

Scaling exponent and dispersity of polymers in solution by diffusion NMR

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Abstract

Molecular mass distribution measurements by pulsed gradient spin echo nuclear magnetic resonance (PGSE NMR) spectroscopy currently require prior knowledge of scaling parameters to convert from polymer self-diffusion coefficient to molecular mass. Reversing the problem, we *utilize* the scaling relation as prior knowledge to uncover the scaling exponent from within the PGSE data. Thus, the scaling exponent—a measure of polymer conformation and solvent quality—and the dispersity (M_w/M_n) are obtainable from one simple PGSE experiment. The method utilizes constraints and parametric distribution models in a two-step fitting routine involving first the mass-weighted signal and second the number-weighted signal. The method is developed using lognormal and gamma distribution models and tested on experimental PGSE attenuation of the terminal methylene signal and on the sum of all methylene signals of polyethylene glycol in D_2O . Scaling exponent and dispersity estimates agree with known values in the majority of instances, leading to the potential application of the method to polymers for which characterization is not possible with alternative techniques.

Keywords:

Pulsed gradient spin echo, pulsed field gradient, Nuclear Magnetic Resonance spectroscopy, Molecular weight distribution, Polymers, DOSY, Polydispersity Index, Self-diffusion, Molar mass, Flory exponent, Lognormal distribution, Gamma distribution, End-group analysis, Scaling law

Synthetic polymers have distributions of molecular masses determined by their synthesis [1]. Measuring the molecular mass distribution rather than its average is important because the dispersity can influence polymer properties [2]. Absolute as opposed to relative measurements are needed when using polymer physics to fully realize the potential applications of a polymer [3]. Only a handful of techniques can measure the absolute molecular mass distribution [3]. The gold standard is size exclusion chromatography (SEC) using universal calibration [4], which does not always work [5, 6]. New techniques must be developed to aid in the advancement of polymer science.

Pulsed gradient spin echo nuclear magnetic resonance (PGSE NMR)[7, 8] is a powerful technique for obtaining the distribution of polymer self-diffusion coefficients D [9], from which the distribution of molecular masses M can be obtained by the scaling law [10]

$$D(M) = KM^{-\nu}; M(D) = K^{1/\nu}D^{-1/\nu}. \quad (1)$$

Access to chemical shift information and ease of sample prepa-

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ration give PGSE NMR a competitive edge with respect to SEC. Chemical shift information [7], e.g. in a diffusion ordered spectroscopy (DOSY) plot [11], provides the ability to observe chemical heterogeneity and impurity. Sample preparation generally does not require filtration because contamination from large particles such as dust do not impact the experiment. However, the scaling parameters of Eq. (1) specific to that polymer-solvent system must be found by measuring $\langle D \rangle$ on fractionated samples of the polymer with known M . Therefore, currently all PGSE NMR-based methods which convert from D to M cannot independently measure the absolute molecular mass distribution [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25].

In this paper we show that ν in Eq. (1) can be directly estimated from a single PGSE experiment in which the extremity (end-group) polymer signal can be spectrally resolved by a chemical shift from the polymer main-chain signal. The scaling exponent, ν , is a measure of the polymer conformation as well as solvent quality [3, 26], with bounds of $\nu = 1/3$ for a perfectly coiled, impenetrable, polymer ball and $\nu = 1$ for a perfectly straight polymer rod [17]. The value of $\nu = 3/5$ for a polymer in a good solvent was first predicted by P.J. Flory by a free energy minimization of the excluded volume and entropic contributions [1]. (For this, ν is also known as the Flory exponent.)

