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ORIGINAL CONTRIBUTION

B. Håkansson
M. Nydén
O. Söderman

The influence of polymer molecular-weight distributions on pulsed field gradient nuclear magnetic resonance self-diffusion experiments

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B. Håkansson · O. Söderman (✉)
Division of Physical Chemistry 1
Center for Chemistry and Chemical
Engineering, Lund University
P.O. Box 124, S-221 00 Lund, Sweden

M. Nydén
Department of Applied Surface Chemistry
Chalmers University of Technology
S-412 96 Gothenburg, Sweden

Abstract The influence of polymer molecular-weight distributions on the outcome of pulsed field gradient (PFG) NMR self-diffusion experiments has been considered. The self-diffusion coefficient, *D*, of monodisperse poly(ethylene oxide) (PEO) polymers has been determined in order to accurately determine the scaling behavior of *D* both with molecular weight and concentration. In order to investigate the influence of polydispersity on the PFG NMR signal, a model system consisting of ten reasonably monodisperse PEO polymers was made, and the PFG NMR signal intensities were recorded at a low total concentration. The data were analyzed using both inverse Laplace transformation and nonlinear least-squares fitting to a prescribed distribution function of *D*. Finally, the molecular-weight distribution was obtained by use of the values of the scaling parameters. We also present some model calculations used to investigate the sensitivity of the degree of polydispersity on the NMR signal decays.

Key words Polymers · Poly(ethylene oxide) · Pulsed field gradient spin-echo nuclear magnetic resonance · Self-diffusion · Polydispersity

Introduction

Polymer self-diffusion coefficients are important physical properties of polymer solutions and melts. For concentrated polymer solutions and melts they provide experimental parameters with which theoretical frameworks describing such systems may be calibrated [1]. In dilute solutions the long-time (implying that the root-mean-square displacements of the polymers are always larger than the size of the polymer) self-diffusion coefficients are important measures of the coil size and, hence, they convey information about the solvent quality. Measurements of the coil size must be carried out at sufficiently dilute concentrations so that polymer–polymer interactions, arising from direct interactions or mediated by the solvent, may be neglected. In addition, any real polymer is polydisperse in size, giving a distribution of self-diffusion coefficients (DSDC). This work addresses these two features of polymer self-diffusion experiments.

We do this by determining the self-diffusion coefficients of poly(ethylene oxide) (PEO) aqueous solutions, covering a concentration regime from dilute to concentrated and a molecular-weight range of 4 orders of magnitude. The self-diffusion coefficients are determined by means of the pulsed field gradient spin-echo (PFG SE) NMR method. The literature treating the influence of polymer molecular-weight distributions (MWD) on self-diffusion measurements is extensive [2–8], but here we build on recent work by Chen et al. [8]. The work presented here can be considered as a complement of that work in the sense that the range of experiments determining the scaling behavior of the self-diffusion coefficient with molecular weight is more extensive and more accurate.

Various NMR methods are central to the study of polymer dynamics. In particular, the PFG NMR self-diffusion experiment is important since it can be used to measure polymer self-diffusion coefficients in solutions and in melts. The experiment is applicable to a wide range of different polymers. It is noninvasive and yields self-diffusion coefficients of high accuracy in reasonable measuring times. The accuracy is only limited by the signal-to-noise (S/N) ratio one can achieve. In addition, due to hardware developments during the last decade it is now possible to measure very low diffusion coefficients (values down to approximately 10^{-15} m^2 s^{-1} have been measured) [9].

An additional advantage of the experiments is that the functional form of the signal decay depends on the degree of the polydispersity in size of the polymer system. Thus, the curvature of the signal decay reflects the DSDC. If the MWD is to be extracted from the DSDC, the scaling behavior of the self-diffusion coefficients with molecular weight must be known. In the dilute regime one often assumes that the self-diffusion coefficient is related to the molecular weight through a scaling relation of the form $D = KM^{-\alpha}$. Some care has to be exercised when using such scaling relations since the values of the scaling parameters depend on the diffusion mechanism and consequently show a concentration dependence which varies with the size of the polymers.

