J. Am. Chem. Soc. **1995,** *117,* 7965–7970

Determination of Molecular Weight Distributions for Polymers by Diffusion-Ordered NMR

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Received April 10, 1995®

Abstract: Diffusion-ordered NMR spectroscopy (DOSY), a technique based on pulsed field gradient NMR (PFGNMR), was used to characterize molecular weight distributions for samples of poly(ethylene oxide) in D_2O. The distribution of diffusion coefficients $G(D)$ was obtained by analysis of PFGNMR data with a modified version of the well-known constrained regularization program CONTIN. Regularization was considerably improved for broad distributions by setting the weights c_m in CONTIN's quadrature formula equal to $(D_m/D_{\max})^{x_m}$ where $D_{\max}$ is the diffusion coefficient corresponding to the maximum in $G(D_m)D_m$ and m is an index. Here x_m varies linearly from +2 to −2 with $\log(D_m)$ across the distribution. This amounts to enhancing low amplitude regions of $G(D)D$ during analysis. The estimated distribution was then converted to the mass weighted distribution of molecular weights by means of the relation $D = 10^{-7.62}\ M^{-0.62}$ (with D in units of $m^2\ s^{-1}$) obtained from experiments on monodisperse reference standards. In this study spin relaxation rates were independent of molecular weights and intermolecular averaging effects were insignificant. As an illustration, molecular weight distributions were determined for two broadly distributed samples. The number and weight average molecular weights and the polydispersities agreed well with values provided by the manufacturer when the PFGNMR data sets had signal-to-noise ratios greater than 500.

Introduction

High polymers are characterized by a distribution of molecular weights. Some information about the width of the distribution can be obtained by measuring different average molecular weights for a polymer, *e.g.* number average and weight average. However, knowledge about the contribution of each molecular size requires that the full molecular weight distribution (MWD) be determined. MWDs are of fundamental importance in polymer science because (a) the distributions give evidence about the type of polymerization employed and (b) the distributions determine the physical properties of polymer mixtures.

The determination of MWDs has been approached by both chemical and physical methods, but for higher molecular weights ($M > 25\,000$) physical methods are more reliable. Gel permeation chromatography (GPC) and dynamic light scattering (DLS) are popular methods for the determination of MWDs.[1,2] Both of these methods detect transport rates that depend on molecular size and require calibration or data transformation to obtain the MWD. Pulsed field gradient NMR (PFGNMR) is also sensitive to molecular size and provides a method for the determination of weight average molecular weights for polymers.[3–7] Through enhancements and extensions of PFGNMR, it is now possible to obtain diffusion ordered NMR (DOSY) spectra of polydisperse samples that display the complete mass weighted distribution of tracer diffusion coefficients at each chemical shift.[8]

In this article we propose a DOSY based method for the determination of MWDs. The constrained regularization program CONTIN[9,10] is used as in previous DOSY studies of polydisperse samples,[8,11] but special modifications are made to obtain accurate descriptions of broad distributions of diffusion coefficients. These modifications give major improvements in the accuracy of measured molecular weight distributions. Extensive analyses of simulated and experimental PFGNMR data sets with various signal-to-noise (S/N) ratios have been performed to establish the range of validity of the DOSY/CONTIN method. Poly(ethylene oxide) (PEO) samples with narrow and broad MWDs were studied, and the scaling law relating mass weighted tracer diffusion coefficients (D) and molecular weights was determined with standard monodisperse PEO samples. For polydisperse samples the distributions of diffusion coefficients were converted to MWDs by means of the scaling relation. The MWDs were then used to calculate average molecular weights and polydispersities for comparison with the results of GPC and viscosity measurements. In all cases the results were in satisfactory agreement with data provided by the manufacturer.

We note that the DOSY method is analogous to the DLS method.[12] Both experiments require the inverse Laplace transformation (ILT) of experimental data sets to determine distributions of diffusion coefficients. Therefore, the improvements reported here in the CONTIN analyses also apply to DLS. In general the DOSY and DLS methods complement each other. Special features of MWD determinations by means of DOSY are the following: (a) the instrumentation (while expensive) is widely available, (b) different molecular species in a mixture can be distinguished by their chemical shifts, and (c) the signal

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® Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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intensity depends on the number of NMR active nuclei in each molecule, a quantity proportional to the molecular mass. In principle, polymer solutions in heterogeneous systems such as turbid suspensions and porous media can be studied. The primary requirements are (a) high S/N ratio (>500), (b) low concentrations so that molecules act independently, and (c) nuclear relaxation times that are long and not strongly dependent on molecular weight. In contrast to this, the DLS method usually gives high S/N ratios for polymers, has signal intensities that depend on the square of the molecular mass, requires transparent samples, and usually permits no resolution of molecular species.