The method uses a mathematical framework which we first presented [27] and applied [28] in 2016. The method builds on

the work of Viéville et al. [19] who showed that the distribution of polymer self-diffusion coefficients is mass-weighted for the main-chain signal and number-weighted for the end-group signal. The key to directly obtaining the scaling exponent is our use of parametric distribution models to fit these two signals. The molecular mass dispersity, defined as M_w/M_n —the ratio between the mass-average and the number-average molecular masses, (and the molecular mass distribution if given M_n) can then be calculated from the parameter values estimated for the chosen model. To build up directly from the work of Viéville et al. [19], we prove this method on the same system: mixtures of polyethylene glycol (PEG) molecular mass standards solvated in D_2O . In this way, M_n and M_w of each mixture are known. In the following, we introduce PGSE NMR and reproduce equations [24] for the application of the lognormal [29, 30, 14] and gamma [21, 31] distribution models. We then explain sample preparation and outline the procedure for obtaining ν , M_w/M_n , and the molecular mass distribution. The method is then applied to three PEG samples and the results are compared to the known values.

In a PGSE NMR measurement of the self-diffusion coefficient D , the signal attenuation of a monodisperse species is given by the Stejskal-Tanner equation,

$$I(b) = I_0 \exp(-bD) \quad (2)$$

where I_0 is the initial signal intensity, and the independent variable b is incrementally increased by stepping up the gradient pulse strength in successive scans [32, 33]. The signal attenuation of a polydisperse species will be multiexponential as a result of the distribution of diffusion coefficients. Such a superposition of exponential decays can be modeled by,

$$I(b) = I_0 \int_0^\infty w(D) \exp(-bD) dD, \quad (3)$$

where $w(D)$ is the distribution model of choice. We refer to $w(D)$ as the mass-weighted distribution of diffusion coefficients, and we note that in general the measured distribution is mass-weighted because it is proportional to the total number of protons and therefore, for a polymer, the total number of repeat units. However, the end-group signal can often be spectrally resolved for low molecular mass polymers (roughly less than 10 kDa [19]). The distribution of diffusion coefficients of the end-group is number-weighted (referred to as $n(D)$) because it is proportional to the number of molecules [19]. If an appropriate model for $w(D)$ is chosen, then $n(D)$ can be obtained by the definition (see, e.g., [34])

$$n(D) = \frac{w(D)/M(D)}{\int_0^\infty w(D)/M(D) dD}. \quad (4)$$

Using Eq. (1) as $M(D)$ brings in ν as an additional parameter of $n(D)$. Note that the parameter K seen in Eq. (1) will always cancel out as a constant in the numerator and denominator of Eq. (4).

Many distribution models exist, and the estimation of the distribution is an inverse problem for which there is no unique so-

lution. We are physically motivated to use the lognormal distribution [14, 29, 30],

$$w(D) = \frac{1}{D\sigma_D\sqrt{2\pi}} \exp\left(-\frac{(\log D - \mu_D)^2}{2\sigma_D^2}\right), \quad (5)$$

for which

$$n(D) = \frac{D^{1/\nu-1}}{\sigma_D\sqrt{2\pi}} \exp\left(-\mu_D/\nu - \sigma_D^2/(2\nu^2)\right) \exp\left(-\frac{(\log D - \mu_D)^2}{2\sigma_D^2}\right), \quad (6)$$

and

$$M_w/M_n = \exp\left(\frac{\sigma_D^2}{\nu^2}\right) \quad (7)$$

and the gamma distribution [21, 31],

$$w(D) = \frac{\beta^\alpha}{\Gamma(\alpha)} D^{\alpha-1} \exp(-\beta D), \quad (8)$$

for which

$$n(D) = \frac{\beta^{\alpha+1/\nu}}{\Gamma(\alpha + 1/\nu)} D^{\alpha+1/\nu-1} \exp(-\beta D), \quad (9)$$

and

$$M_w/M_n = \frac{\Gamma(\alpha + 1/\nu)\Gamma(\alpha - 1/\nu)}{\Gamma(\alpha)^2}, \quad (10)$$

because both distributions meet the criterion that the probability of negative molecular masses must be zero. The complete derivation of equations and case studies for use of the lognormal and gamma distribution models for estimating molecular mass distributions are presented in our previous publication [24]. We reproduce a few more equations for these models, including the molecular mass distribution functions, in the Supplementary Information.

