Chemistry/MatSci 5223W Wednesday, April 12

Assignment 19
Due: *In Lab*, Thursday, April 20/Friday, April 21

In the NMR spectrum of stereochemically pure poly(L-lactide), the α-ester proton is characteristically observed at δ = 5.17 ppm, but stereochemical defects cause shifts in the chemical shift of these protons. Thakur et al. have assigned different shifts to different stereochemical sequences.[1,2] They concluded that α-ester protons in PLLA appear at chemical shifts shown in the chart below, according to the introduction of a minority of R defects:

stereosequence	chemical shift (δ, ppm)
*SS**R**RSS* *SS**S**RRS*	5.23 5.22
*SS**S**RSS*	5.21
*SS**R**SS* *SS**S**SS* *SS**S**SR*	5.17

The δ = 5.23 ppm and δ = 5.22 ppm protons are in the same box because these peaks will probably be indistinguishable in your NMR.

1. In the sequences below, each letter *R* and *S* describes the stereochemistry of an α-proton in poly(lactide). Mark each proton (letter) that would appear at δ = 5.22-5.23 ppm with an X, and each that would appear at δ = 5.21 with an O.

S S S S R S S S S S *S S S S R R S S S S*

(from meso-lactide) *(from D-lactide)*

2. Based on your answer above, how would you expect integrated NMR signals in the δ ≈ 5.2 ppm range to relate to the fraction of *R* stereocenters in the polymer? Write an equation that relates them.

[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. Calculate the fraction of *R* stereocenters in each of the stereochemically impure polymers made by your supergroup from the decoupled NMR spectra. Do the numbers you calculate match the fraction of *rac*-lactide you started with? Attach copies of the NMR spectra to this assignment.