Original Article

Application of ¹H DOSY NMR in Measurement of Polystyrene Molecular Weights

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Abstract: In this work, we studied the applicability of diffusion ordered nuclear magnetic resonance spectroscopy (DOSY NMR) as an alternative method in determination of polystyrene molecular weight. DOSY NMR spectroscopy allows measuring the diffusion coefficient of molecule which directly depend on hydrodynamic radius and so on, average molar mass in weight (M_w). By using commercial polystyrene (PS) standards, an external calibration curve was established. Based on the excellent linear correlation between diffusion coefficient ($logD$) and molecular weight ($logM$), the molecular weight of polystyrene can be predicted using the following equation $logD = -0.6512logM - 7.2686$. The validation was done by comparing with the M_w value obtained by gel permeation chromatography within less than 5% deviation. From the diffusion coefficient, some property of polystyrene in solution, such as Flory coefficient and polymer-solvent interaction, were also studied. The Flory coefficient confirmed that chloroform is a good solvent for PS.

Keywords: Diffusion coefficient, molecular weights, diffusion ordered NMR spectroscopy.

1. Introduction

One of key parameters that affects the physical properties of polymers, thus its application, are the molecular weights (MW) and weight distributions. Because all synthesized polymers have a certain polydispersity, we only concern the term average molecular weight. These average MWs can be revealed through some physical properties under consideration. The most common average MWs can be measured by gel permeation chromatography (GPC). Despite its advantages, this method of characterization still has some drawbacks such as time-consuming and requirement of a large amount of solvent for each measurement. The stability of GPC system can also affect the results obtained; consequently, regular calibration is

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required. Additionally, the problem of solubility could rise when changing solvent and it could damage expensive GPC columns. Finally, it is not possible to get a reliable result of molecular weight with low MW (<2000 g/mol).

Diffusion ordered nuclear magnetic resonance spectroscopy (DOSY NMR) is usually used to measure the diffusion parameter of molecule by applying a gradient pulse (pulse field gradient - PFG). The basic theory of this method has been well described in the literature[1,2]. As the diffusion parameter is sensitive to molecular weight (molecular size and shape), the relationship between molecular weight (here weight average molecular weight, M_w) and diffusion coefficient (D) has been determined as follows:

$$\log D = \log A + \alpha \log M \qquad (1)$$

Where A and α are the constants that depend on the nature of polymer used. To obtain the linear relationship between $logD$ and $logM$, different parameters such as convection, temperature, and viscosity must be well controlled. The highly diluted concentration will ensure the viscosity, density and random movement without interaction condition, so that the linear relationship can be achieved.

Through enhancement and extensions of PFG technique, DOSY NMR provides a versatile tool for the determination of not only molecular weight but also the polydispersity of polymers. Neufeld *et al*. used DOSYNMR technique for molecular weight determination of small molecules [3]. Delsuc *et al*. presented a DOSY method based on maximum entropy method for reveal of weight distribution of polysaccharides and polymer systems[4,5]. Other researchers studied the application of DOSY NMR for controlled-radical polymerization systems [6-8] and block copolymers[9].

In this work, we study the applicability of DOSY NMR as an alternative method in determination of polystyrene molecular weight. The processing method parameters, as well as the calibration with appropriate standards are

also discussed. The method validation is conducted by comparing the DOSY-based molecular weight values with weight average molecular weight (M_w) obtained from GPC measurements.

2. Experimental

2.1. Chemicals

Polystyrene standards were obtained from Sigma-Aldrich. Styrene was obtained from Sigma-Aldrich and redistilled under reduced pressure to eliminate inhibitors. 2,2–azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and purified by recrystallization from methanol. Toluene was purchased from Fisher, refluxed in sodium/benzophenone to remove water and oxygen before redistilled and stocked over molecular sieves (2.4 Å) prior to use. N-hexane was purchased from Fisher and used without further purification.

2.2. Polystyrene synthesis

PS samples were synthesized by Free-Radical Polymerization (FRP) using AIBN as initiator, under nitrogen atmosphere. A solution containing 3.134 g of styrene (3.0×10^{-2} mol) and 17.0 mg of AIBN (1.0×10^{-4} mol) in toluene was introduced in a 100 mL three-neck flask. The reaction solution was then degassed by nitrogen bubbling for 45 minutes. After degassing process, the reaction mixture was heated to 70°C in a constant-temperature oil bath for 24 h. The polymerization was stopped by rapidly cooling in ice water and by opening the polymerization flask to air. This mixture was then precipitated in n-hexane, filtered, and dried under vacuum for 24 h giving a white solid (PS).