The method for estimating ν and M_w/M_n from the PGSE attenuation of the main-chain and end-group signals follows a two-step, least squares fitting routine. Benjamini and Basser found that imposing parameter constraints in a two-step fit of 2-D relaxation and diffusion NMR measurement data restricts the solution set of the second fit and leads to a significant reduction in the amount of data required for a stable fit [35]. By fitting our data in two steps we take advantage of the large signal of the main-chain peak, from which precise parameter estimates are obtained. A global (simultaneous) fit of both signal attenuations is more ill-posed, and thus less accurate. First, the sum of the main-chain and end-group signals is fit with the chosen distribution model. Second, the end-group signal is fit with the associated number-weighted distribution model. Parameter estimates from the first fit are used as constraints such that the only free parameter in the second fit is ν . Given that the model choices are appropriate, we take into account the effect which random noise in the data has on the accuracy of the first fit by bounding the constrained parameters to within the value $\pm 1/2$ the standard deviation from the first fit. The M_w/M_n is defined

by the estimated parameters. It is well known that the number-average molecular mass can be estimated from end-group analysis of a 1-D NMR spectrum [3]. Together, M_n and M_w/M_n define the parameters of the molecular mass distribution function.

The method was tested on three PEG mixtures with $M_n = 822$ g/mol and $M_w/M_n = 1.81$ for mixture 1, $M_n = 667$ g/mol and $M_w/M_n = 2.49$ for mixture 2, and $M_n = 441$ g/mol and $M_w/M_n = 1.41$ for mixture 3. To make each mixture, Polyethylene glycol (PEG) molecular mass standards ($M_w/M_n < 1.2$) (Polymer Standards Services Inc., Germany) were mixed together in defined ratios to create molecular mass distributions which were roughly lognormal in shape (though not continuous). (Refer to the Supplementary Information for standard molecular masses and their fractional makeup of the mixtures.) The designed mixtures were diluted to 0.1 % (w/w) PEG in D_2O (99.9 atom % deuterium, Sigma-Aldrich, USA) and transferred to 5 mm NMR sample tubes.

To measure PEG self-diffusion, pulsed gradient stimulated echo experiments [36] were performed on the mixtures at 20°C using a 600 MHz Avance III HD NMR spectrometer (Bruker BioSpin, Germany) equipped with a Micro5 probe, 5 mm radio frequency coil, and Diff30 (11.7 T/m maximum) gradient set. Sinusoidal gradient pulse shapes were chosen, for which the b in the Stejskal-Tanner equation (Eq. (3)) is

$$b = (\gamma g \delta)^2 \frac{4}{\pi^2} \left(\Delta - \frac{\delta}{4} \right), \quad (11)$$

with proton gyromagnetic ratio γ , time lapse Δ between the leading edges of the gradient pulses, gradient pulse duration δ , and gradient strengths g . The experiments used $\Delta = 50$ ms, $\delta = 1.58$ ms, repetition time = 10 s, 16 scans, and 32 gradient points with g varied linearly to 4 T/m for mixture 1 and mixture 2 and 3.2 T/m for mixture 3. Each experiment took 1½ hours.

The least-squares fitting routine was implemented in MATLAB R2016a (Mathworks, Natick, USA) and incorporated a Monte Carlo error analysis [37]. The 95% confidence intervals were assessed from the distributions of parameter values obtained from the Monte Carlo steps, in which the data was refit after the addition of Gaussian noise with the same standard deviation as that of the initial fit. Monte Carlo estimates of ν incorporated the errors of both fitting steps. The fitting procedure used 100 random parameter initializations and 1000 Monte Carlo steps. The fitting routine and data sets from the three mixtures are available in the Supplementary Information.

We first demonstrate how the method works on PEG mixture 1 and second compare the results of ν and M_w/M_n to the known values for all three mixtures. The PGSE experiment measures the signal attenuation of the main-chain methylene peak at 3.7 ppm and the two sets of triplets arising from the two methylenes closest to the hydroxyl group on the PEG extremity. (The proton spectrum from the smallest gradient (or b) value is shown in Fig. 1a.) We define the mass-weighted signal as the sum of all methylenes (not just the main-chain peak) and the number-weighted signal as the triplet from the terminal methylene. We take the integral values directly from Fig. 1a to obtain $M_n = 900$ g/mol, compared to the known value

