Chem/MatS/ChEn 4223W

Assignment 17
Due: *In Lecture*, Monday, April 22

The Lab 6 instructions explain that different stereochemical sequences in polylactide are observed at different chemical shifts by ^{1}H NMR. Thakur et al. have assigned specific different shifts to these sequences.[1,2,3]

tacticity sequence	chemical shift (δ, ppm)
sis	5.23
sii (or *iis*)	5.22
iis (or *sii*)	5.18
iii	5.17
isi	5.16

Technically, *sii* and *iis* aren't the same; they refer to a defect either at the beginning or the end of a four-unit segment in the (-COOH end)-to-(-OH end) direction.

1. The graphic on the next page shows a hypothetical situation: a section of polymer chain that has four L-lactide monomers and one D-lactide monomer. (So, it represents a polymer that is 80% L-lactide and 20% D-lactide.) There are ten α-protons in this segment, contributing an intensity of "10H" to the δ = 5.1-5.3 ppm region of the NMR spectrum, and ten tacticity sequences that determine the chemical shifts of those ten protons.[4]

   What are the ten sets? I've filled in the blanks for two of the ten--what are the other eight? What chemical shift would you expect each set to appear at? I've filled in one of those—what are the other nine?

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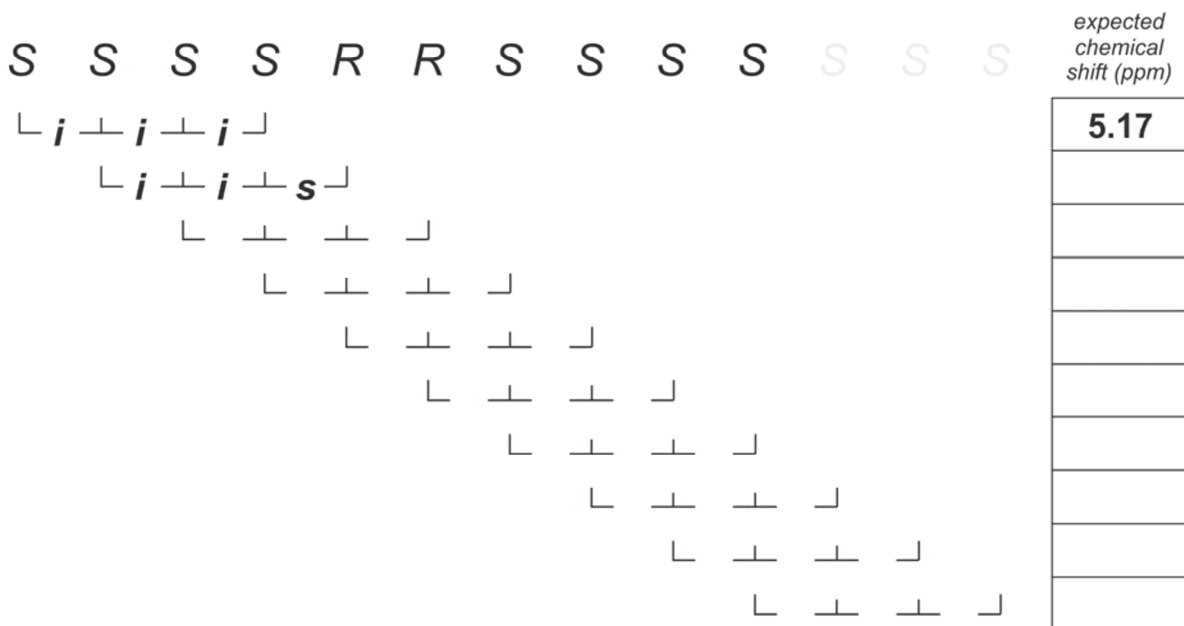
[1] Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Kolstad, J. J.; Lindgren, T. A.; Doscotch, M. A.; Siepmann, J. I.; Munson, E. J. *Macromolecules* **1997**, *30*, 2422.
[2] Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Doscotch, M. A.; Munson, E. J. *Anal. Chem.* **1997**, *69*, 4303.
[3] Zell, M. T.; Padden, B. E.; Paterick, A. J.; Thakur, K. A. M.; Kean, R. T.; Hillmyer, M. A.; Munson, E. J. *Macromolecules* **2002**, *35*, 7700.
[4] You might ask yourself, "which individual proton in a tacticity sequence of four protons is responsible for the peak at δ = 5.17/5.21/5.23 ppm?" Quantum mechanics, unfortunately, tells us we can't think that way. NMR evaluates the difference in energy between spin states, and those states can represent single protons (most of the time), or sets of protons (in this case). So here you will assign chemical shifts to tacticity sets rather than to individual protons.



