APPLICATION NOTE

No. AN52907

Determination of polymer molecular weight and composition using picoSpin NMR spectroscopy

Authors:
Katherine Paulsen and Daniel Frasco,
Thermo Fisher Scientific, Madison, WI

Key words

NMR, polymer, copolymer, number average molecular weight, compositional analysis

Abstract

Polymer molecular weight determination and copolymer compositional analysis involve the integration of the resonance signals from polymer repeating units and end groups, which are inherently broad. A Thermo Scientific™ picoSpin™ 80 NMR spectrometer is well suited for these analyses. In the example of poly (ethylene glycol) (PEG) acetyl triarm, the number average molecular weight was determined with great ease. In the case of the compositional analysis of a commercial PEG-PPG-PEG block copolymer, Pluronic® L-35, the PEG/PPG ratio determined by a picoSpin 80 NMR agrees well with the manufacturer's product specification. Furthermore, the analyses using an 82 MHz and a 300 MHz NMR yielded almost identical results.

Introduction

The control of the molecular weight and molecular weight distribution (MWD) is essential to obtain and improve certain desired physical properties in a polymer product, and is therefore of great importance in material science[1]. In addition to gel permeation chromatography (GPC) and matrix assisted laser desorption ionization mass spectrometry (MALDI MS)[2], end group analysis using nuclear magnetic resonance (NMR) spectroscopy has long been established as a viable analytical technique for determining the number average molecular weight (M_n) of polymers. For polymers with a defined end group structure, the number of repeating units can be deduced by comparing the resonance signals from repeating units to those of end groups, thereby determining the molecular weight. A similar methodology can be adapted for the compositional analysis of copolymers, so long as the resonance signals from different monomers can be clearly differentiated.

Due to poor molecular rotation and marginally different chemical environments in which the repeating units are situated, resonance signals from polymer repeating units often coalesce as a broad peak, even using high-field NMR spectrometers.[3] However, in the molecular weight analysis and compositional analysis, collective signals from polymer repeating units are used for calculation and monomeric resolution is generally not required. To that end, low-field NMR readily lends itself as a low-cost alternative to high-field instruments, with significant savings on both instrument procurement and upkeep.

In this application note, molecular weight determination of poly(ethylene glycol) (PEG) acetyl triarm and compositional analysis of a polyol using a picoSpin NMR spectrometer are presented. The results of the compositional analysis using an 82 MHz NMR were also compared with those using a high-field, 300 MHz NMR spectrometer.

Experimental

The structures of the polymers examined in this study are shown in Figure 1.

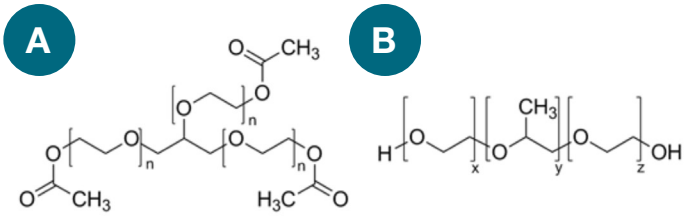

Figure 1: Chemical Structures of: **A)** poly(ethylene glycol) (PEG) acetyl triarm (PEG acetyl triarm), and **B)** poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG).

A Thermo Scientific picoSpin 80 NMR spectrometer was used to acquire the spectra of the polymer materials. The spectrometer is an 82 MHz, pulsed, Fourier transform ^{1}H NMR. The instrument contains a 2 Tesla temperature controlled permanent magnet and is fitted with a 40 microliter capillary cartridge used for sample introduction into the spectrometer.

Poly(ethylene glycol) (PEG) acetyl triarm (PEG acetyl triarm) was a crude reaction mixture provided by Dr. Lei Zhu's group in the Department of Macromolecular Science and Engineering at Case Western Reserve University.

The sample was injected neat and 64 scans were acquired. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG; Pluronic® L-35) was purchased from Sigma-Aldrich.[4] The sample was diluted in equal volume of $CHCl_3$ prior to injection. The data was collected using 16 scans. The 300 MHz NMR data of Pluronic L-35 diluted in $CDCl_3$ was acquired at Case Western Reserve University.