of $M_n = 820$ g/mol. (We do this for simplicity and to point out that all the necessary information is contained within this one PGSE measurement. Weighting effects from spin-spin and spin-lattice relaxation [29], diffusion, and even spectral overlap [38] can be taken into account with more rigorous methods. Using a spectrum from a 1-D free induction decay results in essentially the same M_n value.) Following the methods for use of the lognormal and gamma distribution models outlined above, the experimental results, fits, estimated number and mass-weighted diffusion coefficient distributions, and estimated molecular mass distributions are shown in Fig. 1b-d. The known molecular mass distribution of the mixture is represented by a sum of lognormal distributions, defined by the mass fractions and the reported values of M_n and M_w/M_n of the standards composing the mix. Though the multimodal shape cannot be reproduced, the estimated molecular mass distributions accurately depict the width of the known distribution.

The estimated values of ν and M_w/M_n for this mixture (mixture 1) as well as mixture 2 and mixture 3 are shown in Table 1. The estimates can be compared to the known values of M_w/M_n and ν . The known value of $\nu = 0.50 \pm 0.02$ was obtained from a fit of Eq. (1) to the mean diffusion coefficient values of the individual molecular mass standards (see Supplementary Information) and is comparable to previously published values for PEG in D_2O of $\nu = 0.521 \pm 0.011$ at 25°C [14] and $\nu = 0.539 \pm 0.003$ at 30°C [17].

Table 1: Results of ν and M_w/M_n , with 95 % confidence intervals, compared to the known values for the three PEG mixtures

Mixture	Known	Lognormal	Gamma
	ν	ν	ν
1	0.50 ± 0.02	0.54 ± 0.05	0.50 ± 0.11
2	0.50 ± 0.02	0.49 ± 0.03	0.41 ± 0.07
3	0.50 ± 0.02	0.61 ± 0.04	0.58 ± 0.14
	M_w/M_n	M_w/M_n	M_w/M_n
1	1.81	1.60 ± 0.13	1.71 ± 0.42
2	2.49	2.23 ± 0.23	3.03 ± 1.37
3	1.41	1.38 ± 0.05	1.41 ± 0.24

The estimates of ν from the lognormal and gamma listed in Table 1 differ due to strong sensitivity of the method to model choice. This is evident in Fig. 1c where two very similar mass-weighted diffusion coefficient distributions arise from the first fit, but the constraints lead to drastically different number-weighted diffusion coefficient distributions from the second fit. Certain models in certain instances, such as the gamma for mixture 1 and the lognormal for mixture 2, resulted in accurate ν estimates compared to the known value, which then led to better estimates of M_w/M_n than those of the alternative models. Both models accurately estimated M_w/M_n for mixture 3 even though their estimates of ν were off, potentially because small values of M_w/M_n are less sensitive to errors in ν , as seen by Eqs. (7) and (10). For 8 out of the 12 estimated values of ν

and M_w/M_n in Table 1, the known values are within the 95% confidence intervals.

Estimates were quite successful considering that the method only assumed that M and D scale by Eq. (1) and that the distribution models were appropriate. A wide range of polymers follow the scaling relation [17]. The universal calibration method by which absolute molecular mass can be obtained with SEC [4] relies on an analogous scaling relation known as the Mark-Houwink-Sakurada equation. A major limitation then is the assumption of a distribution shape. Knowledge of the polymerization reaction kinetics can help inform on an accurate model choice. For instance, the gamma—in a parameterization widely known as the Schulz distribution [39, 40]—and lognormal distributions of molecular mass have been derived from certain polymer reaction mechanisms [34]. Relative changes in ν for a given model should not depend on model choice and so the method may be useful for measuring the change in solvent quality as a function of system parameters such as solvent or temperature. Another limitation is the capability to resolve an end-group signal, which diminishes with increasing molecular mass due to increasing peak broadness and decreasing signal.

The scaling exponent and absolute molecular mass are fundamental to realizing the full potential of a polymer. Demands for new applications are driving the complexity of new polymers for which traditional characterization methods do not always work. We show a method by which the scaling exponent and absolute molecular mass distribution characteristics can be obtained directly from a single PGSE measurement performed on a polymer without fractionation.