Background

Standard PFGNMR experiments employ two matched gradient pulses separated by the interval $\Delta - \delta$, each having the effective area $q = \gamma g \delta$ where γ is the magnetogyric ratio, and g and δ are the amplitude and duration of the gradient pulses, respectively.[13] The signal is detected either as a free induction decay (LED experiment) or a half echo (spin echo or stimulated echo experiments). Fourier transformation with respect to time then yields a spectrum in which the peak intensities are given by:

$$f(q) = \int R(T_1,T_2)\, G(D) \exp[-Dq^2(\Delta - \delta/3)]\, \mathrm{d}D \quad (1)$$

where $R(T_1,T_2)$ specifies the attenuation resulting from nuclear spin relaxation and $G(D)$ is the mass weighted distribution of tracer diffusion coefficients (D). For monodisperse samples $G(D)$ is a delta function; and a plot of $\ln[f(q)]$ versus $q^2(\Delta - \delta/3)$ yields a straight line with a slope equal to the diffusion coefficient D. With polydisperse samples, however, this type of plot shows curvature that depends primarily on the characteristics of the distribution function $G(D)$.

The aim of the analysis of PFGNMR data is to obtain a function $G(D)$ that can be converted into $W(M)$, the mass weighted MWD. This goal may be complicated by two factors. First, the relaxation factor $R(T_1,T_2)$ may depend on the molecular weight so that the product $R(T_1,T_2)G(D)$ cannot be easily separated.[6] In the LED experiment where all the time intervals except δ are held constant, molecules with small values of T_1 and T_2 are underrepresented in the integral. In general this complication cannot be ignored, and must be evaluated for each type of polymer sample. However, spin relaxation rates in high polymers are often determined by segmental motion (local) rather than overall tumbling rates so that $R(T_1,T_2)$ is approximately independent of the molecular weight. In the following we assume that $R(T_1,T_2)$ is a constant, an assumption that is consistent with previous experimental studies.[14,15]

The second complicating factor arises from intermolecular interactions. A consequence of these interactions is a "microaveraging effect" in which the effective diffusion coefficient of a molecule depends on the molecular weights of neighboring molecules.[6,16] The solute molecules tend to diffuse at the same rate, and the nonlinearity of the semilog $f(q)$ plots is decreased. All physical methods for the measurement of molecular weights require that the molecules contribute independently.[17] In order to avoid molecular overlap and the resulting averaging effects, the concentrations must be kept low and extrapolation to zero concentration may be required.

Data Transformation

Equation 1 shows that the signal $f(q)$ is the Laplace transform of the distribution function $G(D)$ with respect to D. The inversion of the Laplace transform to obtain $G(D)$ from the signal is an ill-posed problem. This means that the answer cannot simply be extracted from the data, and strategies are required to obtain an estimate of $G(D)$. A number of inverse Laplace transform methods including exponential sampling, constrained regularization, and maximum entropy have been developed for this problem.[18] The constrained regularization program CONTIN is competitive with the other methods, and has the advantage of being widely distributed and extensively tested.[19] Also, CONTIN offers great flexibility through numerous user defined control variables.[10]

According to eq 1, the experimental data set at a given chemical shift can be represented as a set of intensities y_k versus t_k, the incremented values of $q^2(\Delta - \delta/3)$. With the program CONTIN, the inversion of eq 1 to obtain $G(D)$ is handled by solving the set of linear algebraic equations,[9]

$$y_k = \sum_{m=1}^{N_g} c_m\, F_k(\lambda_m,t_k)\, s(\lambda_m) + \sum_{i=1}^{N_L} L_{ki}\beta_i \quad (2)$$

to determine the unknown function $s(\lambda)$ at N_g grid points λ_m. Here the c_m are weights of the quadrature formula, and $F_k(\lambda_m,t_k)$ are known decay functions. The second term on the right-hand side of eq 2 permits a background to be included, *e.g.* a constant background β_1 results from the choice $N_L = 1$ and $L_{k1} = 1$. In the present context, $s(\lambda)$ is associated with the distribution of diffusion coefficients and $F_k(\lambda_m,t_k) = \exp(-\lambda_m t_k)$, where λ corresponds to D.