Experimental

Materials

The PEO polymers $[H(OCH_2CH_2)]_n$ OH, where n is the number of repeating units] were supplied by Aldrich, Milwaukee, USA (polymers in the M_w range 924–8443 g mol^{-1}, Table 1) and from Polymer Laboratories, Shropshire, UK (polymers in the M_w range 9825–904248 g mol^{-1}, Table 1). All polymers were used without further purification. The D_2O (purity above 99.8%) used for mixing the samples was purchased from Dr Glaser, Basel, Switzerland.

Table 1 Characteristics of poly(ethylene oxide) (*PEO*) polymers used in the study. Also given are the self-diffusion coefficients for dilute samples of each polymer as well as the masses used in constructing a model polydisperse polymer system

M_w^a (g mol^{-1})	M_n^a (g mol^{-1})	Polydispersity index	m^b	D^c (10^{-11} m^2 s^{-1})
924	892	1.04		23.4
1856	1795	1.03		16.3
4501	4350	1.03		10.2
8443	8320	1.02		7.24
9825	9548	1.03	0.0214	6.49
18321	17965	1.02	0.0519	4.52
31715	30910	1.03	0.1036	3.30
49206	48327	1.02	0.1412	2.59
73977	72839	1.02	0.1605	2.03
120580	118224	1.02	0.1695	1.64
213793	196001	1.10	0.1459	1.26
291685	274955	1.06	0.1052	1.07
636907	607034	1.05	0.0803	0.648
904248	828032	1.10	0.0205	0.582

[a] Determined by gel permeation chromatography
[b] Relative masses used in the model polydisperse polymer system
[c] Self-diffusion coefficients at a polymer concentration of 0.05 wt %

Self-diffusion measurements

The self-diffusion of the polymers was measured with the Fourier transform PFG SE technique [10]. The measurements of the polymers in the M_w range from 924 to 8443 g mol^{-1} were performed on a Varian Unity 400 spectrometer, equipped with a 360 MHz (8.45 T) Oxford wide-bore magnet, while the measurements of the rest of the polymers were performed on a Bruker DMX 200 spectrometer. The gradient probe used on the Varian Unity 400 was homebuilt and has a gradient strength of approximately 0.18 T m^{-1} per unit current, while a Bruker probe with a gradient strength of approximately 0.22 T m^{-1} per unit current was used on the DMX 200. The pulse sequence, 90°-τ-180°-τ-echo, with a pulsed magnetic field gradient of amplitude g and duration δ inserted on each side of the 180° radio frequency pulse with a time separation of Δ from leading edge to leading edge (where Δ is kept equal to τ) was used throughout.

All measurements were performed in 5-mm NMR tubes. The samples were made by first weighing and then mixing the components properly in small vessels. After an equilibration period of 1–2 days, the solutions were transferred to NMR tubes. The temperature was 25.0 ± 0.1 °C for all measurements.

Results and discussion

How shall we deal with the influence of molecular-weight polydispersity in PFG NMR self-diffusion experiments of polymers? Is it possible to determine the MWD from the NMR signal attenuation recorded in such experiments? These and related questions have been raised and treated in several publications over the years [2, 4–8]. In our opinion some issues remain to be clarified. In order to achieve this objective we have performed very accurate PFG NMR self-diffusion experiments on PEO polymers, covering a wide range of molecular weights and concentrations. In addition, we have also investigated mixtures of monodisperse polymers as models for real polydisperse polymer systems.

Theoretical background

An often-used number to quantify the width of the MWD of a polymer is the polydispersity index, which is defined as M_w/M_n, where M_w and M_n represents the weight-average and the number-average molecular weights, respectively [11]. The method commonly used to determine the polydispersity index is gel permeation chromatography, also called size-exclusion chromatography [12].

Although the actual form of the MWD function is, in general, not known, a common distribution function used to describe polydispersity is the log–normal distribution [5]

$$P(M) = \frac{1}{M\sigma\sqrt{2\pi}} \exp\left(-\frac{[\ln(M) - \ln(M_0)]^2}{2\sigma^2} \right) , \tag{1}$$

where M_0 is the median and σ is a measure of the width of the MWD. The polydispersity index for a log–normal distribution function is given by

$$\frac{M_w}{M_n} = \exp(\sigma^2) . \tag{2}$$

For monodisperse systems ($M_w/M_n = 1$) the signal attenuation in a PFG NMR self-diffusion experiment is given by [13]

