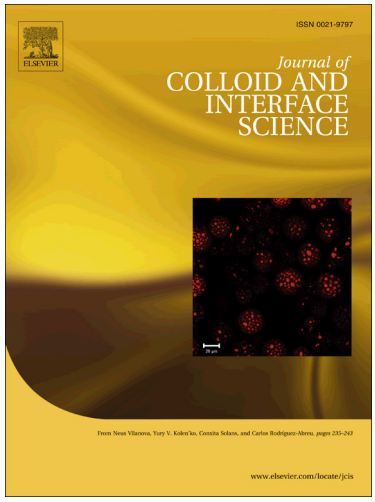

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Nathan H. Williamson, Magnus Röding, Stanley J. Miklavcic, Magnus Nydén

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Scaling exponent and dispersity of polymers in solution by diffusion NMR

Nathan H. Williamson[a,*], Magnus Röding[b,c], Stanley J. Miklavcic[d], Magnus Nydén[a,c]

[a] *Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia.*
[b] *SP Agrifood and Bioscience, Frans Perssons väg 6, 402 29 Göteborg, Sweden.*
[c] *School of Energy and Resources, University College London, 220 Victoria Square, Adelaide, SA 5000, Australia.*
[d] *Phenomics and Bioinformatics Research Centre, School of Information Technology and Mathematical Sciences, University of South Australia, Mawson Lakes, SA 5095, Australia*

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]

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

Access to chemical shift information and ease of sample preparation 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 contaminates 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

*Corresponding author: Nathan H. Williamson, Telephone: +61 (0) 8 8302 3331, Fax: +61 (0) 8 8302 3683, E-mail: nathan.williamson@mymail.unisa.edu.au

Email addresses: nathan.williamson@mymail.unisa.edu.au (Nathan H. Williamson), magnus.roding@sp.se (Magnus Röding), m.nyden@ucl.ac.uk (Stanley J. Miklavcic), m.nyden@ucl.ac.uk (Magnus Nydén)