Applications of CONTIN to simulated data and comparisons with other methods have recently been reviewed by Štěpánek.[18] The basic problem is to eliminate oscillatory solutions which are not filtered by the ILT, but which have no physical meaning. With CONTIN the solution is constrained by (a) absolute prior knowledge, (b) statistical prior knowledge, and (c) the principle of parsimony. Of those solutions not eliminated by (a) and (b), parsimony requires that the simplest be chosen. Essentially this means that solutions are selected for smoothness and the minimum number of peaks. The selection process can be implemented by penalizing solutions on the basis of integrated squared second derivatives.

The standard application of CONTIN is quite successful in recovering distribution functions from simulated data sets in the absence of noise. But in the presence of noise CONTIN tends to give smaller average diffusion coefficients $\langle D \rangle$ and reduced standard deviations $(SD)/\langle D \rangle$ relative to the true values, especially for broad distributions. The finding by Jakeš that the standard application of CONTIN over-smooths the $G(D)$ distribution in the region of small D while seriously undersmoothing for large D values is particularly important for the present study.[20] This effect has to do with the equality of the penalty for different ranges of D values since standard CONTIN penalizes the $G(D)$ function on the logarithmic axis. Note that two separated peaks with identical areas in a plot of $G(D)$ versus D will appear quite asymmetric when $G(D)$ is plotted versus

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log(D). In order to restore the equality of areas, $G(D)D$ instead of $G(D)$ must be plotted with respect to log(D), *i.e.* $G(D)\,\mathrm{d}D = G(D)D\,\mathrm{d}(\ln D)$. The result of unequal smoothing is that noise can produce a secondary peak in the large D region of the $G(D)D$ versus log(D) plot. When $G(D)$ splits into two peaks, $\langle D\rangle$ for the main peak shifts to a smaller value and SD/$\langle$D$\rangle$ decreases.

Regularization can be improved by switching to "integration off" in CONTIN, *i.e.* setting the control parameter IQUAD = 1 so that $c_m = 1$. In this case $G(D)D$ rather than $G(D)$ is analyzed on the logarithmic axis. With this modification, most of the "noise peak" disappears in the CONTIN output and the main peak gives more accurate values of $\langle$D$\rangle$ and SD/$\langle$D$\rangle$. This choice of c_m improves the estimation of $G(D)$ by means of eq 2 and provides a clue for further enhancements. Extending this idea, we propose that c_m be replaced with $(D_m/D_{\max})^{x_m}$ in eq 2 where x_m is incremented from +2 to −2 as log(D) ranges from −12 to −9 in our analyses. The range of log(D) will, of course, depend on the distribution being studied; and in general it must be set as narrow as possible consistent with the distribution having zero amplitude at both limits. Typically at $x_m = \pm 1$, the amplitude of $G(D)D$ is about 10% of the maximum value. With this choice, $c_m = 1$ near the center or maximum of the distribution (where $D = D_{\max}$) while providing the necessary amplitude enhancement where the amplitude is small. Thus, c_m serves as a microscope with adjustable amplification that enhances the ability of CONTIN to analyze regions of low amplitude, here the wings of the diffusion distribution curve. It should be noted that the choice of c_m values depends on the function to be fitted so that special attention can be given to the region of interest. The CONTIN analysis then returns the distribution $G(D_m)D_m/c_m$, and $G(D_m)$ can easily be extracted.

The final step in determining the distribution of molecular weights requires that $G(D)$ be transformed into either the number weighted MWD, $n(M)$, or the mass weighted MWD, $W(M)$, where $W(M) = n(M)M$. For example, $W(M)$ can be obtained with the equation $W(M) = G(D)\,|\mathrm{d}D/\mathrm{d}M|$ if the relationship between D and M is known. The scaling law must be established for each polymer system, but for gaussian random coils we expect a relation of the form:

$$D = AM^{\alpha} \tag{3}$$

In terms of the distributions $W(M)$ and $n(M)$, the number weighted molar mass $\bar{M}_n$ and the mass weighted molar mass $\bar{M}_w$ are given by

$$\bar{M}_n = \frac{\int n(M)\,M\,\mathrm{d}M}{\int n(M)\,\mathrm{d}M};\quad \bar{M}_w = \frac{\int W(M)\,M\,\mathrm{d}M}{\int W(M)\,\mathrm{d}M} \tag{4}$$

and the polydispersity is defined as $\bar{M}_w/\bar{M}_n$.

