**Polymer Characterization: Nuclear Magnetic Resonance Spectroscopy (NMR)**

*Instructor Support Document*

*How to Use This Document*

This document accompanies a set of slides produced by the ACS PolyEd initiative. It is meant to provide deeper explanation of the concepts and content found on these slides, supporting their use in the classroom. For each slide, we suggest how to walk students through the slide to promote learning, then we include background information that will assist you, the instructor, in teaching the material. This document is not intended for dissemination to students, but rather to bring you, the instructor, “up to speed” on this polymer content. You can choose what background information is relevant to your students and course, it is not necessary to include all background information in all teaching contexts.

*The Slides*

These slides are meant to serve as a way to incorporate polymer content into sophomore- or junior-level lecture and lab courses such as organic chemistry or instrumental analysis. The slides assume that students have already been exposed to the theory of NMR, and thus only provide a brief refresher on the technique. Next, the slides cover the limitations of NMR when it comes to analyzing polymer samples. The slides finish with several examples of polymer NMR applications.

*MACRO Content Connections*

Depending upon your and your students’ familiarity with polymers, you may wish to include some or all of the “Polymers: Essential Background and Definitions” slides also found in MACRO. These slides also have an accompanying instructor document for your convenience. This document contains a great deal of fundamental information about polymers and an extensive jargon vocabulary list.

For organic chemistry, especially, these slides pair well with the module “Polymers: Synthesis by Alkene Chemistry”. NMR is a go-to method for analyzing the structures of alkene-based polymers.

*Glossary*

Backbone: The principal chain of a polymer, in which is defined the repeat unit

Block copolymer: A copolymer in which the two different repeat units are arranged in pure blocks of each type of repeat unit, for example 30 repeat units of linear polystyrene bound to 30 repeat units of linear polymethacrylate

Copolymer: A polymer containing more than one type of repeat unit

Degree of polymerization: The number of repeat units in a given chain

End-group: The structures at either end of a polymer chain that are not part of a repeat unit

Gradient copolymer: A copolymer in which one of the chain begins rich in one type of repeat unit, but more of the other repeat unit is gradually added to the sequence until the other end of the chain is predominantly the second repeat unit

Homopolymer: A polymer consisting of only one type of repeat unit

Linear polymer: An unbranched polymer

Macromolecule: A large molecule consisting of linked repeating subunits; may also be a polymer

Molar Mass: The mass of a polymer chain, expressed in various units including g/mol

Monomer: The small molecule from which a polymer is derived

Nuclear Magnetic Resonance Spectroscopy (NMR): A spectroscopic technique that uses radio waves to excite suitable atomic nuclei aligned in a magnetic field. The emitted radiation is put through a Fourier Transform to change the time domain to the frequency domain to generate the spectrum. The chemical environment around the nucleus determines the characteristics of the signal, allowing for structure analysis.

Number-average molecular weight (*M*n): The average molecular weight of polymer chains in the sample, weighted by number of chains that possess a given weight

Percent (%) conversion: The percent of monomer functional groups that have been converted to polymer backbone functional groups

Polymer: A large molecule consisting of covalently linked repeating subunits; created from monomers

Random copolymer: A copolymer in which the sequence of repeat units is random

Repeat unit: The simplest repeating structure in the polymer backbone

Size-Exclusion Chromatography (SEC): A liquid phase characterization method that measures the molar mass and molar mass distribution of a polymer sample

*Slide-by-Slide Guide*

Slide 2: NMR Overview

Student walkthrough: Students should have experience with using NMR to determine or confirm the structure of small molecules, so provide a brief refresher on NMR theory before connecting it to analyzing polymers and other macromolecules.

Additional background: For additional information on NMR as a technique, the authors recommend the following:

Silverstein, R. M., Webster, F. X., Kiemle, D. J., *Spectrometric Identification of Organic Compounds (7th ed.),* John Wiley and Sons, Inc., Hoboken, NJ. 2005

Slide 3: Polymer NMR Limitations

Student walkthrough: Walk students through the simulated example styrene and polystyrene spectra, noting the resonance broadening after polymerization and the shift of the monomer alkene signals between 5-6 ppm to polymer alkane signals between 1-2 ppm. Then draw their attention to the need for solubility unless you have access to advanced instrumentation. Are there other techniques we could use to interrogate the molecular structure of an insoluble polymer?

Additional background: Small molecules produce sharp resonances because they can freely tumble in the sample solution. Each nucleus of the same type (for example, the benzyl hydrogen in styrene) is experiencing the exact same chemical environment, resulting in a clean resonance at 6.63 ppm. Polymers are different from this in two ways: large polymer molecules cannot tumble freely, and there are slight chemical environment differences between the center of a polymer chain and the chain ends. This causes polymer resonances to be mildly to significantly broader than those of their corresponding monomers.

For polymers derived from alkene monomers, 1H NMR is an especially powerful analytical tool. The monomer and polymer backbone resonances are quite chemically distinct, with monomer alkenes showing up in the 4.5-6.5 ppm region and polymer alkanes appearing in the 0-2 ppm region, depending upon the specific solvent.

