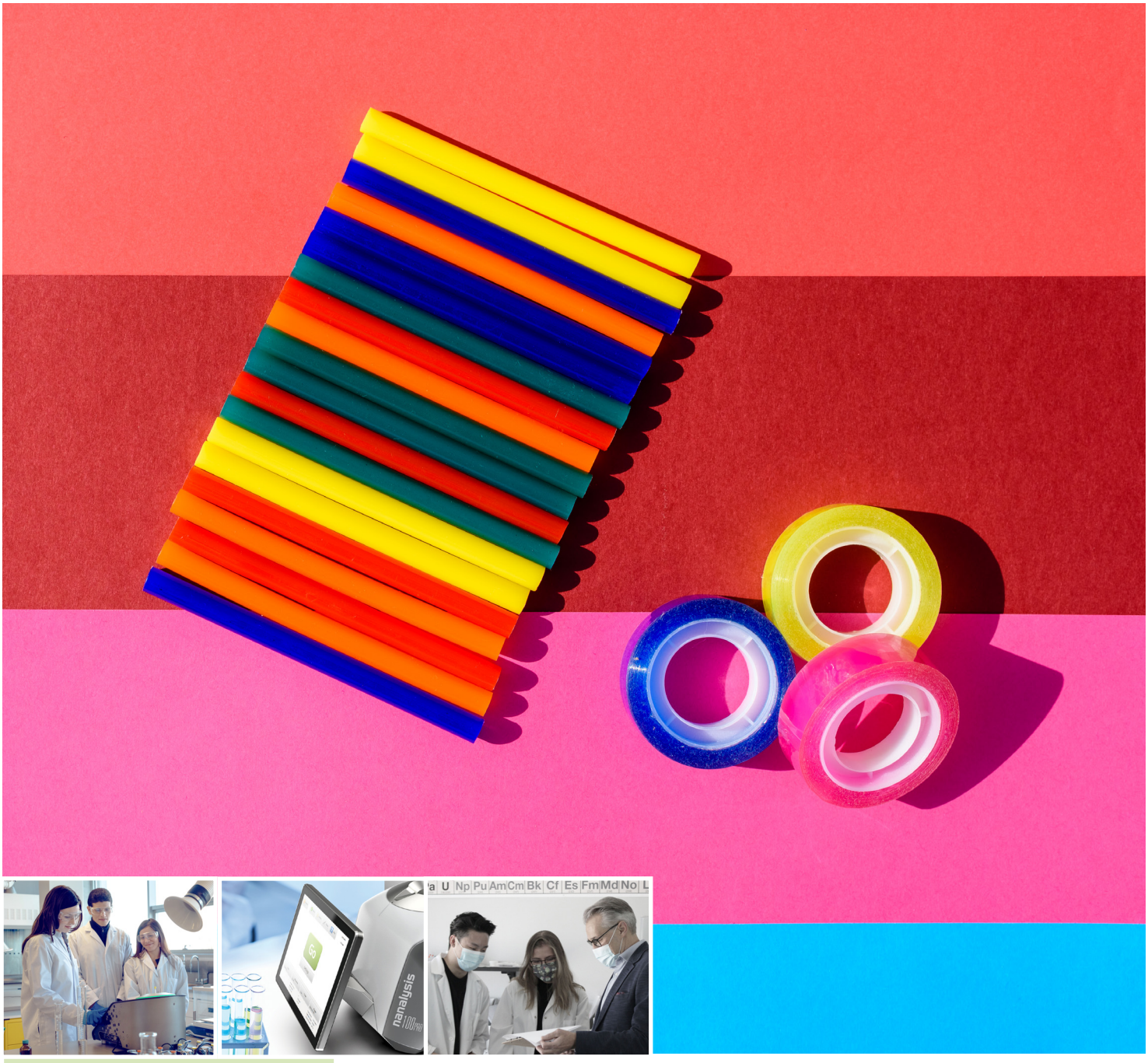
APPLICATION NOTE

Number-Average Molecular Weight (M_n) Determination in Polymers Using Benchtop NMR



nanalysis

Materials & Polymers
APPLICATION NOTE
Feb 2023

Number-Average Molecular Weight (M_n) Determination in Polymers Using Benchtop NMR