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2. Supplementary Information available online

Supplementary Information for: Scaling exponent and dispersity by diffusion NMR—Lognormal and gamma distribution models, Preparation of mixtures, Scaling parameters, End-group analysis estimation of M_n , Experimental acquisition details, Mixture 2 and mixture 3 results.

Matlab R2016a code—Fitting routine code, Data sets for the 3 mixtures, Code for obtaining the I and b vectors from PGSE or PGSTE experiments performed on Bruker spectrometers using the Diff module.

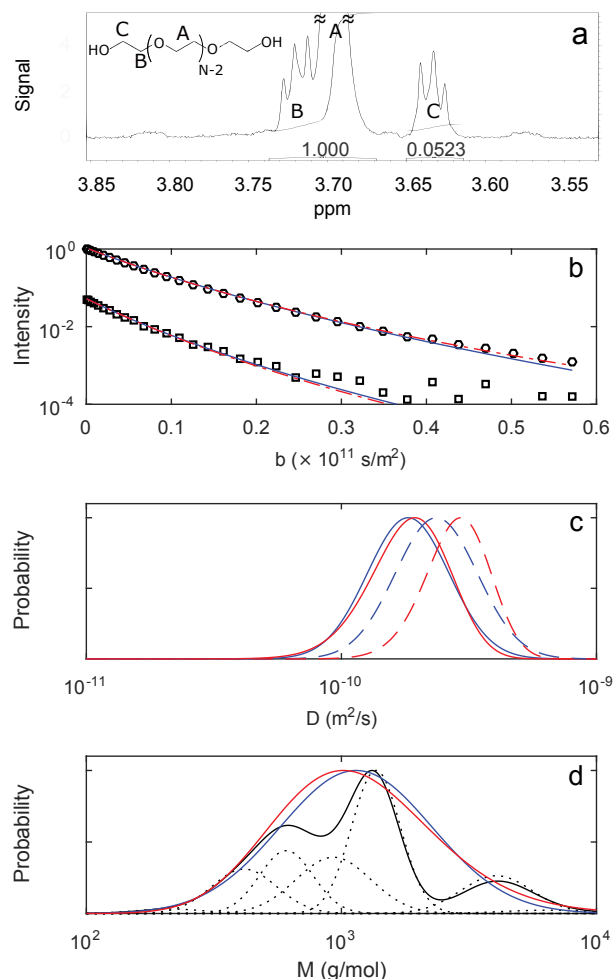


Figure 1: Results for PEG mixture 1 for the lognormal (red) and gamma (blue) models showing (a) the methylene signal integral definitions on the spectrum from the first PGSE gradient point, (b) the experimental signal attenuation for the mass-weighted signal from the sum of all methylenes (circles) and number-weighted, terminal methylene signal (squares), the mass-weighted and number-weighted lognormal (red dot-dash) and gamma (blue solid) model fits, (c) the estimated mass-weighted (solid) and number-weighted (dashed) distributions of diffusion coefficients, and (d) the molecular mass distribution estimates compared to the molecular mass distributions, individually (dotted black) and as a sum (solid black), arising from the standards composing the mix.

