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Nuclear Magnetic Resonance Measurements of Molecular Weights. Self-Diffusion of Poly(methyl methacrylate) in Acetonitrile[†]

Ravi Raghavan,[‡] Tammy L. Maver,[§] and Frank D. Blum*[#]

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104.

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ABSTRACT: The pulsed-gradient spin-echo NMR technique has been used to study the self-diffusion of both monodisperse and polydisperse poly(methyl methacrylate) (PMMA) in 5 wt % solutions in acetonitrile–d_3 at 40 °C. The spin-echo attenuation for the methoxy resonance of monodisperse PMMA is exponential and characterized by a single self-diffusion coefficient, D. The variation in the self-diffusion coefficient with molecular weight of the polymer follows a simple scaling law, with $D = 2.5 \times 10^{-6}(M)^{-0.87}$. For polydisperse PMMA samples nonexponential decays of the spin-echo intensity are observed. By use of the experimental scaling law, the decay curves for the polydisperse polymers could be used to determine the molecular weight of the polymer. It was found that simple exponential (monodisperse), Schulz, combination, and disproportionation models for molecular weight distributions all gave reasonable estimates of the weight-average molecular weight which were consistent with those obtained from gel permeation chromatography measurements. However, the accuracy of the fits for the various molecular weight distributions is such that a weight-average molecular weight is perhaps the most that can be determined with good accuracy in these experiments.

Introduction

The determination of the molecular weight and the molecular weight distribution of a polymer is a complicated task. Most synthetic polymers typically have a wide distribution of molecular weights, and a knowledge of the molecular weight distribution is of fundamental importance in the various properties of the system. Consequently, any new technique of determining polymer molecular weights deserves some consideration. Techniques for determining molecular weights of polymers can be classified into absolute and secondary, the two being differentiated in that the former are based on firm theoretical grounds and are without the need for calibration.[1] Absolute methods include vapor pressure osmometry, light scattering, end-group analysis, and ultracentrifugation. Although these techniques do not require any calibration or the availability of standards, they may require complex, often lengthy, sample preparation and/or expensive instrumentation. Secondary methods of molecular weight determination such as gel permeation chromatography (GPC) and solution viscosity have become widely accepted because of their cost and ease of use. The solution viscosity method requires the knowledge of the Mark–Houwink constants for the polymer–solvent pair and primarily determines the viscosity-average molecular weight, M_v. GPC, on the other hand, fractionates a molecule based on its hydrodynamic volume, and various molecular weight averages can be calculated after a calibration is done relating the elution volume to the molecular weight.[2]

In the present study, we describe how the NMR pulsed-gradient spin-echo (PGSE) technique can be used to determine the molecular weights of polymers in polydisperse systems. The PGSE technique has been widely used to determine the self-diffusion coefficients of polymer molecules in bulk[3–6] and in solution.[7–17] In this laboratory, we have also used the technique to study the self-diffusion of solvents in polymer solutions[18,19] and swollen polystyrene beads.[20] The technique and its applications in polymer and colloidal systems have recently been reviewed.[21,22] In previous PGSE studies investigators have noted, and in some cases[11,16,17,23–26] taken into account, the effects of polydispersity on the experimental results. Whereas these previous studies have largely focused on testing scaling theories, the purpose of this study is to use the PGSE technique to actually measure the molecular weights of polydisperse polymers. The advantages of the PGSE technique are that it does not require much sample preparation and, since most impurities will be resolved with respect to chemical shift, they should not cause any direct interference in determining the self-diffusion behavior of the polymeric species. The measurements can be carried out by using a conventional FT-NMR equipped with a homospoil accessory,[22] as in this case, but its use is then restricted to dilute and semidilute polymer solutions. Smaller diffusion coefficients, such as those often encountered in polymer melts or highly entangled solutions, can be measured by using instruments with stronger gradients but with some loss of chemical resolution.[22,27]

Table I
Monodisperse and Polydisperse PMMA Samples

polymer	M_n	polydispersity[a]
M-1	27 000	1.07
M-2	60 500	1.09
M-3	90 000	1.08
M-4	125 000	1.08
M-5	179 000	1.08
M-6	270 000	1.14
P-1 no. (18 225-7, lot 3)	48 100	1.75
P-2 no. (18 224-9, lot 18)	45 800	1.69
P-3 no. (18 225-7, lot 9)	53 600	1.67

[a] For monodisperse polymers supplied by manufacturer; for polydisperse polymers determined for GPC measurements.

