

Analysis

The Effect of Polydispersity on the Analysis of Optical Tracer Diffusion Experiments

T. P. Lodge¹, L. M. Wheeler¹, B. Hanley², and M. Tirrell²

¹ Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

² Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA

Summary

The recently developed technique of dynamic light scattering from ternary solutions, in which the solvent and matrix polymer are isorefractive, can provide extensive information about the translational diffusion of polymers in semidilute and concentrated solutions. However, the strong molecular weight dependence of diffusion in these regimes has a substantial effect on the observed autocorrelation functions. It is demonstrated that the traditional cumulants approach is inadequate for extracting the desired decay rates, even for narrow distribution samples (i.e. $M_w/M_n \cong 1.05$). Alternative methods of analysis are proposed, and implications for other polymer diffusion experiments are discussed.

Introduction

Dynamic light scattering has proven to be a most useful probe of macromolecular motion, providing rapid and precise measurements of mutual diffusion coefficients (1). Under suitable conditions, internal relaxation modes of single polymer chains may also be examined (2). Although the majority of applications to polymer solutions have been concerned with the dilute regime, the semidilute and concentrated regimes have more recently attracted a great deal of attention. Issues of interest include the molecular weight and concentration dependence of the cooperative diffusion coefficient (3), the origin(s) of the so-called "slow mode" (4), and the use of isorefractive ternary solutions to enable extraction of translational diffusion coefficients (5). In this last example, the "visible", or tracer, polymer is present in dilute amounts, and thus in principle the analysis of the experimental scattered intensity autocorrelation function should proceed in a manner entirely similar to those traditionally employed for dilute solutions. In particular, for a monodisperse tracer polymer a single exponential decay is expected, while for narrow distribution polymers a cumulant expansion would seem a convenient way of accounting for the distribution of decay rates (6). In dilute solution, where the molecular weight dependence of the individual decay rates is approximately $\Gamma \sim M^{-0.5}$ for flexible polymers, the cumulant expansion is generally carried only to a second or perhaps a third term. However, in semidilute or concentrated solutions, where the tracer polymer may be reptating, the decay rates could vary as M^2 . This molecular weight dependence is shown to have a significant effect on the shape of the correlation function, and thus on the extraction of diffusion coefficients.

In this paper we present calculations of the magnitude of the effect of small (i.e. 1.05 - 1.10) and moderate (i.e. 1.10 - 1.50) polydispersities on the correlation function, and we compare these predictions with experimental results on two ternary systems. From these simulations it is clear that the traditional cumulant approach is far from adequate under these conditions. Two particular alternative methods of analysis are proposed, and the implications for related experiments such as forced Rayleigh scattering are discussed.

Experimental

Two ternary systems have been employed in this work: polystyrene in a solvent composed of poly(vinyl methyl ether)/o-fluorotoluene, and poly(styrene-co-acrylonitrile) in poly(methylmethacrylate)/toluene. The polymer samples were: polystyrene (PS) from the Toyo Soda

Co., $M_w = 422,000$, $M_w/M_n = 1.05$; poly(vinyl methyl ether) (PVME), recently synthesized (7), $M_w = 1,300,000$, $M_w/M_n \cong 1.3$; poly(styrene-co-acrylonitrile) (PSAN) from Monsanto Co., $M_w = 120,000$, $M_w/M_n \cong 1.5$, ~ 76% styrene by weight; polymethylmethacrylate (PMMA) from Polysciences, Inc., $M_w = 410,000$, $M_w/M_n \cong 1.7$. The solution preparation, light scattering photometers, and experimental protocol have all been previously described (5).