Simulations

Simulated MWDs with added noise provide a good test of the analysis methods. We have chosen the log normal distribution to represent W(M) for a typical polymer sample. Thus[21]

$$W(M) = \frac{1}{M(\ln\sigma)\sqrt{2\pi}}\exp\left(-\frac{(\ln M - \ln M_0)^2}{2(\ln\sigma)^2}\right) \tag{5}$$

Values of $W(M)$ were calculated at 128 values of ln$M$ equally spaced in the range $\ln M_0 \pm 4\ln\sigma$, and M_0 was set equal to 10^5. The calculations were repeated with σ values ranging from 1.25 to 3.25, and $W(M)$ was converted to G(D) according to the scaling law in eq 3 with $A = 10^{-7.5}$ and $\alpha = -0.6$ when D is in units of m^2 s^{-1}. PFGNMR data sets were then generated by means of eq 1 for sets of q values, and Gaussian noise with RMS deviation of 10^{-3} relative to the largest signal (smallest q value) was added to each data point.

The simulated data sets were analyzed by means of CONTIN with three different choices of weighting factors to obtain $\langle D\rangle$ and SD/$\langle D\rangle$. The results are shown in Figures 1 and 2 as functions of σ for standard CONTIN (△), CONTIN with c_m = 1 (○), and CONTIN with computed c_m values (●). It is clear that for broad distributions ($\sigma > 2$), standard CONTIN loses accuracy. Both $\langle D\rangle$ and SD/$\langle D\rangle$ are usually smaller than the input values (solid curves) as a consequence of the appearance of a noise peak in the computed distribution. This effect is illustrated in Figure 3 which shows a simulated distribution $G(D)D$ (solid line) with $\sigma = 3.2$ for comparison with distribu-

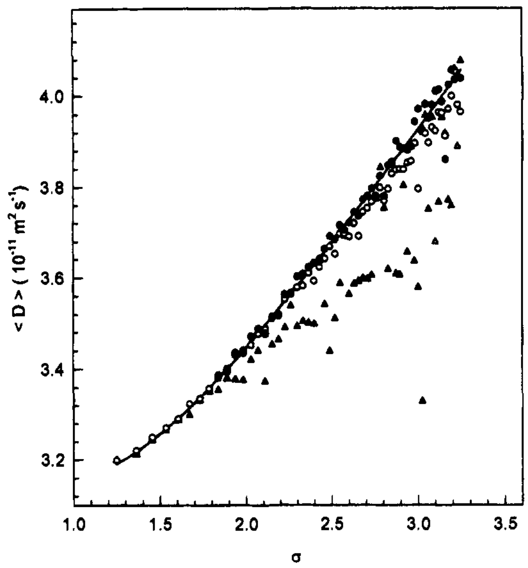

Figure 1. $\langle D\rangle$ versus σ for the simulation (solid line), standard CONTIN analysis (△), CONTIN with c_m = 1 (○), and CONTIN with computed c_m values (●) (see text).

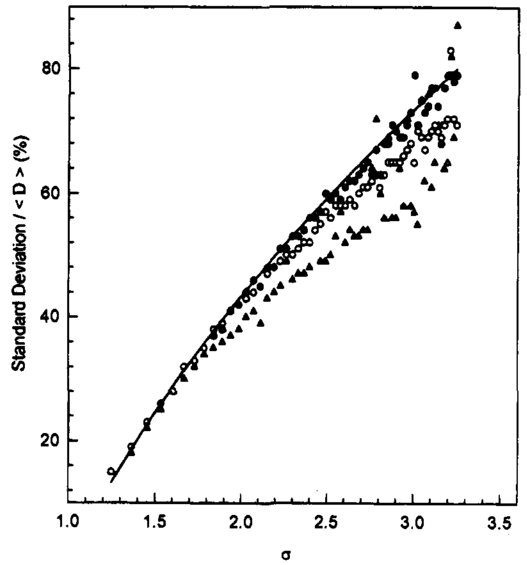

Figure 2. Standard deviation/$\langle D\rangle$ versus σ for the simulation (solid line), standard CONTIN analysis (△), CONTIN with c_m = 1 (○) CONTIN with computed c_m values (●) (see text).

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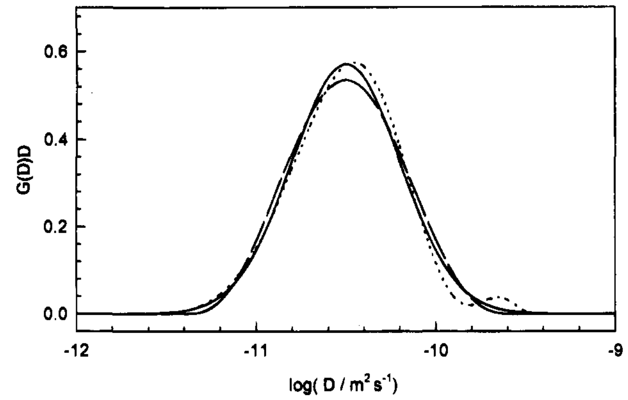

Figure 3. The normalized distribution $G(D)D$. Simulated distribution with $M_0 = 10^5$ and $\sigma = 3.2$ (solid line), the standard CONTIN estimate (dotted line), and CONTIN estimate with $c_m = 1$ (dashed line). The number of grid points N_g in the CONTIN analyses was 31, and cubic splines were used to obtain smooth displays.