Introduction

Polymers represent a significant portion of the entire chemical industry and span materials such as plastics, rubbers, resins, and nylons, among many others.[1-2] As such, the quality control of these products on an industrial scale is crucial and involves a multitude of chemical and physical tests. Some of these include tensile strength, shear tests, thermal behavior and resistance, rheological testing, UV-resistance, chemical composition, and many more.[3] Among these tests, the number-average molecular weight (M_n) determination is essential to determine the average length of a repeating unit in a homopolymer, or of the combined lengths of different repeating units in a block co-polymer.[4]

An important distinction must be made between M_n and the weight-average molecular weight (M_w). While M_n is a summation of the product of the mole fraction of each species and its molecular weight, M_w is instead a summation of the product of the weight fraction of each species and its molecular weight. Nuclear magnetic resonance (NMR) spectroscopy is particularly well-suited to determining the M_n value of polymers, given that:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \sum X_i M_i$$

where $\boldsymbol{X_i}$ and $\boldsymbol{M_i}$ are the mole fraction and molecular weight of species $\boldsymbol{i}$, respectively. Since NMR is an inherently quantitative technique, meaning that the area under the curve is directly proportional to how many chemically equivalent nuclei are giving rise to that signal, the integration area of a given signal is proportional to the molar concentration of this signal in solution. Since all molecules in this solution will have a uniform molar response to the detector:

$$M_n = \frac{\sum A_i}{\sum N_i}$$

where $\boldsymbol{A_i}$ and $\boldsymbol{N_i}$ are the integration area of a given ^{1}H NMR signal and the number of molecules of species $\boldsymbol{i}$, respectively. This equation demonstrates that if a few key parameters about a given polymer are known, and provided some important guidelines are observed, determining M_n for a polymer using NMR is straightforward. It is important that the polymer have a known structure, that it is entirely soluble and stable in the medium of analysis, and that is has a well-defined end-group (*e.g.*, methoxy, vinyl, etc.). Some end-groups, such as hydroxyl substituents, can be problematic due to their tendency to undergo exchange in solution, affecting the accuracy of their corresponding integrations.[5] Finally, at least one of the end-group signals and one of the signals of the repeating unit must not overlap with each other or other signals.

While traditional high-field NMR instruments offer greater sensitivity and signal dispersion, these have large upfront and recurring costs, require cryogens for operation, and necessitate a large operating space. In addition, expert staff is required to maintain the instruments. With the advent of benchtop NMR instruments over the last decade, major accessibility concerns over the introduction of NMR into quality control (QC) workflows have been addressed. Herein, we showcase the use of a 60 MHz benchtop NMR instrument in determining the M_n of some commercial polymers and compare the obtained values to those provided on the label. The general theory underlying this work was adapted from thorough work published by Higginbotham *et al.* in *The Journal of Chemical Education*.[4] For a detailed description of the chemical concepts and mathematics describing these analyses, the reader is highly encouraged to read the original publication.

Results

For this work, five polymers were analyzed, the structures for which are shown in **Figure 1**. These polymers were chosen to represent different scenarios, such as single and multiple repeating units (*i.e.*, poly(ethylene glycol), poly(propylene glycol), poly(D,L-lactide)), varying end-groups (*i.e.*, methoxy, methacrylate, decane, and acrylate), and two different end-groups for the same polymer (*i.e.*, methoxy and methacrylate). Having different end-groups in a polymer allows for the determination of M_n using both end-groups, provided their respective signals are well-resolved, which can provide orthogonal confirmation of the calculated values.