2.3. Characterization

2.3.1. NMR Experiment

NMR experiments were conducted on a Bruker AVANCE III 500 MHz spectrometer

(Faculty of Chemistry, VNU University of Science, Hanoi), using a 5 mm ATMA BBO probe head. Each sample contained 3 mg of polystyrene dissolved in 0.5 mL of deuterated chloroform (CDCl$_3$). Before measurement, all samples were equilibrated at 298 K for at least 5 minutes to avoid a temperature gradient along the sample tube. The spinning could also lead to a convection [1], so it must be deactivated.[1]H and 1D DOSY experiments were performed using*zg30*and *ledbpgp2s1d*pulse program with 16 scans. 2D DOSY experiments were performed using the standard *ledbpgp2s* pulse program employing a stimulated bipolar echo sequence with longitudinal eddy current delay (LED). Smoothed rectangle gradient pulse shapes were used throughout. The gradient pulse duration was varied from 0.5 to 4 ms. Diffusion time were set at $100 - 2000$ ms.8 step increments were defined for all acquisitions.

FID data were processed by Topspin 3.5 software, Bruker Biospin. Fourier transform was performed by the command *xf2,* line broadening 0.3 Hz was applied to all spectra. 2D DOSY spectrum was generated using Lavenberg-Marquardt algorithm. From 2D DOSY spectrum, diffusion coefficients of a chosen narrow chemical shift range can be calculated thank to Topspin 3.5 software [4,5].

2.3.2. GPC Characterization

The average molecular weights of synthesized polystyrene samples were investigated by GPC using a Water 501 pump equipped with a 2690D separation module and two detectors (Refractive-index detector DRI 410 and UV detector Kontron 432). Tetrahydrofuran (THF) was used as eluent at 30°C and at a flow rate of 1.0 mL/min. The polymer molecular weight was compared against narrow standards of PS (M_p from 620 to 3.6×10^5 g/mol).