$$I_n = \exp(-kD) , \tag{3}$$

where k is defined as $k = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ and I_n is the normalized intensity (normalized to 1 for $k = 0$). γ is the magnetogyric ratio of the nucleus studied, δ is the duration of the gradient pulses, Δ is the time between the leading edges of the gradient pulses, and D is the self-diffusion coefficient. For polydisperse systems ($M_w/M_n > 1$), Eq. (3) is no longer valid and the observed signal attenuation becomes the sum of signal decays of different molecular weights

$$I_n = \frac{\sum p_i M_i \exp(-kD_i)}{\sum p_i M_i} , \tag{4}$$

where p_i is the number of molecules with a molecular weight of M_i and a self-diffusion coefficient of D_i. With a continuous distribution in M (e.g. Eq. 1) Eq. (4) can be rewritten as an integral of the form

$$I_n = \frac{\int MP(M) \exp(-kD) \mathrm{d}M}{\int MP(M) \mathrm{d}M} , \tag{5}$$

where $P(M)$ represents the MWD function. In order to evaluate Eq. (5) one must introduce an expression that relates the self-diffusion coefficient to the molecular weight. Such a relation, which is often used, is given by

$$D = KM^{-\alpha} , \tag{6}$$

where K and α are scaling parameters. As we shall see, one has to be careful when using Eq. (6) in the evaluation of polydisperse systems because the scaling parameters are only constant at sufficiently low concentrations.

Instead of using the MWD directly, we can write the signal attenuation in terms of a DSDC. The signal attenuation will then be given by

$$I_n = \int P(D) \exp(-kD) \mathrm{d}D , \tag{7}$$

where $P(D)$ is the probability of finding a component with a self-diffusion coefficient of D. The appearance of Eq. (7) merits two comments. First, the actual form of $P(D)$ is, in general, not known, but it can be obtained from an inverse Laplace transformation (ILT) of I_n. This is the basis of approaches such as CONTIN [14, 15], which is a numerical procedure to obtain the ILT of a multiexponential signal decay. The same approach is used in diffusion-ordered NMR spectroscopy [16, 17]. Secondly, the moments of $P(D)$ may be obtained by a series expansion of Eq. (7)

$$\begin{aligned} I_n &= \int P(D) \left(1 - kD + \frac{k^2}{2} D^2 - \cdots \right) \mathrm{d}D \\ &= 1 - k\langle D \rangle + \frac{k^2}{2} \langle D^2 \rangle - \cdots . \end{aligned} \tag{8}$$

Thus the average self-diffusion coefficient may be obtained from the signal decay at small k values. For a log–normal distribution function in D (Eq. 10) the average self-diffusion coefficient is

$$\langle D \rangle = D_0 \exp\left(\frac{\sigma^2}{2} \right) . \tag{9}$$

An alternative to the ILT approach is to assume a functional form for $P(D)$. As before a log–normal distribution function is often used

$$P(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left(-\frac{[\ln(D) - \ln(D_0)]^2}{2\sigma^2} \right) , \tag{10}$$

where the parameters D_0 and σ of the distribution may be obtained from the experimental signal decay by a nonlinear least-squares fitting procedure of Eqs. (7) and (10) to the data. In this case we obtain the DSDC instead of the MWD (see earlier). The DSDC can be transformed to a MWD (and vice versa) through the following relationship

$$MP(M)\mathrm{d}M = P(D)\mathrm{d}D \int MP(M)\mathrm{d}M . \tag{11}$$

By combining Eqs. (6) and (11) we obtain

$$M^2 P(M) = \alpha D P(D) \int MP(M)\mathrm{d}M . \tag{12}$$

Furthermore, we note that the polydispersity index (Eq. 2) can be obtained directly from $P(D)$ by the following relationship

$$\sigma_{PD} = \alpha\sigma_{PM} \Rightarrow \frac{M_w}{M_n} = \exp\left(\frac{\sigma_{PD}^2}{\alpha^2} \right) , \tag{13}$$

where σ_{PD} is a measure of the width of the DSDC (Eq. 10 and cf. Eq. 2) and σ_{PM} is a measure of the width of the MWD (Eq. 1). One consequence of Eq. (13) is that the scaling constant, α, will determine the effective width of the DSDC. Hence, it is important that α is constant over the entire MWD and this will only be true at sufficiently low concentrations (see Fig. 1a and the following discussion).