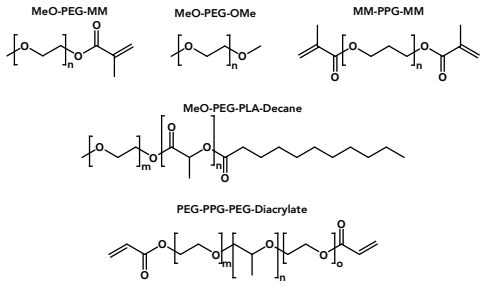


Figure 1. *Polymers analyzed in this work.* ***MeO-PEG-M****: poly(ethylene glycol) methyl ether methacrylate.* ***MeO-PEG-OMe****: poly(ethylene glycol) dimethyl ether.* ***MM-PPG-MM****: poly(propylene glycol) dimethacrylate.* ***MeO-PEG-PLA-Decane****: poly(ethylene glycol) methyl ether-block-poly(D,L-lactide)-block-decane.* ***PEG-PPG-PEG-Diacrylate****: poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) diacrylate.*

In this study, three individual assays were prepared for each polymer, and each assay was analyzed in triplicate, for a total of nine analyses per polymer. For each polymer, very close agreement between the values obtained at 60 MHz and those on the product label were obtained.[6] These results are summarized in **Table 1**.

Table 1. Summary of the M_n values of commercial polymers analyzed using ^{1}H (60 MHz) benchtop NMR, in addition to the values provided on the label.

Polymer	Repeating Unit[a]	End-Group[b]	Assay	M_n 60 MHz[c]	M_n Label[d]	%diff[e]
MeO-PEG-MM	PEG	Methacrylate (Vinyl)	1	1,117 (0.6)	1,076	3.7
			2	1,122 (0.7)		4.2
			3	1,116 (0.9)		3.6
MeO-PEG-OMe	PEG	OMe	1	1,039 (0.3)	1,050	1.1
			2	1,052 (1.9)		0.2
			3	1,030 (0.4)		1.9
MM-PPG-MM	PPG	Methacrylate (Vinyl)	1	570 (0.3)	556	2.6
			2	570 (0.0)		2.6
			3	569 (0.0)		2.2
MeO-PEG-PLA-Decane	PEG	OMe	1	2,012 (0.4)	2,024	0.6
			2	2,035 (1.2)		0.5
			3	2,049 (0.8)		1.2
	PLA	OMe	1	2,431 (1.2)	2,485	2.2
			2	2,462 (1.9)		0.9
			3	2,460 (1.2)		1.0
PEG-PPG-PEG-Diacrylate	PEG+PPG	Acrylate (Vinyl)	1	6,319 (0.5)	6,636	0.7
			2	6,315 (0.5)		0.7
			3	6,636 (0.5)		0.0

[a]Repeating unit being quantified. [b]End-group used for quantification. [c]Average of triplicate analyses, the relative standard deviation (RSD) values for which are provided in parentheses. [d]Values provided on Certificate of Analysis (COA) according to lot# for each polymer. According to the COA, these values were all determined using ^{1}H NMR. [e]%diff=[M_n (60 MHz) – M_n (label)] / [(M_n (60 MHz) + M_n (label))/2].

Calculations

As a specific example of how the M_n values were calculated for the samples analyzed in this work, **Figure 2** illustrates the ^{1}H (60 MHz) NMR spectrum of the **MeO-PEG-PLA-Decane** polymer.

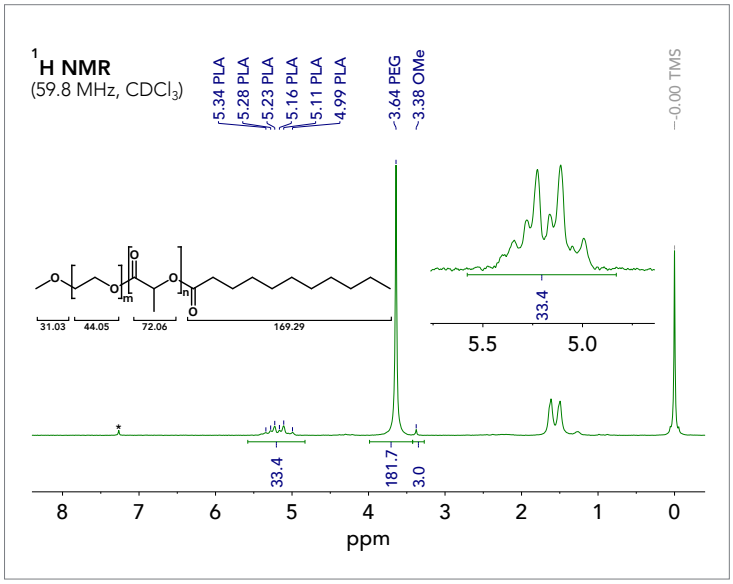


Figure 2. ^{1}H (59.8 MHz) NMR spectrum of MeO-PEG-PLA-Decane polymer, with integration areas used in M_n calculations highlighted. The structure of the polymer is shown, along with the respective molecular weights of the individual sub-units. The asterisk represents the residual solvent peak for chloroform.

