one of the two components (equation (1)), it is possible to estimate the viscosity of the background solution (which in this case was that of the solvent) or the spin–spin relaxation time weighted number concentration. For the polydisperse case, the broad distribution makes this approach impossible, i.e. the weighting factors are unknown. Consequently, no attempt was made to deconvolute these three portions. Indeed, these factors are the precise information that is required and it is tacitly assumed that the weighted self-diffusion coefficient is a representation of those factors. Attempts at deconvolution might inherently remove the required information. It should be noted that the self-diffusion coefficients obtained from this analysis will represent, in some manner, the diffusion properties of the whole sample. Consequently, the initial decay will be dominated by the signal arising from fast-diffusing species, whilst the later decay will be due to species with a slower diffusion. Each portion of the decay was fitted to the diffusion equation (equation (1)) and a weighted value for the self-diffusion coefficient obtained. The concentration behaviours of the three coefficients are plotted in *Figures 5* and *6* for the two polydisperse polymer samples. It is obvious from these raw data that, with increasing polydispersity, a greater spread of self-diffusion coefficients is present and hence the associated errors increase concomitantly. The concentration dependence of each component was analysed in terms of the power series described previously. The infinite-dilution friction, f_0, for each component may be converted to an equivalent monodisperse molecular weight with comparison to calibrants[7]. These 'effective' molecular weights are displayed on the g.p.c. traces of *Figures 7* and *8*. The ratio of these two components increases with polydispersity (see *Table 2*).

In both cases, the slow component lies outside the range of molecular weight present. The fast and medium components, however, fall within the distribution; the fast component falls before the distribution maximum, whilst the medium component falls after the distribution maximum. The initial signal intensity in equation (1), A_0, is a complicated parameter for the case of polydisperse

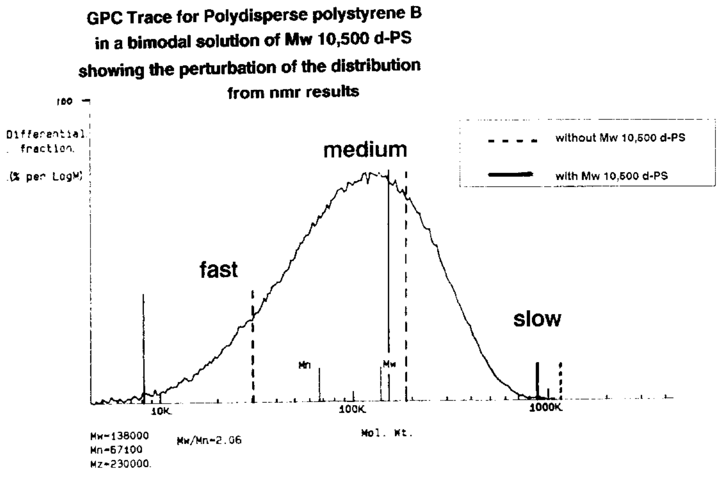

Figure 8 Gel permeation chromatography trace of the molecular-weight distribution of polydisperse polymer B, $M_w/M_n = 2.06$, showing the molecular-weight estimates of the 'fast', 'medium' and 'slow' components and those estimates in the presence of a deuterated polymer of M_w 10 500

Table 2 The polydispersity index calculated from g.p.c. and that from this analysis

Sample	M_w/M_n g.p.c.	$f_0^{\text{medium}}/f_0^{\text{fast}}$
A $M_w = 242\,000$	2.80	3.0 (±0.4)
B $M_w = 138\,000$	2.06	2.4 (±0.3)

samples since it contains a molecular-weight-dependent term. Rewriting in full:

$$A_\delta = \sum_i A_0(i) \exp[-2\Delta/T_2(i)] \times \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D_S(i)] \qquad (4)$$

where T_2 is the spin–spin relaxation time (effectively the lifetime of the signal), which depends on the polymer mobility and hence molecular weight. Essentially, low-molecular-weight species have longer T_2 values and larger self-diffusion coefficients. Consequently, these components contribute significantly to the spin-echo intensity when $\delta = 0$ but these attenuate ($\delta \neq 0$) more quickly. Conversely, higher-molecular-weight species have shorter T_2 values and smaller self-diffusion coefficients. These components contribute disproportionately less to the spin echo but the attenuation is significantly less. The ramifications of these opposing factors is not straightforward if Δ is varied. Consequently, for these experiments Δ was fixed. However, because of the limited range of field gradients available, the nominal self-diffusion coefficient for the higher-molecular-weight component is inaccurate and will not be discussed further. Nonetheless, as found in other studies[8], the presence of a small fraction of high-molecular-weight species has a significant effect on the p.f.g.n.m.r. experiment.

Since this is a purely qualitative approach, the agreement with the M_w/M_n ratio obtained from the g.p.c. data is surprisingly good. With further refinement, currently underway, it may be possible to estimate the polydispersity index from these sorts of measurements.

The addition of a monodisperse *deuterated* polymer offers the opportunity to systematically alter the distribution without complicating the p.f.g.n.m.r. experiment. Such an attempt was made by studying the (M_w^{prot} polydisperse B–M_w^{deut} 10 500) system (see *Figure 8*). Estimates of the new molecular-weight distribution were obtained from the self-diffusion coefficient–concentration behaviour as in the previous analyses. All three components were shifted to lower molecular weights. This behaviour is in accord with the approach discussed previously; the diffusion of the protonated polymer is enhanced by the reduction in viscosity due to the smaller deuterated component. Two important points arise: (a) the higher-molecular-weight species are perturbed the least, i.e. some power-law dependence on molecular weight must determine the averaging process such as viscosity; and (b) that analysis in terms of a summation of monodisperse behaviours tends to give reasonable predictions as the observed distribution.

CONCLUSIONS

The self-diffusion coefficients of polymers in model bimodal systems have been shown to follow dilute-solution behaviour; the concentration dependence is well described by a power series and a molecular-weight exponent of 0.5 (±0.05).

Similar behaviour was observed in model polydisperse systems where these analyses were used to extract qualitative information on the molecular-weight distribution. For the case of *real* polydisperse systems, good agreement is found with g.p.c. values.

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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