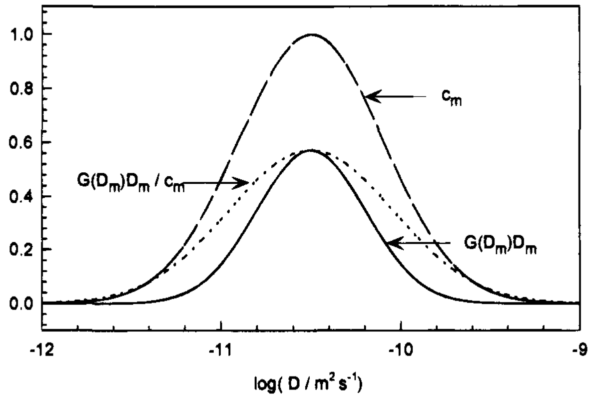

Figure 4. The simulated distribution $G(D)D$ with $M_0 = 10^5$ and $\sigma = 3.2$ (solid line), computed c_m values (dashed line), and the effective distribution to be estimated by CONTIN with the computed c_m values (dotted line). Cubic splines were used to obtain smooth displays from the 31 c_m values.

tions obtained with standard CONTIN (dotted line) and CONTIN with $c_m = 1$ (dashed line).

We note that even with noise levels as low as 1 part in 10^3 the results calculated for the main peak returned by standard CONTIN fluctuate wildly as σ changes. More accurate averages can be obtained from the bimodal distributions by including both peaks in the calculation. However, the secondary peak tends to vanish and the averages show considerable improvement when $c_m = 1$; and even more accurate and consistent results are obtained with computed c_m values as described above. In Figure 4 we show the simulated curve $G(D_m)D_m$ (solid line), the c_m values (dashed line), and the effective function $G(D_m)D_m/c_m$ analyzed by CONTIN (dotted line). The actual distribution $G(D)D$ recovered from the CONTIN analysis with a computed c_m set is shown in Figure 5 (●) with the simulated log normal distribution (solid line).

After analysis with CONTIN, the $G(D)$ curves are converted to $W(M)$ distributions and the averages $\bar{M}_n$ and $\bar{M}_w$ and the polydispersity $\bar{M}_w/\bar{M}_n$ are calculated. The results are displayed in Figures 6 through 8. In the $\bar{M}_n$ calculation (Figure 6), standard CONTIN shows unacceptable large errors for $\sigma > 2$. CONTIN with $c_m = 1$ is better and CONTIN with computed c_m's gives the best estimate. However, the situation is different for $\bar{M}_w$ (Figure 7) where larger molecules (lower diffusion coefficients) receive heavier weighting. Here standard CONTIN, which emphasizes the region of low diffusion coefficients, is more accurate than the calculation with $c_m = 1$. But as before, the calculation with computed c_m's is clearly the best. The calculated polydispersity versus input σ plot in Figure 8 also reveals differences in the accuracy of the calculation methods. In all cases examined, the method with computed c_m's provides the best estimate of $G(D)$ and $W(M)$. Further simulations with different levels of noise show that this method can improve the fitting results for the signals with S/N ratios greater than 500.

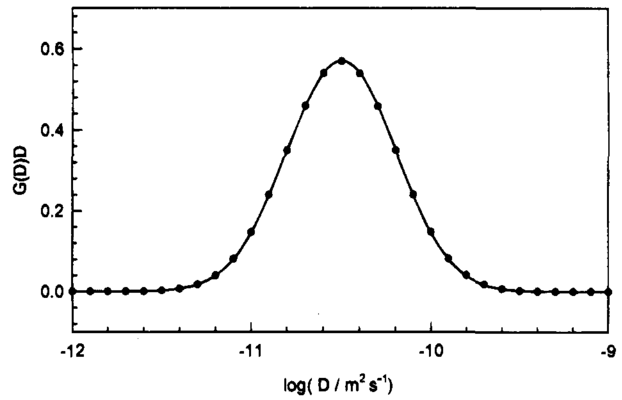

Figure 5. The simulated distribution $G(D)D$ (solid line) and the estimate obtained by CONTIN with computed c_m values (●).