3. Results and Discussion

3.1. Optimization of ^{1}H DOSY NMR measurement

The ^{1}H NMR spectrums of PS synthesized (above) and a standard PS (below) in Figure 1 shows four main signals in two regions. In the first region, from 1.0-2.0 ppm, there are two peaks corresponding to the protons of aliphatic chains of polymer. The second region, from 6.2-7.1 ppm, contains signals corresponding to the aromatic protons. Before running 2D DOSY experiment, the gradient pulse length δ and the diffusion time Δ were optimized to detect whole decay function properly. The optimization was done by 1D DOSY measurements. The first 1D DOSY started with value of 50 ms for Δ and 1.4 ms for $\delta$and with 2% amplitude of gradient pulse (1.0 G/cm). Then the gradient strength was increased up to 95% amplitude (45.78 G/cm), and the values of $\delta$and Δ were changed until the signal dropped to at least 5% of the residual signal. The Figure 2 showed spectra of two 1D DOSY of the standard PS (M_w = 4130 g/mol) at 2% (above) and 95% (below) amplitude of gradient pulse, where the signal obtained at 95% amplitude was already multiplied by 93 times. It must be noted that increasing δ results bigger reduction in signal, but this value is limited at 2.5 ms with SMSQ10.100 shape. After optimizing, 2D DOSY can be run with 8 increments, 32 scans each, and a linear gradient ramp. The total duration of a 2D DOSY is 12 minutes. After Fourier transform, the AU program DOSY in Topspin 3.5 give a pseudo-2D *chemicalshift − logD* spectrum. The diffusion parameter can be obtained as the center of the cross peaks. All signals of the same kind of molecule will have a similar diffusion coefficient value (Figure 3). If there was an overlap of the peaks, the signal on the 2D spectrum was convected [4,5] (signals at 1.2 ppm and 7.1 ppm).
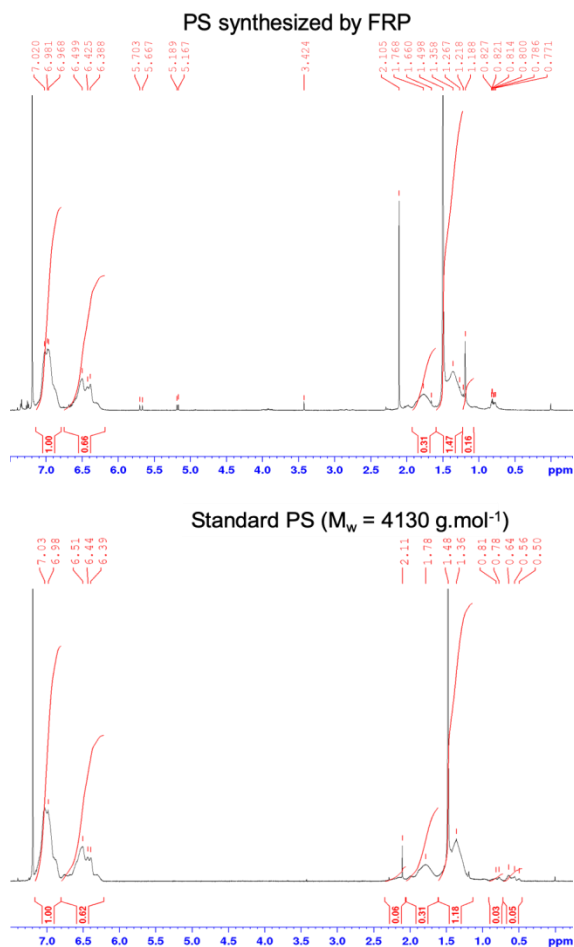
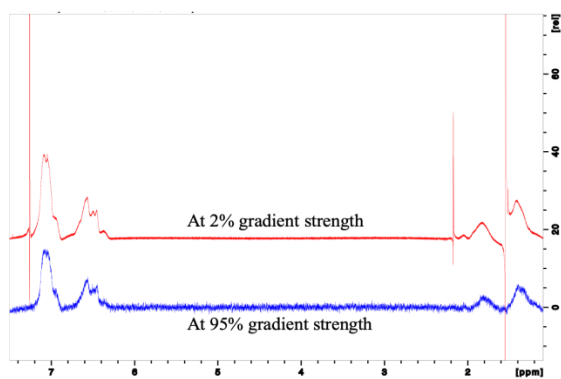Figure 1. ^{1}H NMR spectrum of PS synthesized by FRP and a standard PS (M_w = 4130 g/mol).

Figure 2. Signal attenuation at gradient strength 2 % (above) and 95% (below) amplitude (PS standard, M_w = 4130 g/mol).
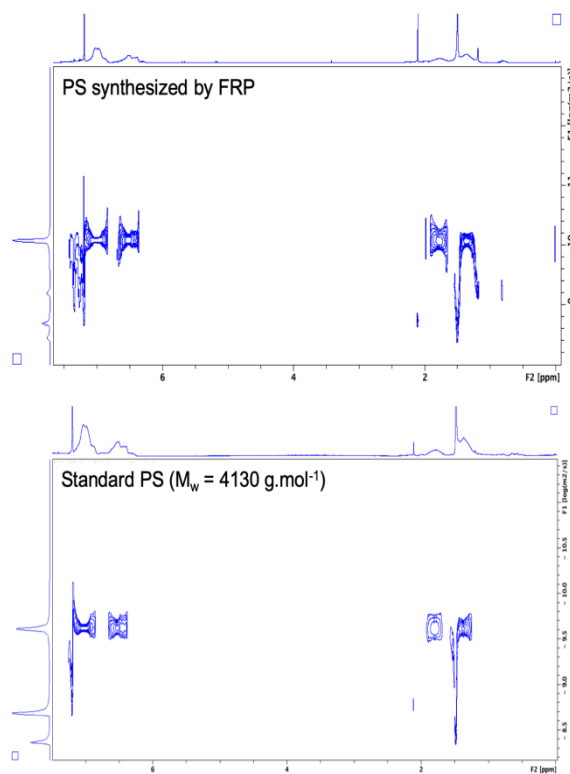

Figure 3. 2D DOSY NMR spectrum of PS synthesized by FRP and a PS standard (M_w = 4130 g/mol).