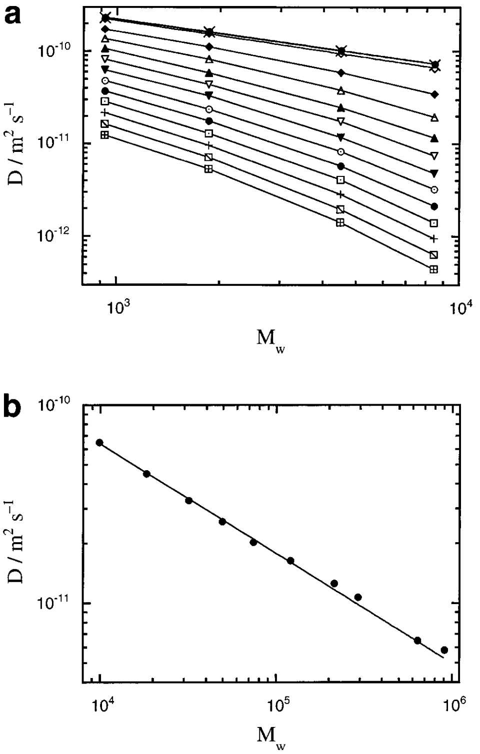

Fig. 1 **a** D versus M_w for four poly(ethylene oxide) (*PEO*) polymers of M_w 924, 1856, 4501, and 8443 g mol^{-1} at concentrations of 0.05, 0.1, 1, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, and 55 wt% (from *top* to *bottom*). The *solid lines* for the concentrations 0.05–1.0 wt% are nonlinear least-squares fits of Eq. (6) to the data (see Table 2), while the *solid lines* for the concentrations 5–55 wt% are guides for the eye. Note, that the symbols of the two lowest concentrations almost fall on top of each other. **b** D versus M_w for ten PEO polymers (in the M_w range 9825–904248 g mol^{-1}) at a concentration of 0.05 wt%. The *solid line* represents a nonlinear least-squares fit of Eq. (6) to the data (see Table 2)

In summary, one can obtain the MWD in PFG NMR self-diffusion measurements directly by assuming a functional form of $P(M)$ and by fitting Eqs. (5) and (6) to the NMR signal decay. This procedure yields the parameters describing the $P(M)$ as well as the scaling parameters of Eq. (6). Alternatively one may use the ILT in order to obtain $P(D)$ directly from the signal decay or one may assume a functional form for $P(D)$ and fit Eq. (7) to the NMR signal decay. Equation (12) can then be used to transform $P(D)$ to $P(M)$. For the latter case one must know the scaling behavior of the self-diffusion coefficient with molecular weight in order to obtain the MWD. The scaling behavior will not be the same for all polymers, as the solvent quality will determine the scaling parameters of Eq. (6). Consequently, the latter approach becomes more cumbersome as the scaling behavior must be known and has to be determined for each system in separate experiments.

Scaling behavior

As previously noted when using Eq. (12) to obtain the MWD for polymer systems we must know the scaling behavior of the self-diffusion coefficient with the molecular weight. In a practical situation the procedure would be to first determine the values of the parameters of Eq. (6) in separate experiments on monodisperse polymers. A critical question is then under what conditions and, in particular, for which polymer concentrations are the values of the scaling parameters constant? This issue is very important in the evaluation of polydispersity data.

To investigate this issue in some detail we performed experiments on a number of (reasonably) monodisperse polymer systems as a function of both M_w and concentration. The characteristics of the polymers used are given in Table 1. All samples yielded straight lines in semilogarithmic plots of I_n versus k (data not shown), indicating that the polymer self-diffusion of the samples investigated could be described with a single self-diffusion coefficient. The self-diffusion coefficients versus M_w of four PEO polymers at 14 concentrations are displayed in a double-logarithmic plot in Fig. 1a. As can be seen from Fig. 1a, the deviation from Eq. (6) starts at very low concentrations. Only the three lowest concentrations, 0.05, 0.1, and 1 wt%, can be considered to follow the functional behavior of Eq. (6). The parameters of nonlinear least-squares fits of Eq. (6) to the data of the three lowest concentrations are presented in Table 2. At concentrations as low as 1 wt%, we obtain a different scaling exponent of Eq. (6). This means that PFG NMR self-diffusion measurements must be carried out at sufficiently low concentrations to ensure that the molecules diffuse independently of each other.