Results and Discussion

In dynamic light scattering one obtains a normalized intensity autocorrelation function, $C(t)$, which in the homodyne case is related to the scattered electric field autocorrelation function, $g(t)$, by

$$C(t) = 1 + \beta\{g(t)\}^2 \quad (1)$$

For a monodisperse sample,

$$g(t) = e^{-\Gamma t} \quad (2)$$

where $\Gamma = Dq^2$, with D the diffusion coefficient and q the scattering wave vector defined as $q = (4\pi n/\lambda_0)\sin(\theta/2)$. For a polydisperse system, a distribution of decay rates, Γ , is observed with

$$g(t) = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \quad (3)$$

and

$$\langle \Gamma \rangle = \int_0^\infty G(\Gamma) \Gamma d\Gamma \quad (4)$$

where $\langle \Gamma \rangle$ is the mean decay rate. One approach to analyzing $g(t)$ is in terms of the moments and/or cumulants of $G(\Gamma)$ (6). A prescription for calculating the i^{th} cumulant in terms of the i^{th} and lower moments has been given (8). For the ternary solution light scattering experiment, where the "visible" tracer is present only in small quantity, $G(\Gamma)$ may be written as

$$G(\Gamma) = \int_0^\infty w(M) M P(\theta, M) \delta(\Gamma - \Gamma(M)) dM / \int_0^\infty w(M) M P(\theta, M) dM \quad (5)$$

where $w(M)$ is the weight fraction of tracer species in the visible polymer sample, $P(\theta, M)$ is the corresponding scattering form factor, and $\delta(x)$ is the Dirac delta function. In the following, it is assumed that θ is sufficiently small so that $P(\theta, M) = 1$ for all M . Substitution of specific expressions for $w(M)$ allows explicit calculation of the moments and cumulants, and thus $g(t)$.

The Schultz and the log-normal distributions are commonly employed functions for describing molecular weight polydispersity (9). The corresponding expressions for $w(M)$ for these two distributions may be written as

$$w(M) = y^{z+1} M^z e^{-My} / H(z+1) \quad (6)$$

and

$$w(M) = (1/\sigma M_0 \sqrt{2\pi}) \exp(\sigma^2/2) \exp\{-(\ln M - \ln M_0)^2/2\sigma^2\} \quad (7)$$

respectively. In equation (6), y and z are parameters of the distribution which are related to the number and weight average molecular weights by $M_n = z/y$ and $M_w = (z+1)/y$; thus the polydispersity, M_w/M_n , is given by $(z+1)/z$. $H(x)$ is the familiar gamma function. In equation (7), M_0 and σ are the corresponding parameters related to the number and weight average molecular weights by $M_n = M_0 \exp(\sigma^2/2)$ and $M_w = M_0 \exp(3\sigma^2/2)$, so that $M_w/M_n = \exp(\sigma^2)$.

Substitution of an expression like (6) or (7) into (5) and subsequently into (3), with the postulate that $\Gamma \sim M^{-\nu}$, allows evaluation of the moments and thus the cumulants of the electric field autocorrelation function in terms of the polydispersity and the molecular weight power law exponent. It should be noted that when a two parameter distribution such as those given in equations (6) and (7) is substituted into (3), equation (3) can be put into a form that is independent of absolute molecular weight. Thus, for a given power law exponent, ν , dimensionless master curves for the autocorrelation functions can be developed which do not depend upon absolute molecular weight, but only upon the breadth of the molecular weight distribution.

For estimating the relative values of the cumulants in various diffusion regimes, three molecular weight power law exponents are of particular interest: $\nu = 0.5$, 1.0 , and 2.0 , corresponding

to the Zimm, Rouse, and reptation predictions respectively. These exponents were chosen for illustration only; there is considerable evidence that the molecular weight power law exponent varies smoothly as a function of matrix concentration. In general, the correlation function itself is best evaluated by numerical integration, but for the particular case of the Schultz distribution, the normalized cumulants can be calculated quite simply, for small polydispersities. The normalized i^{th} cumulant, κ_i/κ_1^i , is the relevant quantity in the Taylor series expansion of the natural logarithm of $g(t)$:

$$\ln(g(t)) = \sum_{i=1}^{\infty} (-1)^i (\langle \Gamma \rangle t)^i (1/i!) \kappa_i/\kappa_1^i \quad (8)$$