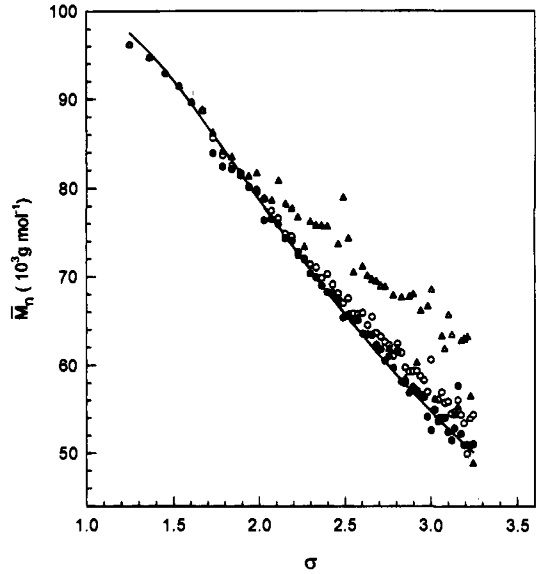

Figure 6. The number average molecular weight $\bar{M}_n$ versus the width σ of the simulated distribution obtained by standard CONTIN analysis (△), CONTIN with $c_m = 1$ (○), and CONTIN with computed c_m values (●). The solid line indicates the input values.

Experimental Section

Deuterium oxide (D, 99.9%) from Cambridge Isotope Laboratories was used as the solvent for all samples. The poly(ethylene oxide) samples (PEO1K, PEO3K, PEO5K, PEO27K), kindly provided by Professor J. M. DeSimone, were prepared with the standard living anionic polymerization technique.[22] The molar masses for these samples were obtained by GPC on a Waters 150-C gel permeation chromatograph with Ultrastyra-gel columns having pore sizes of 100, 500, 10^3, 10^4, and 10^5 Å and using THF as eluant. Polystyrene standards (Showa Denko) were used to calibrate the molar masses. Other PEO samples were purchased from American Polymer Standards Corp. The samples and their reported molecular weights are listed in Tables 1 and 2. All PEO samples were used as received without further purification.

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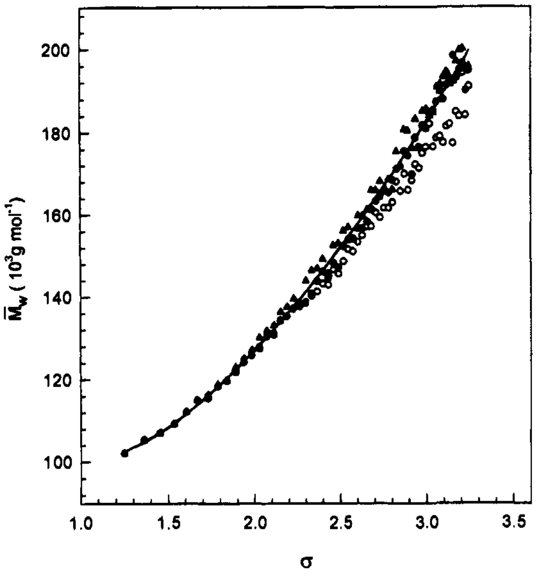

Figure 7. The weight average molecular weight $\bar{M}_w$ versus the width σ of the simulated distribution obtained by standard CONTIN analysis (△), CONTIN with $c_m = 1$ (○), and CONTIN with computed c_m values (●). The solid line indicates the input values.

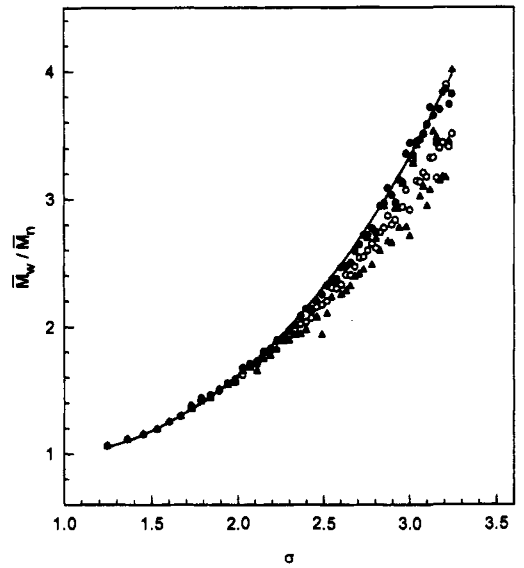

Figure 8. The polydispersity $\bar{M}_w/\bar{M}_n$ versus the width σ of the simulated distribution obtained by standard CONTIN analysis (△), CONTIN with $c_m = 1$ (○), and CONTIN with computed c_m values (●). The solid line indicates the input values.