For our experiments we have chosen a system containing poly(methyl methacrylate) (PMMA) in deuteriated acetonitrile (CD_3CN). The system lends itself to measurement of the polymer self-diffusion coefficients because of the well-resolved, narrow resonance from the methoxy group which has a relatively long spin–spin relaxation time, T_2. We report the self-diffusion scaling law for 5 wt % solutions of monodisperse PMMA in CD_3CN at 40 °C from which preliminary data at ambient temperature have been

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* Author to whom all correspondence should be addressed.

[†] Presented at Polymer 85, Melbourne, Australia, Feb 1985.

[‡] Present address: Sevak Publications, Dadar, Bombay 400014, India.

[§] Present address: Rohm and Haas Co., Spring House, PA 19477.

[#] Present address: Department of Chemistry, University of Missouri—Rolla, Rolla, MO 65401.

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reported.[28] These data are then used to fit the PGSE results for polydisperse PMMA in CD_3CN in order to determine the weight-average molecular weight and the polydispersity for certain distributions. The results are compared to those obtained from GPC measurements.

Experimental Section

Monodisperse PMMA samples (M-1 to M-6) for PGSE NMR and GPC were purchased from Pressure Chemical Co. (Pittsburgh, PA). Three polydisperse samples from Aldrich Chemical Co. (Milwaukee, WI) were also studied (P-1 to P-3). Table I lists the monodisperse and polydisperse polymers that were used for the NMR and the GPC studies. Acetonitrile-d_3 (99% D) was obtained from Stahler Isotope Chemicals (Cambridge, MA). All polymers and solvents were used without further purification.

Polymer solutions for NMR analyses were prepared at 5 wt % polymer by directly weighing the vacuum-dried polymer into a 5-mm NMR tube and adding solvent. The tubes were sealed to maintain accurate concentration as a function of time. The diffusion coefficients were measured by using a JEOL FX-90Q multinuclear FT-NMR spectrometer equipped with a homospoil accessory. By adjustment of the current to the homospoil coils the gradient strength was found to be 0.047 ± 0.002 T/m. Calibration of the gradient was done before each series of measurements by using cyclohexane as a standard, $D(25\ °C) = 1.475 \times 10^{-9}\ m^2/s$.[29] The temperature was controlled at 40 ± 1 °C during the experiment by using a JEOL variable-temperature accessory.

The self-diffusion coefficients were measured by using the method of Stejskal and Tanner,[30] and the pulse sequence used was similar to that developed by Stilbs et al.[31] with some modifications.[22] The pulse sequence consists of a standard 90°–Δ–180°–Δ–echo sequence with two field gradient pulses of duration δ during the Δ periods. In this case the echo amplitude, I, for a simple molecule in an isotropic solution is given by[22]

$$I = I_0' f(J) \exp(-2\Delta/T_2) \exp(-\gamma^2 G^2 D \beta) \qquad (1)$$

where I_0' is the signal intensity for $\Delta = 0$, $f(J)$ is the J-modulation effects, T_2 is the transverse relaxation time, D is the self-diffusion coefficient; G is the field gradient strength, and $\beta = \delta^2(\Delta - \delta/3)$. It is assumed in this analysis that background field gradients are negligible. Multiple spectra are collected by varying δ, the time the gradient is turned on, while keeping Δ constant and J-modulation effects minimized. Consequently, the first three factors in eq 1 can be combined into a single constant, I_0, to yield

$$I = I_0 \exp(-\gamma^2 G^2 D \beta) \qquad (2)$$

Thus for a simple molecule in isotropic solution a semilog plot of I/I_0 vs. β yields the self-diffusion coefficient of the species under consideration provided there are no other complicating effects such as a distribution of molecular weights. A log–linear least-squares fit was used to calculate D for the monodisperse polymers. The PGSE data for the polydisperse polymers were also fit to various distributions by using the least-squares program ZXSSQ (IMSL, Houston, TX).