As a good S/N ratio is important in these kinds of experiments, the fact that one has to use low concentrations is a drawback and will be a limiting factor in the accuracy one can achieve in the derivation of the MWD. In the present study we chose to work at a concentration of 0.05 wt%, where the molecules diffuse independently

Table 2 Scaling parameters of Eq. (6) obtained from the data in Fig. 1a and b. System I represents data for four PEO polymers in the M_w range 924–8443 (see Fig. 1a) and system II represents data for ten PEO polymers in the M_w range 9825–904248 (see Fig. 1b). The errors are given by a 90% level of confidence and were obtained from Monte Carlo calculations [19]

System	Concentration (wt%)	K (10^{-9} m^2 s^{-1})	α
I	0.05	8.4 ± 0.3	0.525 ± 0.005
I	0.1	8.1 ± 0.6	0.521 ± 0.009
I	1.0	9.8 ± 0.7	0.55 ± 0.01
II	0.05	10 ± 2	0.55 ± 0.02

of each other (Fig. 1, Table 2). The self-diffusion coefficients versus M_w of ten PEO polymers (in the M_w range from 9425 to 904248 g mol^{-1}) are displayed in a double-logarithmic plot in Fig. 1b. The parameters of a nonlinear least-squares fit of Eq. (6) to the data are presented in Table 2. The values are in reasonable agreement with those of other studies [18].

Model calculations

We have performed model calculations of Eq. (5) (assuming a log–normal distribution function in M) to investigate how sensitive the PFG NMR self-diffusion data are to the magnitude of the polydispersity. The model calculations were performed by rewriting Eq. (5) as

$$I_n = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp\left(X - X_0 - \sigma^2/2\right) \times \exp\left[-(X - X_0)^2/2\sigma^2\right] \exp[-kK\exp(-\alpha X)]\,dX \quad , \tag{14}$$

where $X = \ln(M)$ and $X_0 = \ln(M_0)$. Equation (14) was solved numerically. Signal decays for three different polydispersity indices (1.05, 1.4, and 2) are displayed in Fig. 2, using the parameters $M_0 = 1000$ kD and the values of the scaling parameters of Eq. (6) were $K = 8.4 \times 10^{-9}$ m^2 s^{-1} and $\alpha = 0.525$ (as obtained from data in Fig. 1a). Also included in Fig. 2 are nonlinear least-squares fits of Eq. (3) (i.e. the case of a monodisperse polymer solution) to the data. The fitting parameters obtained are given in the figure caption, with the errors being obtained by Monte Carlo calculations [19], using a confidence level of 90%. We infer from Fig. 2 that the deviation from a straight line (recall that for a monodisperse sample the signal decay is given by a straight line in the representation of Fig. 2) is quite small even for the largest polydispersity index used ($M_w/M_n = 2$). Note that the data in Fig. 2 are plotted on a logarithmic scale and that the systematic deviations from the fits of Eq. (3) are indeed small. This is further corroborated by the nonlinear least-squares fits of Eq. (3), which give quite small errors in D (approximately 2% for $M_w/M_n = 2$, see also the caption of Fig. 2). In practice the deviation from linear behavior may be difficult to observe in PFG NMR self-diffusion experiments as a poor S/N ratio may blur out the nonlinearity. Furthermore, the signal decay has to be monitored over a wide range of intensities (at least 2–3 orders of magnitude). As a consequence, the PFG NMR self-diffusion experiments have to be very accurate in order to detect polydispersity effects, at least at moderate polydispersities.