The need for soluble samples is the main drawback of NMR as a tool for polymer analysis. Many acyl-substitution based polymers, especially polyamides, are very insoluble, as can be poyolefins like polyethylene and polypropylene. There are NMR instruments that can analyze solid samples, but these are advanced instruments only available at larger research institutions. Fourier Transform Infrared Spectroscopy (FTIR) can handle solid samples in powder, film, or KBr pellet form, and can serve as a complementary method when NMR is not available. The main drawback of FTIR is the greater degree of difficulty in getting quantitative, rather than qualitative, structure data. For more information on using FTIR in polymer analysis, check out the MACRO module “Polymer Characterization: Fourier Transform Infrared Spectroscopy”.

Slide 4: Determining % Conversion

Student walkthrough: Explain that NMR can be used to determine the extent of a reaction

(% conversion) for polymerizations just as it can for small molecule reactions. Show them how the integrations of the residual monomer alkene resonance are compared to that of a chemically distinct resonance in the repeat unit to calculate the percent conversion.

Additional background: Intelligent selection of the particular resonances to use is the most important part of calculating % conversion by NMR. With most common instruments, the resolution of the technique is limited to determining up to 99.9% conversion.

Slide 5: End-Group Analysis

Student walkthrough: Show students how a similar calculation can be used to get the ratio of repeat units to end groups to calculate Mn for a polymer. You may need to introduce the term “degree of polymerization (DP)” and the units Dalton (Da, 1 g/mol) and kiloDalton (kDa, 1,000 g/mol).

Additional background: The molecular weight is one of the most important properties to know about a polymer sample. NMR is a good way to obtain an absolute measure of Mn, the number-average molecular weight. Because of the resolution of most instruments, this technique only works for polymers up to about 20 or 30 kDa. As with determining % conversion, choosing your resonances carefully is critical.

In this example, the end group resonance from the hydrogen nuclei alpha to the trithiocarbonate (marked with an orange asterisk) at 3.27 ppm is compared to that of the nuclei alpha to the ester in the repeat unit (marked with a blue plus) between 4.3-3.9 ppm. Note that this polymer resonance shows the expected broadening. The integration of the end group resonance was specifically set to 2.00 to reflect the number of nuclei generating that signal in a single molecule. Dividing the integration of the repeat unit resonance by that of the end group provides the mole ratio of repeat unit to end group. This number is also called the “degree of polymerization” (DP), representing the average number of repeat units in a single chain. By multiplying the DP by its molar mass and adding the molar mass of the end groups, we can obtain an absolute measurement of Mn. This is the appropriate molar mass to use for stoichiometric calculations to post-modify a polymer chain.

Other methods for obtaining Mn include Size Exclusion Chromatography (SEC), Matrix-Assisted Laser Desorption (MALDI) Mass Spectrometry, and techniques based upon colligative properties like viscometry and osmometry. You can learn more about these methods in the MACRO modules “Polymer Characterization: Size Exclusion Chromatography” and the upcoming “Methods for Determining Polymer Molecular Weight”.

Slide 6: Copolymer Composition

Student walkthrough: You may need to remind students of the term “copolymer”. Explain that many material properties are dependent on the ratios of different repeat units in the copolymer, then walk them through the example calculation. At the end of the lesson is an optional problem asking students to extend their knowledge, bringing in additional stoichiometry concepts.

Additional background: Copolymers are a rich class of materials with fascinating and useful material properties. Random copolymers can have tunable glass transition temperatures or serve as additives to stabilize polymer blends. Block copolymers can phase segregate into nanometer-scale patterns and self-assemble into nano- and micro-particles with a wide variety of applications. Knowing the exact ratios of the monomers involved is key to understanding their behavior. For example, a block copolymer in which one block is much larger than the other will assemble into spheres of the minor block embedded in a continuous matrix of the major, while a copolymer with a 50:50 composition will assemble into alternating sheets called lamellae.

Determining copolymer composition by NMR is another application of the same concepts we have already covered. This time, you’re comparing two nuclei or sets of nuclei that are distinct between the two repeat units. This is especially easy if you can pick two resonances that are being caused by the same number of nuclei. If you can’t, you just need to normalize the resonance integrations by the number of nuclei causing them.

The given example is a block copolymer of acrylamide (AM) and hydroxyethyl methacryate (HEMA). The full name of this material is poly(acrylamide)-*b*-poly(hydroxyethyl methacrylate) or PAm-*b*-PHEMA. The italicized “*b*” means it’s a block copolymer. Other copolymer naming conventions include *co* for a generic copolymer, *ran* for a random copolymer, and *grad* for a gradient copolymer. If the number of repeat units is known, it can be placed as a subscript outside the repeat unit’s parentheses in the structure.

The resonance around 7 ppm is from the two hydrogens on the nitrogen atom in the acrylamide repeat unit, while those between 2.4-1.1 ppm are from the six hydrogen atoms on the polymer backbone of both repeat units. The sharp resonance at 1.8 ppm is residual diethyl ether and was not integrated. The NH2 resonance was integrated to 2.00. Stoichiometrically, this means that there should be 3.00 integration for the backbone hydrogens associated with this repeat unit. By adding the two backbone integrations, we find there is a total of 4.21 integration units of backbone hydrogens. From that we subtract the 3.00 associated with the acrylamide, meaning that the 1.21 units remaining are from the HEMA repeat units. The rest of the calculation is analogous to using mole amounts to calculate mole fraction, except in terms of integration units.