Gel permeation chromatography measurements on monodisperse and polydisperse PMMA were carried out by using 0.5 wt % solutions in freshly distilled tetrahydrofuran (THF). An IBM instruments LC 9521 isocratic modular pump and an LC/9525 refractive index detector were used with two columns packed with styrene–divinylbenzene cross-linked polymer (IBM SEC columns, pore type E, B). All GPC measurements were carried out at 30.0 ± 0.2 °C with a flow rate of 1.0 mL/min. Monodisperse PMMA samples were used to generate the calibration curve relating molecular weight to elution volume. Number- and weight-average molecular weights for the polydisperse samples were calculated by the method of curve summation.[32]

Results

The normal proton NMR spectrum of a 5 wt % solution of PMMA in acetonitrile-d_3 is shown in Figure 1. The methoxy peak, being well resolved and narrow, is well suited for diffusion measurements. This peak is not affected by the tacticity of the polymer and exhibits no spin–spin coupling, thus leading to a better signal/noise ratio and fewer complications from the spin-echo sequence. The experimental T_2 of the methoxy resonance for the monodisperse polymers was measured to be 188 ± 3 ms at 40 °C and independent of the polymer molecular weight for all the polymers studied (i.e., in the range 27 000–270 000).

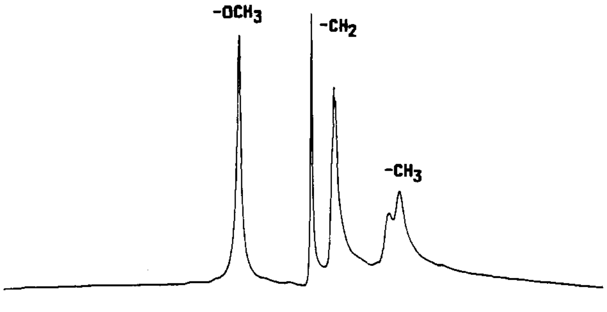

Figure 1. Proton NMR spectra of a 5 wt % solution of PMMA (M_n = 60 500) in acetonitrile-d_3 at 40 °C. The methoxy peak is used for the PGSE experiments.

Shown in Figure 2 are the results of the PGSE experiment on monodisperse samples of PMMA. The signal attenuation for each of the polymers shown can be represented with a simple exponential decay characterized by a single diffusion coefficient, D. von Meerwall[23] has reported observing significant departures from exponential attenuation even in systems where the polydispersity, M_w/M_n, is as small as 1.1. In our experiments only minor effects from polydispersity are observed, possibly due to the small field gradients (0.047 T/m) employed, except for the M-4 sample which showed nonexponential decay at low β values. This could be attributed to the presence of a small fraction of low molecular weight impurity in this sample. The precision of the measured diffusion coefficients is approximately 10% as estimated from several runs on the same sample. As expected, with increasing molecular weight the slopes of the ln I vs. β plots decrease and are indicative of lower self-diffusion coefficients. Figure 3 shows the variation in the self-diffusion coefficient, D, with the molecular weight M of the monodisperse polymer. The values shown are the means of at least three separate runs each. From a least-squares analysis of the dependence of D on the molecular weight of the polymer, M, the following scaling law was established:

$$D = (2.5 \pm 0.5) \times 10^{-6} (M)^{-0.87(\pm 0.10)} \quad (m^2/s) \qquad (3)$$

The uncertainties are given as ±1 standard deviation.