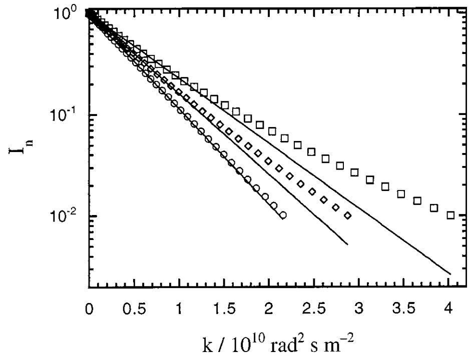

Fig. 2 Calculated signal intensities assuming a log–normal distribution function (in M) with different polydispersity indices (1.05, 1.4, and 2, from *left* to *right*). Parameters used were $M_0 = 1000$ kD, $K = 8.4 \times 10^{-9}$ m^2 s^{-1}, and $\alpha = 0.525$. Also included are nonlinear least-squares fits of Eq. (3) to the data and the parameters obtained are 1.05: $D = 2.171\ (\pm 0.003) \times 10^{-10}$ m^2 s^{-1}; 1.4: $D = 1.83\ (\pm 0.02) \times 10^{-10}$ m^2 s^{-1}; 2.0: $D = 1.48\ (\pm 0.03) \times 10^{-10}$ m^2 s^{-1}

Data for a mixture of monodisperse polymers

In order to further investigate the influence of polydispersity on the PFG NMR signal decays, we produced a mixture of 10 monodisperse PEO polymers (Table 1). The weight fraction of each polymer is given in Table 1 and the distribution is presented in Fig. 3. The distribution was made so that it would resemble a log–normal distribution with respect to the mass of each M_w. The polydispersity index of the (discrete) mixture is 2.8.

The echo decay from a 0.05 wt% (in total) polymer solution with the mass distribution as given in Fig. 3 is presented in Fig. 4. Also included in Fig. 4 are the predictions of three different approaches for the echo decay. In the first, we have taken the self-diffusion coefficients as measured in ten separate experiments of 0.05 wt% solutions (Table 1) of the monodisperse polymers and added ten exponentials according to Eq. (3) with appropriate weights (Table 1) together.

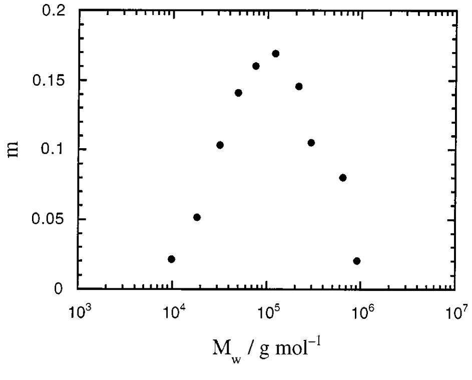

Fig. 3 The mass distribution (see Table 1) of the discrete polymer mixture used as a model for a polydisperse polymer system

There are thus no adjustable parameters in this approach. The agreement with the experimental curve is excellent, showing that indeed each polymer of a given molecular weight can be assigned a self-diffusion coefficient as determined from a separate experiment for each polymer under the same conditions; thus, the relation implied by Eq. (6) should be valid. The second prediction is the result of performing an ILT directly on the echo decay, using the CONTIN approach [14, 15]. The DSDC obtained from the CONTIN analysis is given in Fig. 5. Finally, the third prediction included in Fig. 4 is the result of fitting a log–normal distribution in D (i.e. Eqs. 7, 10) to the data. The resulting distribution is given in Fig. 5 and the values of the parameters D_0 and σ are given in the caption. Both the CONTIN approach and the approach based on Eqs. (7) and (10) give excellent predictions of the echo decay (Fig. 4). They also produce effectively the same DSDC (Fig. 5).

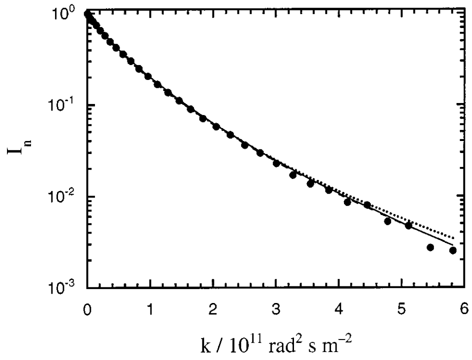

Fig. 4 The echo intensities versus k (see text for the definition of k) for the (discrete) mixture as given in Table 1. The *solid line* represents the sum of ten exponentials (according to Eq. 3) with the weights obtained from the masses in Table 1. The *broken line* is the result of an inverse Laplace transformation (*ILT*) of the echo decay. The *dotted line* represents a nonlinear least-squares fit of Eqs. (7) and (10) to the data. Note, that the result of the sum of ten exponentials and the result of an ILT almost fall on top of each other

We also note that the average self-diffusion coefficient obtained at low k values using the expansion of Eq. (8) yields $\langle D\rangle = 2.6\times10^{-11}$ m^2 s^{-1}, while the first moment of the distributions in Fig. 5 gives $\langle D\rangle = 2.0\times10^{-11}$ m^2 s^{-1} using the CONTIN approach and $\langle D\rangle = 2.2\times10^{-11}$ m^2 s^{-1} using the log–normal approach. The agreement between the three approaches is reasonable.