The results of these calculations are presented in Table I. The crucial condition for successful application of cumulant analysis is that the series converge quickly, i.e. that only one or two terms in the expansion are necessary to fit the data. It can be seen immediately from Table I that in the reptation regime the coefficients are not decreasing rapidly enough. In a typical experiment, the sample time is chosen to give several e-folds of decay over the available data channels; in other words the data extend to $\langle \Gamma \rangle t \cong 3-6$. Thus, in the reptation regime, for a polydispersity of 1.05, even though the coefficient of $(\langle \Gamma \rangle t)^5$ in equation (8) is only about 1% of the coefficient of $\langle \Gamma \rangle t$, the term itself is equal in magnitude to the first term when $\langle \Gamma \rangle t \cong 3$. For higher polydispersities, the situation is much worse.

The effect on the autocorrelation function can be seen directly from the plots in Figures 1 and 2, for the Rouse and reptation cases respectively. In these figures the natural logarithm of the correlation function (normalized to 1 at $t=0$) is plotted against the dimensionless time, $\langle \Gamma \rangle t$. In each case the correlation functions, as expressed in equation (3), have been evaluated numerically for polydispersities of 1.00, 1.05, 1.10, 1.20, 1.50, using the Schultz distribution. The correlation functions obtained via the log-normal distribution for small polydispersities are virtually indistinguishable from these (at higher values of the polydispersity there is some deviation at larger $\langle \Gamma \rangle t$). Analysis of individual cumulant terms for each distribution, for a given polydispersity, reveals that the mean decay rate, $\langle \Gamma \rangle$, is the same for both distributions regardless of the power law exponent, ν , but that the higher cumulant terms can be quite different (see Table I). One implication of this observation is that if data were to be fit successfully to a cumulant expression based on a particular approximate molecular weight distribution, no particular significance should be attached to the values obtained for the second or higher cumulants. This contrasts with the dilute solution case, where the normalized second cumulant or "quality factor" is frequently considered a measure of data reliability - in short, a large "quality factor" is not necessarily indicative of a broad molecular weight distribution in cases where the diffusion coefficient depends strongly upon molecular weight.

In Figure 3 an experimental autocorrelation function is shown, along with calculated correlation functions based on the Schultz distribution. These data were obtained for a solution with a polystyrene concentration of 0.79 mg/ml and a poly(vinyl methyl ether) concentration of 0.061 g/ml. The scattering angle was 90° , the sample time 120 microseconds, and 96 real-time channels were used.

In Figure 4 a typical experimental autocorrelation function is shown for the toluene/PSAN/PMMA system, along with the appropriate calculated correlation functions. In this case the PSAN concentration was 0.65% by weight and the PMMA 38% by weight. The scattering angle was 90° , the sample time was 10 milliseconds, and 64 real-time channels were employed.

TABLE I
 κ_i/κ_1^i for $M_w/M_n = 1.05$

	$\nu=1$	1	2	3	4	5	6
Schultz	1	0.05	1.05×10^{-2}	4.34×10^{-3}	2.79×10^{-3}	2.47×10^{-3}	
Log-normal	1	0.05	7.63×10^{-3}	2.10×10^{-3}	-8.53×10^{-4}	4.68×10^{-4}	
	$\nu=2$	1	0.228	0.212	0.420	1.446	8.042
Schultz	1	0.1025	0.488	-0.375	-1.348	-1.389	
Log-normal	1	0.1025	0.488	-0.375	-1.348	-1.389	