The results of the application of the PGSE technique to three polydisperse PMMA polymers are shown in Figure 4. The curves show significant deviations from simple exponential behavior due to the polydisperse nature of the samples. For a polydisperse system, a distribution of diffusion coefficients also exists and the spin-echo intensity in eq 2 is readily modified as a weighted sum of the intensities arising from the individual molecules with molecular weights M_i, each with a diffusion coefficient, D_i. Since each repeating unit in a polymer molecule contributes equally to the echo intensity, the weight fraction of i-mer, w_i, is used, giving[11,17,23]

$$I/I_0 = \sum_{i=1}^{\infty} w_i \exp[-\gamma^2 G^2 D(M_i) \beta] \qquad (4)$$

No individual weighting of echo intensities by the T_2 term in eq 1 arises because T_2 is not dependent on the molecular weight of the polymer. This independence is to be expected because local segmental reorientation is the dom-

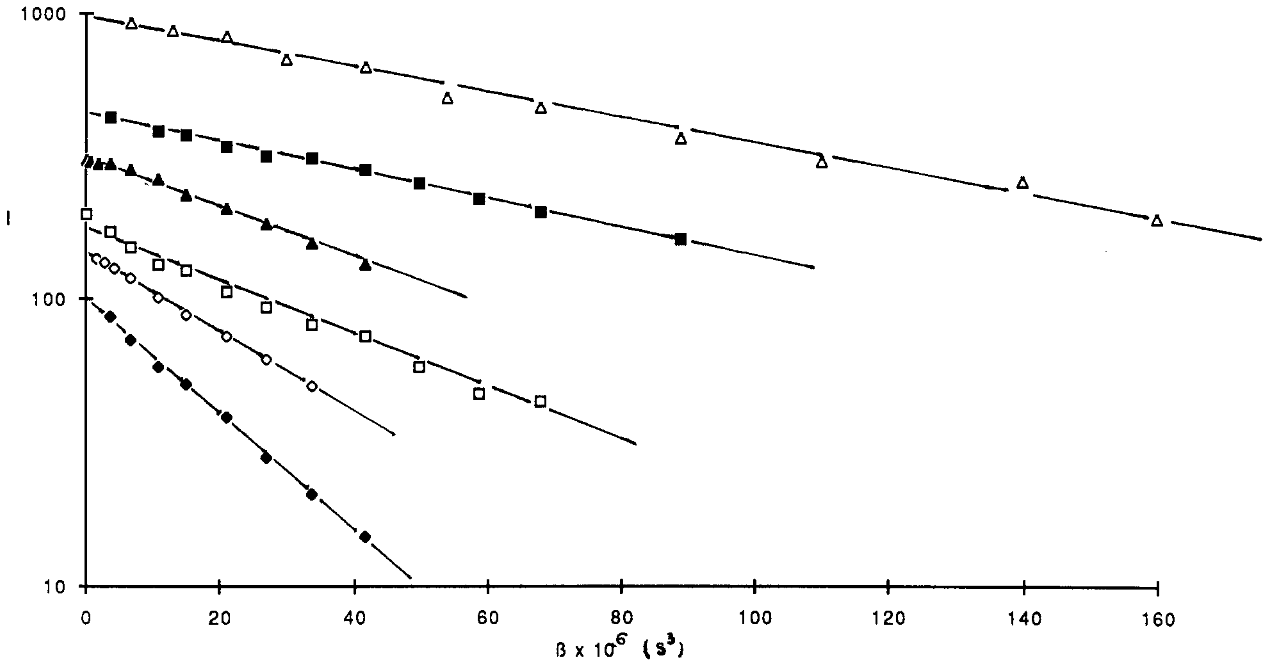

Figure 2. Plot of intensity I (log scale, arbitrary units) vs. β for monodisperse PMMA in acetonitrile-d_3: (●) M-1; (○) M-2; (▲) M-3; (□) M-4; (■) M-5; (△) M-6. Lines drawn are to single-exponential fits of the data.