Each tacticity set—each box you filled in above in the column on the right—contributes 10% to the total NMR intensity of this polymer segment. Given your answer, for the hypothetical 20% D-lactide polymer, what fraction of the 10H total integral is at each chemical shift in the chart on the previous page?

% of total intensity at	
% of total intensity at 5.23 ppm:	
% of total intensity at 5.22 ppm:	
% of total intensity at 5.18 ppm:	
% of total intensity at 5.17 ppm:	
% of total intensity at 5.16 ppm:	

Okay, let's pretend you are a NatureWorks employee, and you don't know how much D-lactide there is in your polymer. So you measure a ^{1}H NMR spectrum of the polymer, and you get the % intensities in the five boxes above. To calculate the % D-lactide in the polymer, you could take the % of the total NMR intensity at

________ ppm and multiply that number by ______ .

(You could probably solve this problem more accurately by averaging multiple integrals, but I'll just ask for one here.)

2. Open and process the ^{1}H-decoupled NMR data (posted to the NMR server, in the /*data* directory) for your group's "stereoimpure" polymer. What % of the total intensity in the δ = 5.1-5.3 ppm region region do you measure in each of the ranges we've been talking about?

% of total intensity at 5.23 ppm:	
% of total intensity at 5.22 ppm:	
% of total intensity at 5.18 ppm:	
% of total intensity at 5.17 ppm:	
% of total intensity at 5.16 ppm:	

Notes on problem 2:

If you were a group that had a low % of impurities, you will probably be looking for peaks with low intensity relative to the main peak at δ = 5.17 ppm. Along with the peaks you are looking for, you may find additional peaks in the δ = 5.2 ppm region that are artifacts of the NMR experiment—especially if they are matched with identical, mirror-image peaks on the other side of the δ = 5.17 ppm peak. These include:

- *Spinning sidebands.* If the non-spin shims in the NMR experiment aren't perfectly shimmed, small peaks or shoulders will appear to the left and right of each peak, with a chemical shift difference that is proportional to the sample spin rate.[5,6]

- *^{13}C satellites.* ^{13}C-^{1}H coupling is not usually observed in ^{1}H NMR, because 99% of all naturally occurring carbon is ^{12}C. This means, however, that every singlet in ^{1}H NMR for a ^{12}C-attached proton will have an overlapping doublet with 1% intensity corresponding to a ^{13}C-attached proton. ^{13}C-^{1}H coupling constants can be much larger than ^{1}H-^{1}H coupling constants, and so the peaks of this doublet are sometimes far from the singlet. As is the case with spinning sidebands, ^{13}C satellites appear symmetrically on the left and right sides of the main ^{1}H peak.

Make sure that your integrals have enough significant digits to answer this question. The ACD/NMR software may report only one significant digit, but I think your integrals will have more precision than this.

Peaks in your NMR spectrum will be overlapped, and this will make it challenging for you to set appropriate integral limits. One way you might address this problem is to fit your NMR spectral data to multiple Gaussian (peak) functions, and then to use those functions to calculate areas for each peak independently, without integrating in

[5] Bammel, B.; Evilla, R. F. *Anal. Chem.* **1980**, *52*, 1999.
[6] Borer, M. W.; Maple, S. R. *J. Magn. Reson.* **1998**, *131*, 177.

the usual way. ACD/NMR Processor has this functionality, in the “PeakFitting” menu. To fit your data:

- Open your Fourier-transformed NMR spectrum in ACD/NMR Processor.
- In the menu bar above your spectrum, click **PeakFitting**.
- To select the peaks you want to model, click **Peaks**. Then, click your cursor on the top of each peak you would like to include in your fit. The software will make initial, poor guesses for your peakshapes as you click; ignore these, and keep clicking until you’ve marked all of your peaks.
- Click **Auto** to perform your fit. If things went well, the software should show the fitted peaks in blue, and an error calculation (any part of the spectral data that couldn’t be accounted for by the peak modeling) in red.
- In the shortcut toolbar (right above the menu toolbar), there are five symbols that look like tables. The left-most one is **Show Table of Peaks**. (You can confirm this by putting your cursor over it—the name will pop up.) Click on this button. In the table that pops up, each peak you’ve tagged will be listed, along with relative areas under each peak. You can use these values in your calculations.

3. From your NMR data, what % D-lactide is your group’s “impure” polymer? How does that compare to what you predicted for your impure polymer in Assignment 15?

	% L-lactide	**% D-lactide**
By NMR, I measured:		
In Assignment 15, I predicted:		