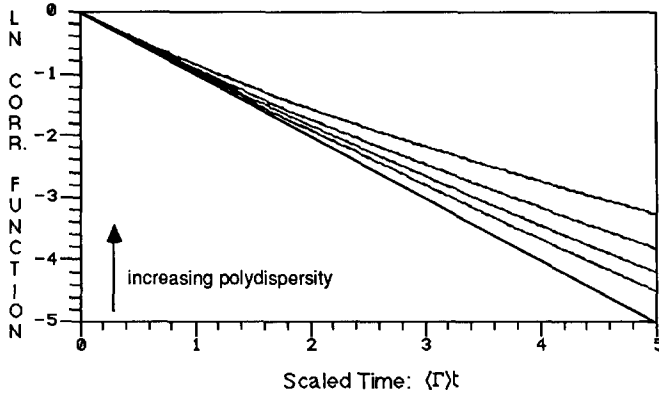


Figure 1 : Variation of the autocorrelation function with polydispersity for a system exhibiting Rouse-like behavior: $D \sim 1/M$.

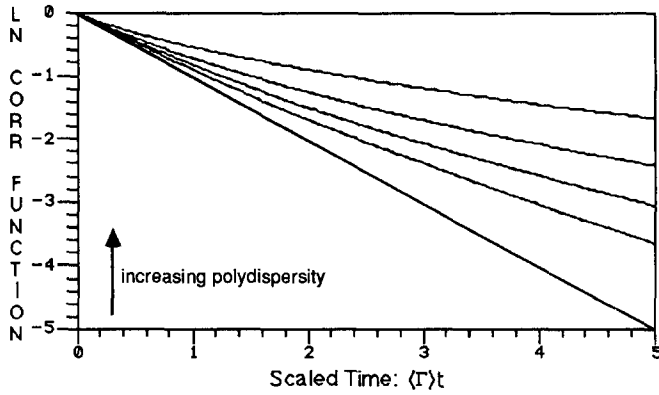


Figure 2 : Variation of the autocorrelation function with polydispersity for a system exhibiting reptation behavior : $D \sim 1/M^2$.

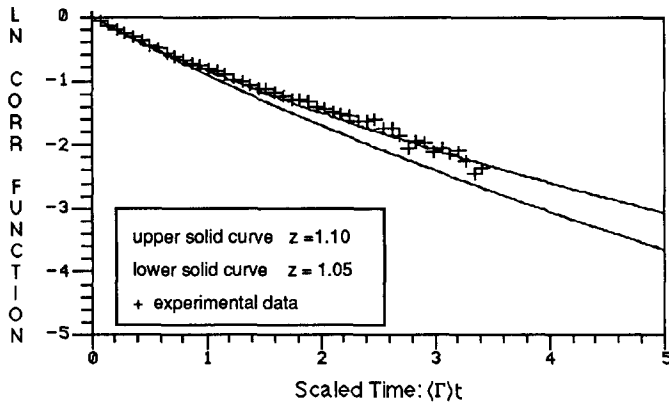


Figure 3 : Comparison of the deviation from single exponential behavior predicted by the Schultz distribution with experimental data on the system o-fluorotoluene/PS/PVME.

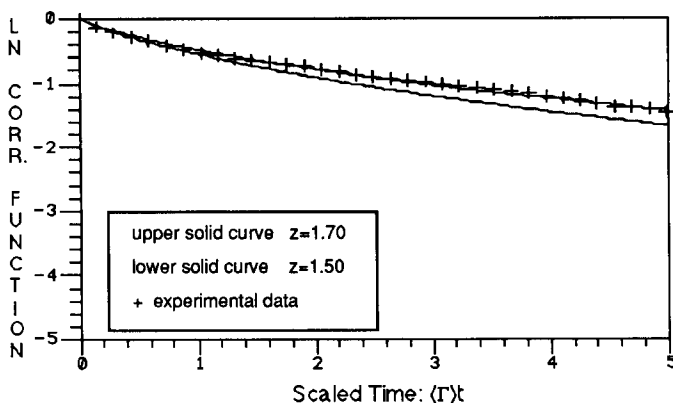


Figure 4 : Comparison of the deviation from single exponential behavior predicted by the Schultz distribution with experimental data on the system toluene/PSAN/PMMA.