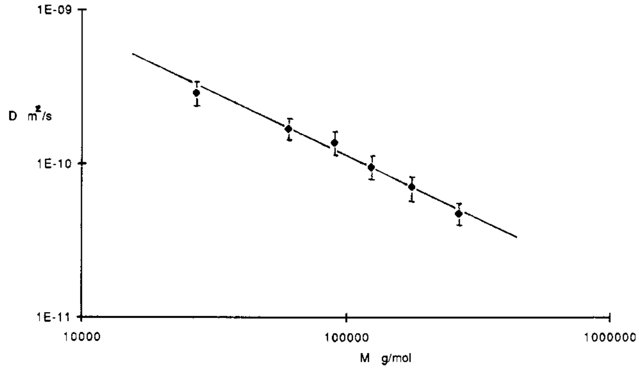

Figure 3. Plot of self-diffusion coefficient, D, vs. the number-average molecular weight, M_n, of monodisperse PMMA in acetonitrile-d_3 (log–log scale). Line drawn is obtained by a weighted least-squares fit to the data and has a slope of −0.9.

inant mode of spin–spin relaxation[33–35] in the methoxy group.

Since the self-diffusion coefficient is a function of the molecular weight of the polymer, the D term in eq 4 could be replaced by the scaling law given in eq 3. We have used this approach to fit our data for the polydisperse samples to the following four distributions: (a) free radical polymerization terminated by combination of the reacting chains which results in a polydispersity of 1.5 and a weight fraction given by[36]

$$w_i = i(i-1)(1 + 1/v)^{-i}/(2v^3) \qquad (5)$$

where i is the degree of polymerization, v is the kinetic chain length, and w_i is the weight fraction of the i-mer; (b) free radical polymerization with termination by disproportionation resulting in a polydispersity of 2.0[36] and a weight fraction given by[36]

$$w_i = i(1 + 1/v)^{-i}/(2v^3) \qquad (6)$$

(c) the Schulz distribution which is a two-parameter fit using both the number-average (or weight-average) molecular weight and the polydispersity[37] with the weight fraction for the i-mer for this distribution given by

$$w_i = a/[X_n\Gamma(a + 1)][ai/X_n]^a \exp(-ai/X_n) \qquad (7)$$

Table II
NMR and GPC Molecular Weight Results for Polydisperse PMMA Samples

polymer	M_n	M_w	polydispersity
polymer P-1			
GPC	48 100	84 100	1.75
Schulz	37 900	79 900	2.11
combination	51 200	76 800	1.5
disproportionation	43 500	87 000	2.0
exponential		80 300	
polymer P-2			
GPC	45 800	77 300	1.69
Schulz	30 000	63 000	2.1
combination	41 600	62 400	1.5
disproportionation	31 300	62 600	2.0
exponential		68 000	
Polymer P-3			
GPC	53 600	89 700	1.67
Schulz	49 100	103 700	2.1
combination	62 200	93 300	1.5
disproportion	53 500	107 000	2.0
exponential		86 500	

where $X_w/X_n = 1 + 1/a$, Γ is the gamma function, and X_n and X_w represent the number- and weight-average molecular weights of the sample; (d) an exponential function (i.e., the spin-echo amplitude decay was fit to an exponential and the diffusion coefficient so obtained was then substituted into the scaling law so as to obtain a single "average" molecular weight). A number of other distributions are possible, but those tested in this study were sufficient to illustrate the usefulness and limitations of this approach.

The results obtained by fitting the nonexponential decay to a scheme assuming termination by combination alone are shown in Figure 4. The solid line drawn through the points represent the best fits to the data for this model. The results for the other models were all qualitatively similar to those obtained for combination. The GPC results for the three polymers provided an independent test of the NMR results. Shown in Table II are the results from GPC along with the results, from all four models chosen, for number- and weight-average molecular weights.