The MWD can now be obtained using the transformation indicated by Eq. (12). The result is given in Fig. 6. Since the M_w of the polymers making up the test solution are not evenly spaced (Table 1), a comparison to the continuous distribution implied in Fig. 5 cannot be made directly. To overcome this subtlety, we proceeded as follows. Each polymer with a M_w is taken to represent polymers with M_w spanning an interval of ΔM around M_w. The weight factor, $P(M)$, for this range is obtained from the relation $P(M) = m/\Delta M$ (where m is the value given in Table 1). The transformed discrete weights of the polymer mixture are included in Fig. 6: the agreement is reasonable.

Concluding remarks

We have shown, as have others before us, that the PFG NMR method is capable of producing MWDs from samples of polydisperse polymers. The method requires accurate data of high quality. It also requires that the scaling relation implied by Eq. (6) holds. In addition, we note that the method requires polymers that are reasonably polydisperse.

The procedure to obtain the MWD is then to produce a DSDC, either through an ILT-based approach or by assuming a certain form of the DSDC, such as a log–normal distribution. From the work presented here it is shown that both procedures give almost equivalent results. We note that ILT-based procedures do not rely on any assumption about the form of the DSDC, which

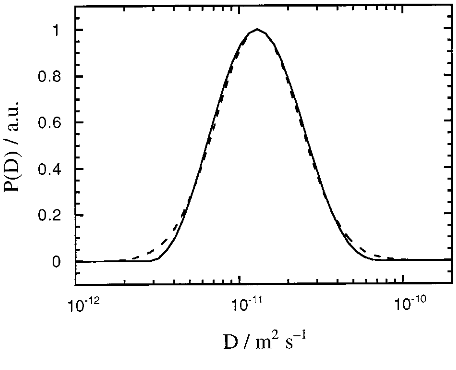

Fig. 5 The distributions obtained from the ILT approach (*solid line*) and from the fit of Eqs. (7) and (10) (*broken line*). The fitted parameters of $P(D)$ are $D_0 = 1.84\times10^{-11}$ m^2 s^{-1} and $\sigma = 0.59$

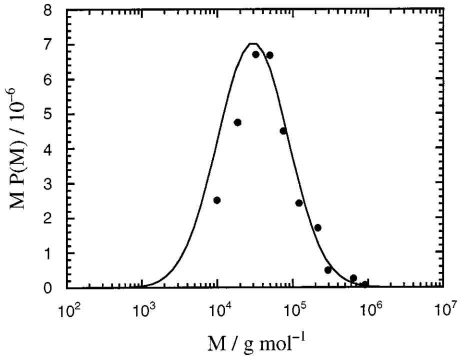

Fig. 6 The molecular-weight distribution from the transformation of $P(D)$ (see Fig. 5) using Eq. (12). Also included are the modified weights obtained from the weights given in Table 1 (see text for details)

would suggest that such procedures are preferable over approaches based on a particular form of the DSDC. We also note that ILT procedures yield DSDCs of finite width also for species which are described by a single value of *D*, which would imply that some care should be exercised when using ILT approaches for polymer solutions with small polydispersity indices. Perhaps a combination of both methods is preferable in order to ensure that a reasonable DSDC is obtained.

The final step is then to transform the DSDC to a MWD by using carefully determined scaling parameters. An alternative would be to assume a functional form of the MWD and to obtain the parameters of the assumed distribution through a fit of Eq. (5) to the data, either by keeping the scaling parameters constant or, alternatively, by evaluating the value of the scaling parameters directly. The latter alternative thus requires no prior knowledge of the scaling parameters, but it does of course require that the data are obtained at low enough concentrations so that Eq. (6) is valid.

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