The liquid samples were injected into the capillary cartridge using 1 mL slip-tip polypropylene syringes and 22 gauge blunt-tipped needles. Back-to-back sample injection and data acquisition was separated by a solvent/air/solvent/air flush to thoroughly clean the capillary. Samples were either referenced to chloroform ($CHCl_3$, δ7.26 ppm) or another known signal in the spectrum.

All spectra were acquired using the following acquisition parameters: 90° excitation pulse, 750 ms acquisition time and 5 second recycle delay. Spectral data were processed using the Mnova™ NMR analysis software with a standard set of processing parameters including: Zero filling and phase correction. Apodization was not used.

Results and discussion

Number average molecular weight (M_n) determination. In ^{1}H NMR spectroscopy, the area under each resonance signal is proportional to the molar concentration of the protons being analyzed. Number average molecular weight (M_n) determination by end-group analysis using ^{1}H NMR therefore involves identifying and integrating distinguishable proton signals originating from end-groups and repeating units.

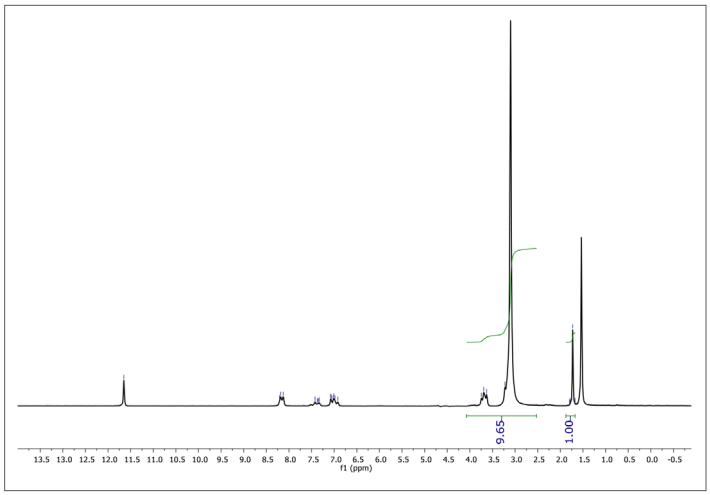

Figure 2: 82 MHz ^{1}H NMR spectrum of PEG acetyl triarm reaction mixture.

Figure 2 shows the ^{1}H NMR spectrum of PEG acetyl triarm obtained using an 82 MHz picoSpin NMR. The acetyl (-$OCOCH_3$) end-group protons resonate as a sharp singlet at δ 1.8 ppm with a normalized peak area of 1.00. The three acetyl moieties contain a total of 9 protons. The PEG repeating group (-OCH_2CH_2-) protons and the glycerol protons resonate between δ 3.1-3.8 ppm with a normalized peak area of 9.65. Each repeating group of PEG contains 4 protons, and the glycerol linkage (–CH_2CHCH_2–) contains 5 protons. Since there are three arms for the polymer, the total number of protons contributing to the signal between δ 3.1-3.8 is 12n+5.

$$\frac{\text{peak area of repeating units and glycerol linkage}}{\text{\# of protons in repeating units and glycerol linkage}} = \frac{\text{peak area of end groups}}{\text{\# of protons in end groups}}$$

$$\frac{9.65}{12n+5} = \frac{1.00}{9},\ n = 6.82 \approx 7 \text{ repeating monomer units}$$

$$M_n = FW_{\text{glycerol linkage}} + FW_{\text{end groups}} + FW_{\text{repeating units}} = 41 + 177 + (44 \times 7 \times 3) = 1142$$

Based on the end group analysis using an 82 MHz picoSpin NMR spectrometer, the number average molecular weight of the PEG acetyl triarm is 1142 g/mol.

Compositional analysis of a PEG/PPG block copolymer.