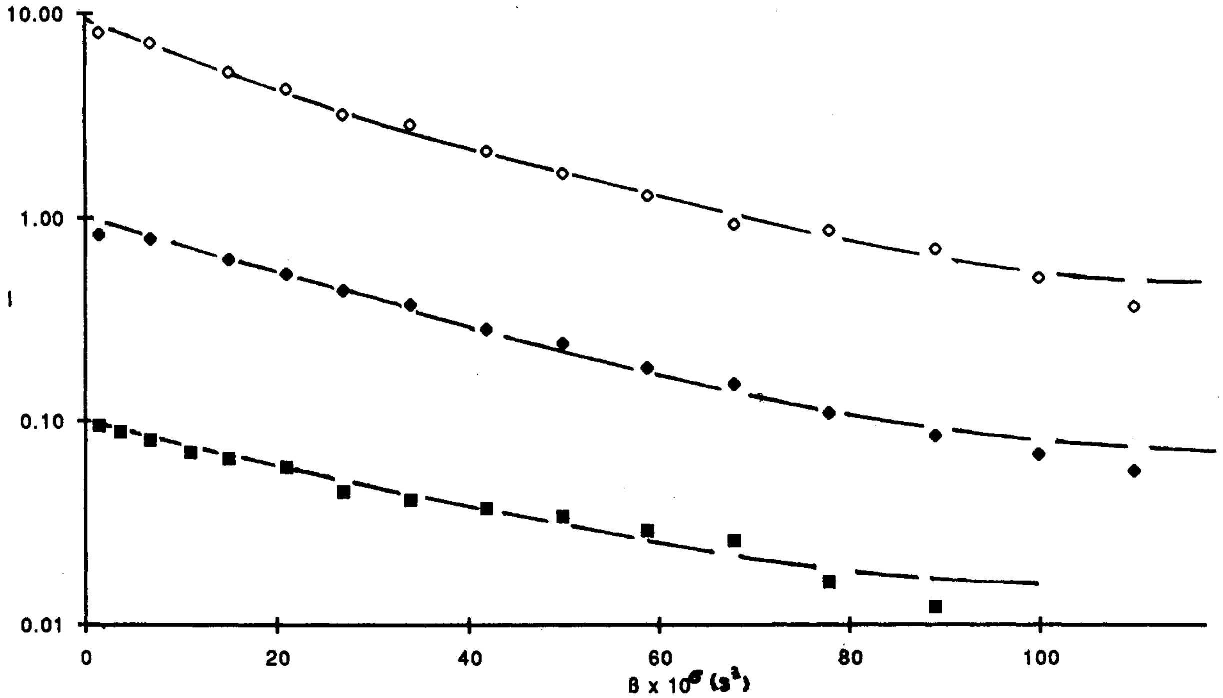

Figure 4. Plot of intensity *I* (log scale, arbitrary units) vs. β for polydisperse PMMA in acetonitrile-d_3: (●) P-1; (○) P-2; (□) P-3. Curves drawn are the best fits to the data assuming that termination occurs by combination only.

Discussion

The power law dependence of the self-diffusion coefficient, D, of the polymer on the molecular weight, M, for monodisperse PMMA samples (eq 5) has also been observed in a number of other systems. The general form of the dependence is

$$D = kM^{-\alpha} \tag{8}$$

where k and α are constants dependent on the type of system. For example, in entangled polymer systems the exponent α is predicted to be 2.[38,39] This has been verified by several techniques including microdensitometry,[40,41] neutron scattering,[42] and NMR for polymers in bulk[5,6,25] and in solution.[7,15] At the other extreme, for a random coil polymer in an infinitely dilute solution, the Flory theory predicts $0.5 \leq \alpha \leq 0.6$.[43,44] This has been verified for the mutual-diffusion coefficient of PMMA in acetone where $\alpha = 0.56$[45] and for tracer diffusion as a function of molecular weight.[46] NMR measurements extrapolated to infinite dilution also show this limiting behavior.[8,10,11,13,14]