The main conclusion to be drawn from these data is that indeed the experimental autocorrelation functions display a strong deviation from single exponential behavior, and that this deviation is comparable in form and magnitude to that predicted. It is apparent that in both of these examples the data are in better agreement with calculations using a higher polydispersity index than that supplied by the manufacturer. It is not yet possible to determine whether this observation really reflects a greater polydispersity, or whether the theoretical analysis is not complete. Furthermore, there are sources of uncertainty in the way these plots are generated. In the first instance, a value of $\langle \Gamma \rangle$ must be estimated *a priori* to plot the data versus the reduced time $\langle \Gamma \rangle t$. Also, the molecular weight exponent ν must be assumed; for the PS/PVME solution in particular, there is evidence that this system at the specified concentrations does not fall in the reptation regime (10). It is worth noting that these results are not very sensitive to uncertainties in the baseline determination.

The problem of extracting the mean decay rate in this type of experiment is another example of the very general problem of analyzing a decay curve consisting of a continuous distribution of exponentials. A wide variety of possible algorithms have been proposed and found to be effective under various circumstances (11, 12). For the case of diffusion in ternary solutions, the general problem is reduced to a more tractable one by two facts, namely that the only desired piece of information is a well-characterized mean decay rate, and that an *a priori* estimate of the width of the molecular weight distribution coupled with some knowledge of the applicable regime of diffusion behavior allows one to estimate the expected deviation of the correlation function from a single exponential. In addition to the various methods referenced above, at least two other approaches merit consideration because of their potential simplicity: a modified cumulants technique, and an integration method. A sufficiently broad range of data (in terms of polydispersities and known diffusional regimes) are not yet available to permit detailed assessment of the success of these procedures.

The modified cumulants technique may be appropriate for samples with smaller polydispersities (for example, < 1.10), and takes advantage of the multiple sample time option found on certain commercially-available correlators. The basic concept is the recognition of the fact that as $\langle \Gamma \rangle t \rightarrow 0$ a given cumulant expansion (1st, 2nd, 3rd, or 4th order) should become progressively more capable of describing the correlation function accurately. Clearly, in practice this will not always result in a better fit as the range of the independent variable is contracted. However, for a given set of data extending over approximately 5 e-folds, the fit can be repeated over successively smaller ranges of $\langle \Gamma \rangle t$ (truncating at the high end). The resulting $\langle \Gamma \rangle_a$ values (where $\langle \Gamma \rangle_a$ is the apparent average decay

rate) can be plotted against the $\langle \Gamma \rangle_a t_{\max}$ value of the last point included in the fit. In our experience, this type of plot frequently has a plateau over a considerable range (for example, $\langle \Gamma \rangle_a t_{\max} \cong 0.5$ to 2), with the plateau value being taken as the best estimate of $\langle \Gamma \rangle$. In less favorable cases it may be desirable to extrapolate the $\langle \Gamma \rangle_a$ values to $\langle \Gamma \rangle_a t = 0$, but not including those $\langle \Gamma \rangle_a$ values obtained at very short reduced times, which are demonstrably in error. Confidence in the results thus obtained can be increased by performing the same operation using different order expansions, and ensuring that the results are identical within acceptable limits. To improve the reliability of the data at smaller $\langle \Gamma \rangle$ values, the multiple sample time option can be used to concentrate the available real-time channels into the early portion of the correlation function. The adequacy of the final fit can also be checked by comparing the full correlation function to a calculated one, as in Figure 3, if the polydispersity and molecular weight power law exponent are known. Furthermore, linearity of a plot of $\langle \Gamma \rangle$ versus q^2 can be taken as additional evidence of the correctness of the fit.