Figure 3 shows the ^{1}H NMR spectra of Pluronic L-35, a PEG-PPG-PEG copolymer, using (a) an 82 MHz picoSpin NMR spectrometer; and (b) a 300 MHz NMR spectrometer. The two spectra are very similar. In the 82 MHz spectrum, the signals at δ ~0.8 ppm with a normalized peak area of 3.0 are attributed to the methyl (-CH_3) group of PPG. The CH- and CH_2- proton signals from both PPG and PEG are located at δ ~ 3.1-3.4 ppm, with a normalized peak area of 7.65. The contributions to these signals include 3 protons from PPG (one CH- and one CH_2-) and 4 protons from PEG (2 CH_2- groups). The 300 MHz ^{1}H NMR spectrum is essentially the same: the signal from the methyl group resonates at δ 1.1 ppm with a normalized peak area of 3.0, and the CH- and CH_2-proton signals are located at δ ~ 3.3-3.7 ppm with a normalized peak area of 7.77. The minor variances in chemical shift between the two spectra are likely due to the difference in sample concentrations. Because of the higher sensitivity of a 300 MHz NMR instrument, the samples were used in a lower concentration; hence, the difference in chemical shift. The 300 MHz spectrum also offers greater resolution than the 82 MHz one. The increased resolution, however, should have little to no bearing on the results of the compositional analysis, because the collective signals are integrated for the ensuing calculations.

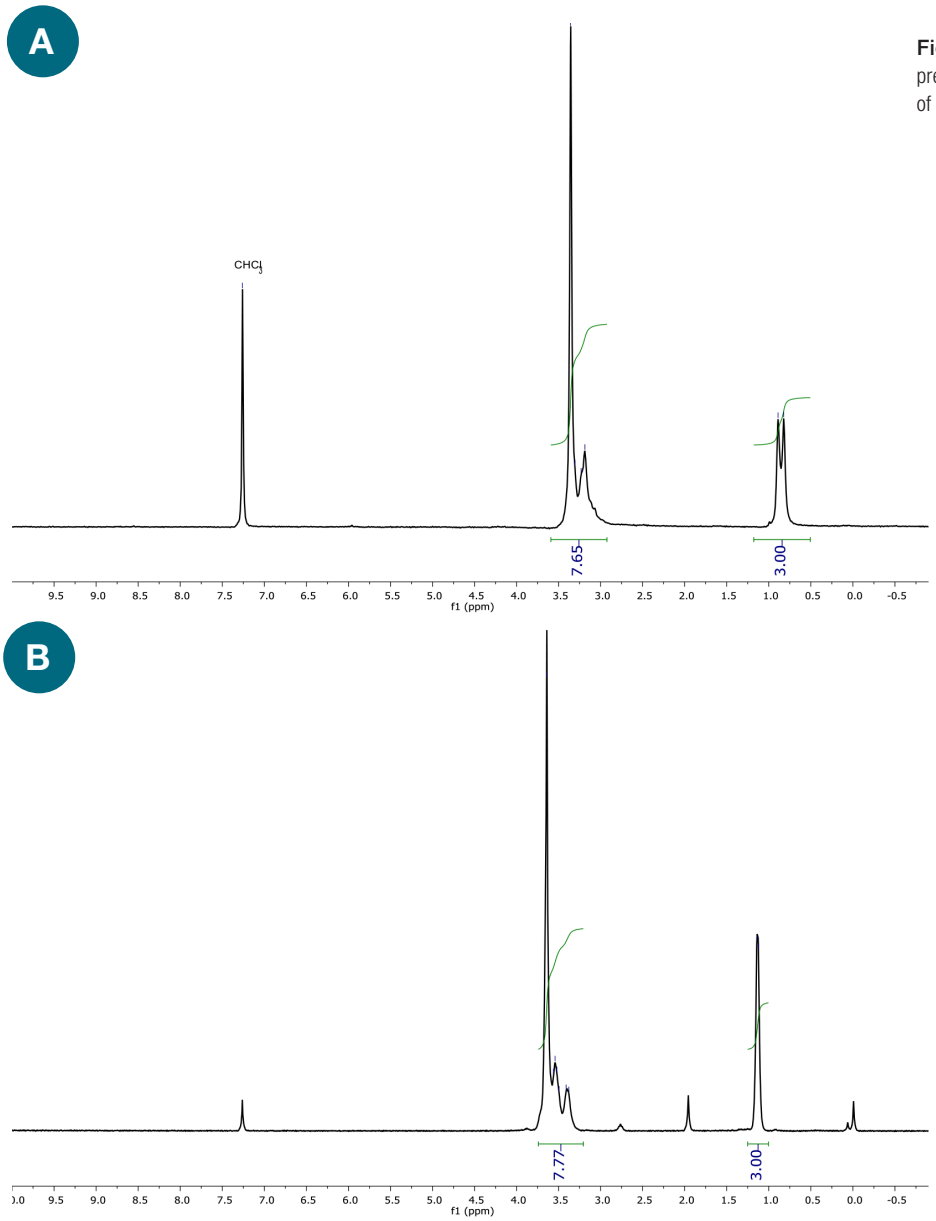

Figure 3: A) 82 MHz ^{1}H NMR spectrum of PEG-PPG-PEG prepared 50:50 (v/v) in $CHCl_3$. **B)** 300 MHz ^{1}H NMR spectrum of PEG-PPG-PEG prepared in $CDCl_3$.