To calculate the M_n values for the PEG and PLA chains using the data in **Figure 2**, the following equations are used:

$$n_{PEG} = \frac{a_{PEG} \times m_{OMe} \times n_{OMe}}{a_{OMe} \times m_{PEG}}$$

where n_{PEG} is the number of repeating PEG units, a_{PEG} is the integration area for the PEG signals, m_{OMe} is the number of protons associated with the OMe end-group, n_{OMe} is the number of repeating OMe units, a_{OMe} is the integration area for the OMe signal, and m_{PEG} and is the number of protons associated with the PEG group. As such:

$$n_{PEG} = \frac{181.7 \times 3 \times 1}{3 \times 4} = 45.4 \approx 45$$

Finally, because we know the molecular weight of each repeating PEG fragment, the M_n value can be calculated using the number of repeating PEG units:

$$M_{n(PEG)} = 45 \times 44.05 = 2{,}001 \ g/mol$$

Using the same approach, the M_n value for the PLA fragment can be calculated:

$$n_{PLA} = \frac{33.4 \times 3 \times 1}{3 \times 1} = 33.4 \approx 33$$

$$M_{n(PLA)} = 33 \times 72.06 = 2{,}407 \ g/mol$$

While only the M_n values for the PEG and PLA repeating units are provided for this polymer, it is common for suppliers to also include the M_n of the entire polymer. In this case, this would involve a summation of the individual M_n values for each individual sequence of repeating units, in addition to the molecular weights of the end-groups, which are methoxy (31.03 g/mol) and decane (169.29 g/mol) functionalities in this case:

$$M_{n(polymer)} = 31.03 + 2{,}001 + 2{,}407 + 169.29 = 4{,}608.32 \ g/mol$$

As evidenced by the results of this study, the number-average molecular weight test for polymers is well-suited to analysis via benchtop NMR spectroscopy. While only the work for the **MeO-PEG-PLA-Decane** polymer is explicitly shown here, the exact same approach was used for the other four polymers. If you have any questions about the incorporation of benchtop NMR into your polymer workflows, or about the work presented herein, please don't hesitate to contact us!

References

(1) Billmeyer, F. W. in *Textbook of Polymer Science*, 3rd ed.; John Wiley & Sons Ltd: New York City, New York, USA, **1984**.

(2) Hart, D. J.; Hadad, C. M.; Craine, L. E.; Hart, H. in *Organic Chemistry: A Short Course*, 13th ed.; Brooks/Cole, Cengage Learning: Belmont, California, USA, **2012**.

(3) van Krevelen, D. W.; te Nijenhuis, K. in *Properties of Polymers*, 4th ed.; Elsevier: Amsterdam, Netherlands, **2009**.

(4) Izunobi, J. U.; Higginbotham, C. L. *J. Chem. Educ.* **2011**, *88*, 1098–1104.

(5) Amin, N.; Claridge, T. *Quantitative NMR Spectroscopy*; **2017**.

(6)Polymers were received from MilliporeSigma and used without further purification. **(a)** poly(ethylene glycol) methyl ether methacrylate p/n: 447951, lot: MKCP5234. **(b)** poly(ethylene glycol) dimethyl ether p/n: 445894, lot: BCBV5276. **(c)** poly(propylene glycol) dimethacrylate p/n: 455032, lot: MKCP9597. **(d)** poly(ethylene glycol) methyl ether-block-poly(D,L-lactide)-block-decane p/n: 764736, lot: MKBP5197V. (e) poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) diacrylate p/n: 915858, lot: MKCM7406.

nanalysis™

Bay 1, 4600 – 5 Street NE
Calgary, Alberta, Canada
T2E 7C3

Tel: +1.403.769.9499

nanalysis.com

sales@nanalysis.com