Table 1. Monodisperse Poly(ethylene oxide) Samples

sample no.	data source	$\bar{M}_n$ (10^3 g mol^{-1})	$\bar{M}_w$ (10^3 g mol^{-1})
PEO1K	GPC	1.2	1.4
PEO3K	GPC	3.4	3.8
PEO5K	GPC	5.1	5.6
PEO27K	GPC	27.3	33.4
PEO100K	manufacturer	103	110
PEO240K	manufacturer	240	250
PEO500K	manufacturer	486	510

Table 2. Polydisperse Poly(ethylene oxide)

sample type	$\bar{M}_n$ (10^3 g mol^{-1}) (manufacturer)	$\bar{M}_w$ (10^3 g mol^{-1}) (manufacturer)	$\bar{M}_n$ (10^3 g mol^{-1}) (DOSY)	$\bar{M}_w$ (10^3 g mol^{-1}) (DOSY)
PEO200K	47.0	204	46	180
PEO120K	36.5	123	35	110

The DOSY experiment has been described in detail elsewhere.[23,24] Instrumentation for the PFGNMR experiments includes a Bruker AC-250 spectrometer with computer controlled gradient drivers designed and constructed in-house.[25] Two probes custom built by Cryomagnet Systems, Inc., with actively shielded gradient coils (coil constants: 0.156 T m^{-1}A^{-1} and 0.1785 T m^{-1}A^{-1}) were used in these experiments.[26] In all NMR experiments, the probe temperature was maintained at 298 ± 1 K by the standard Bruker temperature control unit, and 5 mm sample tubes were used.

From 20 to 40 FIDs, each associated with a different q value (1×10^4 to 3×10^6 m^{-1}), were collected with an ASPECT-3000 computer in each experiment. In each case the maximum attenuation reduced the signal [illegible]% or less of its original intensity so that polydisperse polymer samples could be completely characterized. The LED pulse sequence[27] was employed with diffusion time ($\Delta = 105.5$ ms) and eddy current delay time ($T_e = 50$ ms). The data files were transferred via Bruknet from the ASPECT-3000 to a Silicon Graphics (SGI) workstation; and software package FELIX (Hare Research, Inc.) was used for Fourier transformations, phasing, and polynomial baseline corrections. All the analysis programs were written in FORTRAN on SGI workstations, and the diffusion coefficients and their distributions were determined with a version of CONTIN modified in-house.

Results and Discussion

Microaveraging. In order to test for microaveraging effects under our experimental conditions, a mixture of equal weights of the PEO5K ($\bar{M}_w \cong 5000$) and PEO100K ($\bar{M}_w \cong 100\,000$) samples at a total concentration of 1 g/L in D_2O was studied with PFGNMR. The best fit to a plot of $\ln[f(q)]$ versus $q^2(\Delta - \delta/3)$ for the methylene peak of PEO was found to contain fast and slow components with the diffusion coefficients 1.3×10^{-10} and 1.9×10^{-11} m^2 s^{-1}, respectively. This result matches within experimental error the diffusion coefficients obtained for samples containing only PEO5K (1.1×10^{-10} m^2 s^{-1}) and PEO100K (1.9×10^{-11} m^2 s^{-1}) at the same total weight percent of PEO. Therefore, we conclude that the microaveraging effect on diffusion coefficients resulting from intermolecular interactions is insignificant at concentrations of 1 g/L or lower.

Scaling Relation. The relationship between the mass weighted tracer diffusion coefficient D and mass average molar mass $\bar{M}_w$ was established for monodisperse PEO samples (1 g/L of PEO in D_2O) by measuring the diffusion coefficients for monodisperse samples with PFGNMR.[5] The results shown in Figure 9 verify that $\log(D)$ changes linearly with $\log(\bar{M}_w)$, and as expected the scaling relationship has the form $D = AM^{\alpha}$. Analysis of the data in Figure 9 shows that $A = 10^{-7.62}$ and $\alpha = -0.62$ with D in units of m^2 s^{-1} in good agreement with previous studies.[28]

Molecular Weight Distribution for PEO. As a test of the computed c_m method, MWD's were determined for two polydisperse PEO samples. The large amplitude of the methylene peak in these samples ensured that signal-to-noise ratios greater than 1000 could easily be achieved with concentrations as low as 1 g/L. The procedure was to analyze the $f(q)$ data set for the methylene signals first with standard CONTIN. Then based on the computed distribution function $G(D)$, $\langle D \rangle$, and SD values, a set of c_m values was generated. A CONTIN analysis was