thermo scientific

A detailed compositional analysis using the 82 MHz NMR spectrum is outlined below.

1. Determine the relative moles of PPG, denoted as x, using the signals at δ ~0.8.

$$x = \frac{\text{integral of methyl protons}}{\text{\# of methyl group protons}} = \frac{3.00}{3}$$

$$x = 1.0 \text{ relative moles of propylene glycol}$$

2. Determine the relative moles of PEG, denoted as y, using the signals at δ ~3.1-3,4.

$$\frac{7.65}{4y+3} = \frac{3.00}{3}$$

$$y = 1.16 \text{ relative moles of ethylene glycol}$$

3. Calculate the weight percentages of PEG and PPG.

$$\text{weight \% PEG} = \frac{\text{relative moles PEG} \times \text{MW}_{\text{PEG}}}{\text{relative moles PEG} \times \text{MW}_{\text{PEG}} + \text{relative moles PPG} \times \text{MW}_{\text{PPG}}} \times 100\%$$

$$= \frac{1.16 \times 44}{1.16 \times 44 + 1.0 \times 58} \times 100\% = 46.8\%$$

$$\text{weight \% PPG} = \frac{\text{relative moles PPG} \times \text{MW}_{\text{PPG}}}{\text{relative moles PEG} \times \text{MW}_{\text{PEG}} + \text{relative moles PPG} \times \text{MW}_{\text{PPG}}} \times 100\%$$

$$= \frac{1.0 \times 58}{1.16 \times 44 + 1.0 \times 58} \times 100\% = 53.2\%$$

Based on the 82 MHz NMR spectrum, Pluronic L-35 copolymer contains 46.8 % of PEG and 53.2 % of PPG. The results using the 300 MHz spectrum are essentially the same: 47.4 % of ethylene glycol and 52.6 % of propylene glycol. Both results are in good agreement with the product specification[4], where PEG/PPG (w/w) = 1.

Thermo Scientific picoSpin 80 NMR spectrometer

Conclusions

^{1}H NMR spectroscopy has been established as a powerful tool for polymer characterization, including molecular weight determination and copolymer compositional analysis. Both analyses involve the integration of the resonance signal from polymer repeating units, which are inherently broad. The Thermo Fisher Scientific picoSpin 80 NMR spectrometer is well suited for these investigations. In the example of poly(ethylene glycol) (PEG) acetyl triarm, the number average molecular weight was determined with great ease. In the case of the compositional analysis of a commercial PEG-PPG-PEG block copolymer, Pluronic® L-35, the PEG/PPG ratio determined by a picoSpin 80 NMR agrees well with the manufacturer's product specification. Furthermore, the analyses using an 82 MHz and a 300 MHz NMR yielded almost identical results. The Thermo Fisher Scientific picoSpin 80 NMR spectrometer has proven to be a low-cost alternative to high-field NMR spectrometers for polymer molecular weight determination and compositional analysis.

References

1. Higginbotham, C. L.; Izunobi, J.U. J. Chem. Ed. 2011, 88, 1098-1104

2. Skoog, D. A.; Holler, J. F.; Crouch, S. R. *Principles of Instrumental Analysis*, 6th ed.; Brooks Cole: Pacific Grove, 2006.

3. Bovey, F. A.; Mirua, P. A. *NMR of Polymers*, 1st ed.; Academic Press: San Diego, 1996.

4. Sigma-Aldrich. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG; Pluronic L-35; CAS No. 9003-11-6). www.sigmaaldrich.com/catalog/product/aldrich/435414

Find out more at **www.thermofisher.com/nmr**

ThermoFisher SCIENTIFIC