- [1] P. J. Flory, *Principles of polymer chemistry*, Cornell University Press, 1953.
- [2] M. Nilsson, B. Håkansson, O. Söderman, D. Topgaard, Influence of polydispersity on the micellization of triblock copolymers investigated by pulsed field gradient nuclear magnetic resonance, *Macromolecules* 40 (23) (2007) 8250–8258.
- [3] M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, 2003.
- [4] Z. Grubisic, P. Rempp, H. Benoit, A universal calibration for gel permeation chromatography, *Journal of Polymer Science Part B: Polymer Letters* 5 (9) (1967) 753–759.
- [5] D. Berek, Size exclusion chromatography a blessing and a curse of science and technology of synthetic polymers, *Journal of Separation Science* 33 (3) (2010) 315–335.
- [6] A. T. Sutton, E. Read, A. R. Maniego, J. J. Thevarajah, J. D. Marty, M. Destarac, M. Gaborieau, P. Castignolles, Purity of double hydrophilic block copolymers revealed by capillary electrophoresis in the critical conditions, *Journal of Chromatography A* 1372 (2014) 187–195.
- [7] P. Stilbs, Fourier transform pulsed-gradient spin-echo studies of molecular diffusion, *Progress in NMR Spectroscopy* 19 (1987) 1–45.
- [8] P. Callaghan, *Translational Dynamics and Magnetic Resonance Principles of Pulsed Gradient Spin Echo NMR*, Oxford University Press, 2011.
- [9] H. Walderhaug, O. Söderman, D. Topgaard, Self-diffusion in polymer systems studied by magnetic field-gradient spin-echo NMR methods, *Progress in nuclear magnetic resonance spectroscopy* 56 (2010) 406–425.
- [10] P. de Gennes, *Scaling concepts in polymer physics*, Cornell University Press, 1979.
- [11] K. F. Morris, C. S. Johnson, Diffusion-ordered two-dimensional nuclear magnetic resonance spectroscopy, *Journal of the American Chemical Society* 114 (8) (1992) 3139–3141.
- [12] R. Raghavan, T. L. Maver, F. D. Blum, Nuclear magnetic resonance measurements of molecular weights. self-diffusion of poly(methyl methacrylate) in acetonitrile, *Macromolecules* 20 (4) (1987) 814–818.
- [13] A. Chen, D. Wu, C. Johnson, Determination of molecular weight distributions for polymers by diffusion-ordered NMR, *Journal of the American Chemical Society* 117 (1995) 7965–7970.
- [14] B. Håkansson, M. Nydén, O. Söderman, The influence of polymer molecular-weight distributions on pulsed field gradient nuclear magnetic resonance self-diffusion experiments, *Colloid and Polymer Science* 278 (2000) 399–405.
- [15] S. Viel, D. Capitani, L. Mannina, A. Segre, Diffusion-ordered NMR spectroscopy: A versatile tool for the molecular weight determination of uncharged polysaccharides, *Biomacromolecules* 4 (6) (2003) 1843–1847.
- [16] M. Mazarin, S. Viel, B. Allard-Breton, A. Thévand, L. Charles, Use of pulsed gradient spin-echo NMR as a tool in maldi method development for polymer molecular weight determination, *Analytical Chemistry* 78 (8) (2006) 2758–2764.
- [17] S. Augé, P. O. Schmit, C. A. Crutchfield, M. T. Islam, D. J. Harris, E. Durand, M. Clemancey, A. A. Quoineaud, J. M. Lancelin, Y. Prigent, F. Taulelle, M. A. Delsuc, NMR measure of translational diffusion and fractal dimension. Application to molecular mass measurement, *The Journal of Physical Chemistry B* 113 (2009) 1914–1918.
- [18] C. Barrère, M. Mazarin, R. Giordanengo, T. N. T. Phan, A. Thévand, S. Viel, L. Charles, Molecular weight determination of block copolymers by pulsed gradient spin echo NMR, *Analytical Chemistry* 81 (19) (2009) 8054–8060. doi:10.1021/ac9018654.
- [19] J. Viéville, M. Tanty, M. Delsuc, Polydispersity index of polymers revealed by dosy NMR, *Journal of Magnetic Resonance* 212 (2011) 169–173.
- [20] X. Gong, E. Hansen, Q. Chen, A simple access to the (log/normal) molecular weight distribution parameters of polymers using PGSTE NMR, *Macromolecular Chemistry and Physics* 212 (2011) 1007–1015.