Another way to get the value of D is using Topspin T1/T2 package. If the values of δ and Δ were correctly optimized, an exponential free decay was observed. Otherwise, the free decay could be too fast or too slow [6]. The calculated diffusion coefficients of all four peaks of a standard PS (M_w=4130 g/mol) are shown in Table 1 as example. It is shown that the diffusion coefficients of all peaks of the same molecule had a similar value of D. The diffusion coefficient of peak at 6.50 ppm was chosen for further calculation, because this signal was not overlapped, therefore there was no convection.

Table 1. Diffusion coefficients of four peaks of PS (M_w = 4130 g/mol) calculated by Topspin 3.5 T1/T2 package

Peak (ppm)	7.03	6.50	1.77	1.36
D (10^{-10} m^2/s)	2.36	2.31	2.35	2.52

3.2. Calibration

Commercial narrow standards of PS (GPC standards) were selected to construct the calibration curve. Table 2 and Figure 4 show detailed results of calibration curve in chloroform. The R^2 value equal to 0.993 provided an excellent linearity of the *log D-log M* curve, over a very wide range of molecular weight. From calibration curve, the value of d_f is determined as 0.65. This value is close to the theoretical value, so the Flory coefficient of PS in chloroform is $1/d_f = 1.54$. It can be confirmed that chloroform is a good solvent for PS [10].

Table 2. D-M_w results of PS standard calibration curves

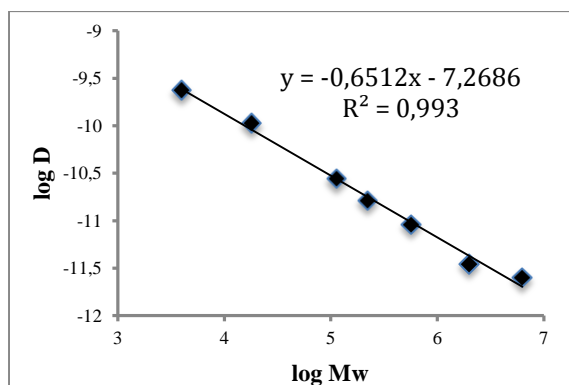| Sample	M_w(GPC) (g/mol)	D (10^{-11} m²/s)	Log D	Log M_w
PS	4130	23.6	-9.63	3.62
PS	19300	10.6	-9.97	4.28
PS	114000	2.75	-10.56	5.04
PS	223000	1.63	-10.79	5.35
PS	567700	0.91	-11.04	5.75
PS	2000000	0.35	-11.46	6.30
PS	6300000	0.25	-11.60	6.80

Figure 4. Calibration curve of *log D – log M*.

Table 3. D – M_w of PS standard validation and PS (FRP) prediction

Sample	M_w (GPC) (g/mol)	D (10^{-11}) (m²/s)	M_w (DOSY) (g/mol)	Dev.
PS	9000	14.79	8577	4.50 %
PS	50000	1.03	51000	2.00 %
PS (FRP)	23228	7.64	23779	2.30 %

3.3. Validation and Application

We applied the calibration curve with two another narrowly dispersed standard samples for validation. First, the molecular weight of two standard samples were measured by GPC, and we obtained the results matched the specification of standards, confirming the accuracy of GPC (Table 3). Second, the 2D DOSY of two commercial samples and a PS synthesized by FRP were measured. From the calibration curve, the M_w values obtained show a good correlation with small deviation (< 5 %). It is noted that all samples, including the calibration curve, were not measured at the same time, same day, but in several weeks. With the very stable of magnetic and gradient field, it is no need to recalibrate but we can use the calibration curve for a long time.

4. Conclusion

^{1}H DOSY NMR is a simple and convenient method for the determination of the molecular weight of PS and its hydrodynamic properties in chloroform. This method is used to measure the average diffusion coefficient D of PS samples of increasing M_w ranging from thousands to millions gram per mole, with the deviation below 5%. The highly linear and stable calibration curve could be used for monitoring the M_w value of various types of PS. With a Flory coefficient value equal to 1.54, it is confirmed that $CDCl_3$ is a good solvent for PS.

In complementary with GPC, Light Scattering (LS) and MALDI-TOF-MS, ^{1}H DOSY NMR appearsto be an interesting tool for the determination of polymer molecular weights.

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