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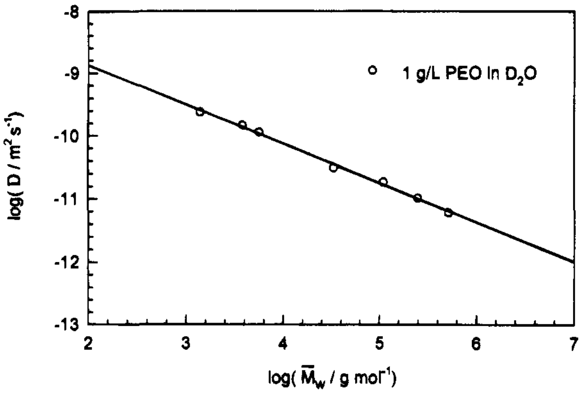

Figure 9. Log(D/m^2 s^{-1}) versus log($\bar{M}_w$/g mol^{-1}) for monodisperse PEO samples.

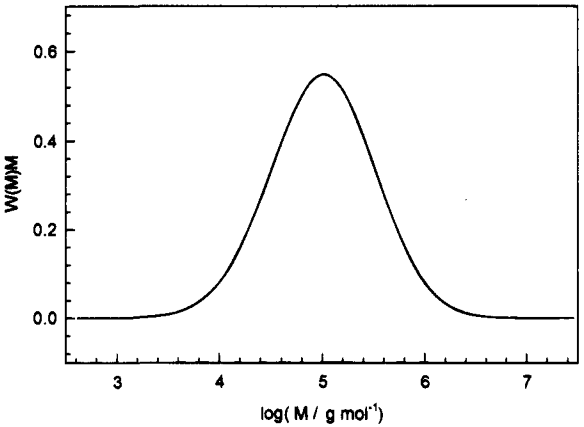

Figure 10. The MWD function $W(M)M$ for PEO200K obtained from CONTIN analysis with computed c_m values. The curve is a cubic spline display of 31 data points.

then performed with these weighting factors to obtain a better estimate of $G(D)$. After converting to MWD, the resulting $W(M)M$ for PEO200K is shown in Figure 10. Also, the molecular weights $\bar{M}_n$ and $\bar{M}_w$ of the two PEO samples obtained from CONTIN analyses with computed c_m's are listed in the Table 2 along with the data provided by the American Polymer Standards Corp. The agreement is quite satisfactory for these samples; and when appropriate conditions (described above) are met, the DOSY/CONTIN technique may be the method of choice for the determination of MWD's.

Diffusion ordered NMR offers several advantages for the determination of MWD's compared with standard methods. Sample preparation is simple and switching solvents is easy. Dust and impurities in the solution do not interfere as long as any additional signals can be resolved from the polymer peaks. Also, mixtures of polymers can be analyzed simultaneously if their chemical shifts are different. Finally, the relationship between the measured quantity (here diffusion coefficient) and molecular weight is not instrument dependent and can be used universally.

Conclusion

An improved pulsed field gradient NMR method has been reported for the determination of molecular weight distributions of polymer samples. This method makes use of the constrained regularization program CONTIN with a set of weighting factors (c_m) in the quadrature formula that depend explicitly on diffusion coefficients. With this modification, CONTIN gives a better estimate of the distribution of diffusion coefficients over the whole diffusion dimension, especially at the extremes where the amplitudes are low. Extensive simulations also show that the mass weighted molecular weight distribution $W(M)$ derived from $G(D)$ gives more accurate estimates of both weight average and number average molecular weights than can be obtained with standard applications of CONTIN. Weighting factors (c_m) that are dependent on the decay rate (diffusion coefficient) can also be used to improve CONTIN analyses in other applications, *e.g.* dynamic light scattering. Finally, we have demonstrated that diffusion-ordered NMR with the improved CONTIN analysis can provide accurate molecular weight distributions for polymers. The success of this method depends on good S/N ratios, relatively long (mass independent) nuclear relaxation times, and low concentrations so that microscopic averaging effects can be avoided. It should be noted that PEO is a particularly favorable example. In addition to mass independent relaxation rates, PEO has a strong ^{1}H signal and a simple NMR spectrum. Some other polymers may be less amenable to this type of analysis. However, sensitivity can be improved by using a modern high-field spectrometer in place of the 250 MHz system.

Acknowledgments. This work was supported in part under National Science Foundation Grant No. CHE 9222590. The authors thank Dr. Jun Lin in Prof. DeSimone's laboratory at UNC for PEO samples and GPC measurements.

JA951150Q