For 5 wt % PMMA in acetonitrile, the exponent, α, was found to be intermediate between the values for entangled and infinitely dilute solution. Callaghan and Pinder[10] have shown a well-defined scaling region for 230 kg/mol polystyrene in CCl_4 for concentrations greater than about 5 wt % polymer. They also found a weaker concentration dependence below 5 wt %. von Meerwall et al.[7] have shown an $\alpha = 1$ dependence for polystyrene in a mixed solvent system below 10% polymer for nonentangled solutions. This behavior is quite consistent with the present result, although it is not known if there is any theoretical significance in the $\alpha = 1$ result. Clearly at 5 wt % PMMA and molecular weights less than 210 the polymer does not undergo reptation as its dominant diffusion mechanism. Regardless of the theoretical significance of the exponent, the scaling law may still be used as the basis for the molecular weight measurements.

As previously mentioned, the fits for all polydisperse distributions were qualitatively similar. The deviation of the experimentally observed intensities from the calculated values becomes more apparent at β values greater than ca. 10^{-4} s^3. The experimental data correspond to a narrower distribution of diffusion coefficients than what would be predicted by a model based on the scaling law and a knowledge of the molecular mass distributions. Such behavior is observed for all three distributions and is consistent with the microscopic averaging of the diffusion coefficients previously seen by Callaghan and Pinder[16] and others.[24] In our case we find this effect to be smaller than that found by others as the curvature in Figure 4 is quite apparent. Nevertheless, we find that the molecular weights obtained by these schemes (Table II) are in reasonable agreement with those obtained by GPC, particularly for the weight-average molecular weight. In this case no single distribution chosen can describe the entire molecular weight spread. The Schulz distribution yields an unexpectedly high polydispersity.

The results from the polydisperse samples have also been effectively fitted to a single exponential. This yields diffusion coefficients that when substituted into the scaling law give molecular weight averages intermediate between the number- and the weight-average molecular weights obtained by GPC. Callaghan and Pinder observed that in bimodal blends of polystyrene the ensemble-average diffusion coefficient lies closer to $D(M_w)$ than to $D(M_n)$. In the present case, the estimated M_w lies within ca. 5% for two samples and 10% for the other sample of the GPC M_w. This agreement is good considering typical accuracies of molecular weight measurement. McDonnell and Jamieson[47] have also addressed the problem of how a distribution of molecular weights affects the molecular weight average determined by using a combination of quasi-elastic light scattering techniques to measure polymer diffusion coefficients and intrinsic viscosity measurements. They report that a characteristic molecular weight can be determined for any combination of polymer–solvent and, provided the Mark–Houwink parameters for that system are known, it is possible to determine the polydispersity. Finally, it is important to note that the three polydisperse samples in our study were chosen to be very close to each other in terms of their molecular weights. As can be seen from Table II the NMR PGSE experiment has no difficulty distinguishing between all three, with perhaps the most reasonable results from the forced fits to a monodisperse distribution.

Conclusion

The present work has shown that polydispersities $M_w/M_n < 1.10$ have a small effect on the exponential behavior of the decay of the methoxy peak in PMMA in the PGSE experiment. The diffusion coefficients of monodisperse PMMA in CD_3CN obtained by a single-exponential fit to the decay follow a scaling law with molecular weight of the polymer and have an exponential factor of -0.9 ± 0.1. In polymer systems of higher polydispersity, $M_w/M_n > 1.5$, a nonexponential decay is observed. The weight- and number-average molecular weights have been calculated for these polymers by using kinetic schemes which presume a termination by combination or disproportionation alone and the Schulz distribution. The results obtained are consistent with those obtained by GPC measurements, with the Schulz distribution giving the least satisfactory results. A single-exponential fit to the data for the polydisperse system gave perhaps the best results and indicates that even for these systems the weight-average molecular weights can be obtained by ignoring the effects of polydispersity and force fitting the nonexponential decay to a single-exponential fit. Furthermore, the PGSE technique is sensitive enough so that even polymers with molecular weights close to each other can be distinguished by their diffusion behavior at low concentrations. Provided molecular weight standards are available, this technique should be appropriate for other systems as well.

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