- [21] M. Röding, D. Bernin, J. Jonasson, A. Särkkä, D. Topgaard, M. Rudemo, M. Nydén, The gamma distribution model for pulsed-field gradient NMR studies of molecular-weight distributions of polymers, *Journal of Magnetic Resonance* 222 (2012) 105–111.
- [22] W. Li, H. Chung, C. Daefler, J. A. Johnson, R. H. Grubbs, Application of 1H DOSY for facile measurement of polymer molecular weights, *Macromolecules* 45 (24) (2012) 9595–9603.
- [23] P. Lewinski, S. Sosnowski, S. Kazmierski, S. Penczek, l-lactide polymerization studied by 1H NMR with diffusion-ordered spectroscopy (DOSY): a “one NMR tube experiment” providing data on monomer conversion, polymer structure, M_n and M_w , *Polymer Chemistry* 6 (2015) 4353–4357.
- [24] N. H. Williamson, M. Nydén, M. Röding, The lognormal and gamma distribution models for estimating molecular weight distributions of polymers using PGSE NMR, *Journal of Magnetic Resonance* 267 (2016) 54–62.
- [25] X. Guo, E. Laryea, M. Wilhelm, B. Luy, H. Nirschl, G. Guthausen, Diffusion in polymer solutions: Molecular weight distribution by pfg-nmr and relation to sec, *Macromolecular Chemistry and Physics* 218 (1) (2017) 1600440. doi:10.1002/macp.201600440. URL <http://dx.doi.org/10.1002/macp.201600440>
- [26] M. Doi, S. Edwards, *The theory of polymer dynamics*, Oxford University Press, 1988.
- [27] M. Röding, S. J. Bradley, N. H. Williamson, M. R. Dewi, T. Nann, M. Nydén, The power of heterogeneity: Parameter relationships from distributions, *PLoS ONE* 11 (5) (2016) 1–11.
- [28] N. H. Williamson, M. Röding, P. Galvosas, S. J. Miklavcic, M. Nydén, Obtaining $T_1 - T_2$ distribution functions from 1-dimensional T_1 and T_2 measurements: The pseudo 2-D relaxation model, *Journal of Magnetic Resonance* 269 (2016) 186–195.
- [29] G. Fleischer, The effect of polydispersity on measuring polymer self-diffusion with the NMR pulsed field gradient technique, *Polymer* 26 (1985) 1677–1682.
- [30] P. Callaghan, D. Pinder, Influence of polydispersity on polymer self-diffusion measurements by pulsed field gradient nuclear magnetic resonance, *Macromolecules* 18 (1985) 373–379.
- [31] M. Röding, N. Williamson, M. Nydén, Gamma convolution models for self-diffusion coefficient distributions in PGSE NMR, *Journal of Magnetic Resonance* 261 (2015) 6–10.
- [32] E. Stejskal, J. Tanner, Spin diffusion measurements: Spin echoes in the presence of a time-dependent field gradient, *The Journal of Chemical Physics* 42 (1962) 288–298.
- [33] E. Hahn, Spin echoes, *Physical Review* 80 (1950) 580–594.
- [34] L. H. Tung, Treatment of data, in: M. J. R. Cantow (Ed.), *Polymer Fractionation*, Academic Press Inc., 111 Fifth Avenue, New York, New York 10003, 1967, Ch. E, pp. 379–413.
- [35] D. Benjamini, P. J. Basser, Use of marginal distributions constrained optimization (MADCO) for accelerated 2D MRI relaxometry and diffusometry, *Journal of Magnetic Resonance* 271 (2016) 40–45.
- [36] J. E. Tanner, Use of the stimulated echo in NMR diffusion studies, *The Journal of Chemical Physics* 52 (5) (1970) 2523–2526.
- [37] J. Alper, R. Gelb, Standard errors and confidence intervals in nonlinear regression: comparison of Monte Carlo and parametric statistics, *Journal of Physical Chemistry* 94 (1990) 4747–4751.
- [38] P. Stilbs, K. Paulsen, P. C. Griffiths, Global least-squares analysis of large, correlated spectral data sets: application to component-resolved FT-PGSE NMR spectroscopy, *The Journal of Physical Chemistry* 100 (20) (1996) 8180–8189.
- [39] G. V. Schulz, On the relationship between the rate of reaction and composition of the reaction products in macro polymerisation processes, *Zeitschrift für Physikalische Chemie B30* (1935) 379–398.
- [40] P. J. Flory, The mechanism of vinyl polymerizations, *Journal of the American Chemical Society* 59 (2) (1937) 241–253.