The second method of data analysis to be considered here consists of an appropriate numerical integration of the autocorrelation function, $g(t)$. Consider

$$\int_0^{\infty} t^x g(t) dt = \int_0^{\infty} t^x dt \int_0^{\infty} G(\Gamma) e^{-\Gamma t} d\Gamma ; \quad x > -1 \quad (9)$$

Reversing the order of integrations, and performing the time integration yields:

$$\int_0^{\infty} t^x g(t) dt = H(x+1) \int_0^{\infty} \frac{G(\Gamma)}{\Gamma^{x+1}} d\Gamma = H(x+1) \langle 1/\Gamma^{x+1} \rangle \quad (10)$$

which, for $x=0$, reduces to

$$\int_0^{\infty} g(t) dt = \langle 1/\Gamma \rangle \quad (11)$$

where $\langle 1/\Gamma \rangle$ is the mean inverse decay rate. $\langle 1/\Gamma \rangle^{-1}$ can thus be considered a type of mean decay rate. Of course, for a single exponential decay $\langle 1/\Gamma \rangle^{-1} = \langle \Gamma \rangle = \Gamma_0$. For the Schultz distribution, it is straightforward to show that

$$\langle \Gamma \rangle / \langle 1/\Gamma \rangle^{-1} = H(z+2-v) H(z+2+v) / H^2(z+2) \quad (12)$$

The ratio of $\langle \Gamma \rangle / \langle 1/\Gamma \rangle^{-1}$ is approximately 1.01 for $M_w/M_n=1.05$ and $v=0.5$, and 1.20 for $v=2$. Clearly, this method yields a different average decay rate than those methods based upon differentiation of the correlation function, but the simplicity with which $\langle 1/\Gamma \rangle^{-1}$ can be extracted - without reliance upon any particular theoretical or empirical fitting function or upon any particular distribution function - makes this method an attractive alternative for extracting a well-characterized decay rate. This decay rate will differ from $\langle \Gamma \rangle$ in absolute magnitude, but it may exhibit the same dependence upon concentration, molecular weight, and scattering wave vector.

For real data, the numerical integration cannot be carried out to $t = \infty$, so that the numerical integration procedure yields an approximation to $\langle 1/\Gamma \rangle$. However, for a single exponential decay, it can be shown that

$$\langle 1/\Gamma \rangle_a^{-1} = \Gamma_0 / [1 - \exp(-\Gamma_0 t_{\max})] \quad (13)$$

where $\langle 1/\Gamma \rangle_a^{-1}$ is inverse of the apparent inverse decay rate. For $\Gamma_0 t_{\max} = 3$, $\langle 1/\Gamma \rangle_a^{-1} \cong 1.05 \Gamma_0$. Termination of the integration at the last "reliable" value of the correlation function should result in no appreciable error in the value of the decay rate. In any event, the errors inherent in this technique can be readily estimated by numerical integration over a given distribution, so that bounds on the errors involved can be evaluated. In addition, an extrapolation might also be possible by plotting $\langle 1/\Gamma \rangle_a$ versus t_{\max} .

It is reasonable to consider whether the dramatic effect of even a small polydispersity on the experimental signal, as demonstrated here, is observed in other experiments employed to measure translational diffusion in entangled polymer systems. In particular, the forced Rayleigh scattering and pulsed-field gradient NMR techniques have been used extensively in this area (13,14). In the NMR case, the influence of polydispersity has very recently been considered by Fleischer, with a similar conclusion, i.e. the effect is important and correctable (15). In the forced Rayleigh scattering case, the deviation from a single exponential decay for reptating polymers has been predicted by

Bernard and Noolandi (16); however, we are not aware of any extensive comparison of data and theory which utilizes this kind of approach. The situation is more complicated, from a practical point of view, than the dynamic light scattering experiment because of the nature of the experimental signal. Specifically, the presence of a coherent background term adds another parameter to the nonlinear regression fit which can interact strongly with the cumulant terms to make convergence to a unique solution difficult. Furthermore, the case considered by Bernard and Noolandi was for singly-labelled chains, resulting in a number-averaged signal. Presumably the multiply-labelled molecules used in some studies would lead to a weight-averaged signal, resulting in a different influence of polydispersity.

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