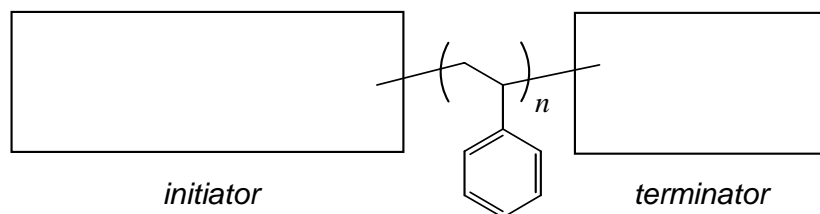


Assignment 11**Due:** *In Lecture*, Wednesday, February 22

1. In Lab 4, you will be using NMR data to determine \overline{M}_n for your polystyrene homopolymer. Because

$$\overline{M}_n = \frac{N_M}{N_I} \times \text{MW}(M),$$

where N_M/N_I is the ratio of monomer units to initiator (or terminator) units in a polymer and $\text{MW}(M)$ is the monomer molecular weight. Because N_M/N_I can be measured by NMR integration, NMR is easily used to determine molecular weight for polymers. In the boxes below, draw the structures of the initiator and terminator groups in your PS homopolymer.



2. Next, in the sample polystyrene NMR on the following page, find peaks that correspond distinctly to a particular set of protons in either the initiator or terminator in the structure you drew above. Given your assignments, what is \overline{M}_n for this polymer?

PS sample

University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

Date: Feb. 18, 2005

Solvent: CDCl3

File: 050218v3_2402

Starting Time: 17:52:34

Completion Time: 18:00:28

Total acq. time 1 minute

UNIRYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 2.000 sec

Width 5998.8 Hz

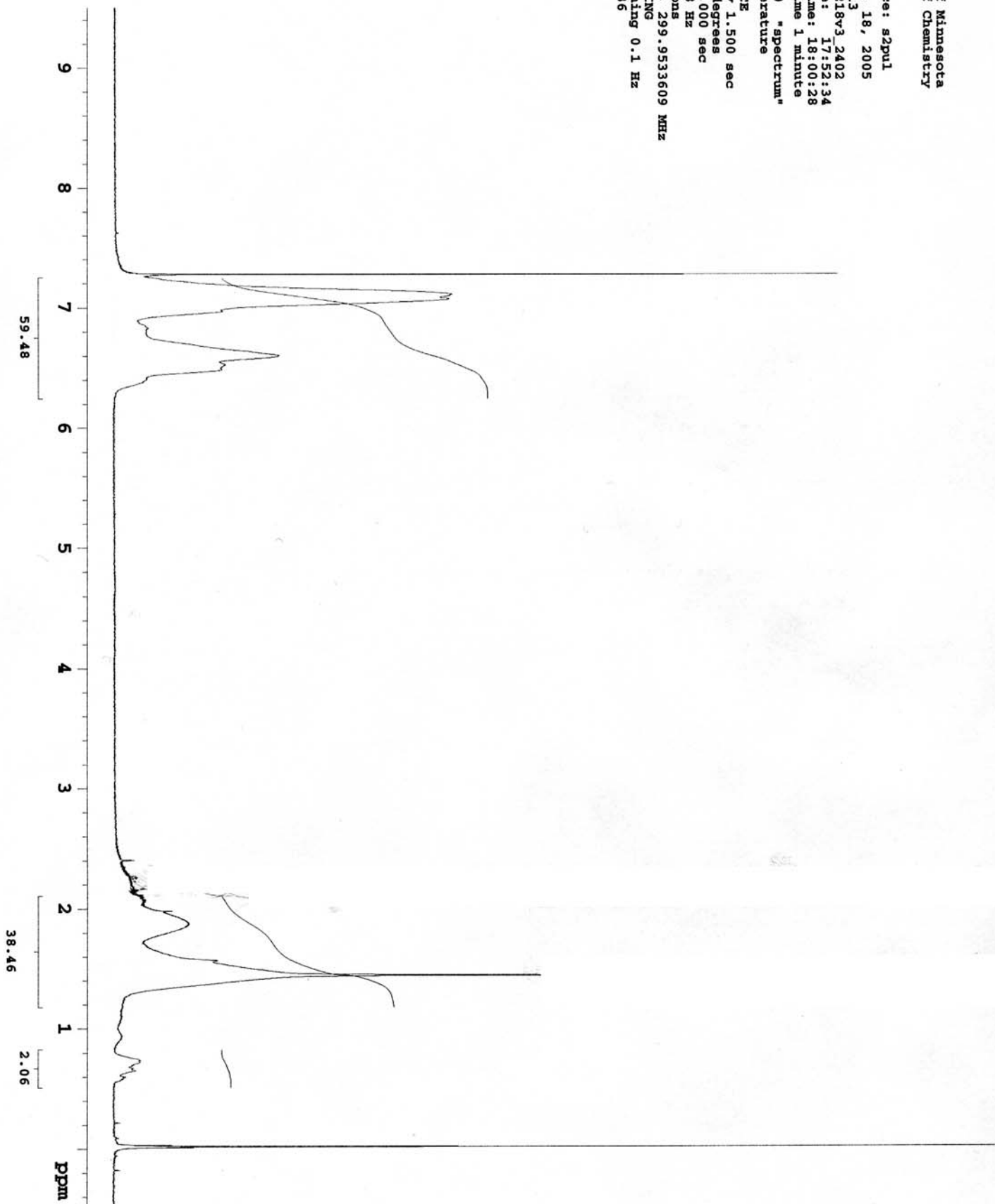
16 repetitions

OBSERVE H1, 299.9533609 MHz

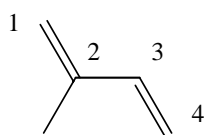
DATA PROCESSING

Line broadening 0.1 Hz

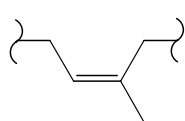
FT size 65536



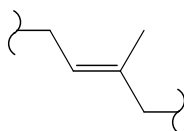
3. Last week you also synthesized polymers containing polyisoprene blocks. The connectivity of every styrene unit in polystyrene is the same— C_α of one styrene is connected C_β of the next, and so on. However, isoprene can be incorporated into a growing polyisoprene chain in a number of regiochemically distinct ways. The connectivity of isoprene units is described by the numbers of the isoprene carbons:



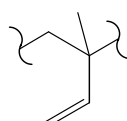
isoprene



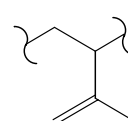
cis-(1,4)



trans-(1,4)



(1,2)



(3,4)

Which regiochemistry predominates in a particular polymerization depends sensitively on solvent(s), counterion, and reaction conditions. You can find a good review of this subject in “Stereochemistry of Polymerization”, Chapter 9 of *Anionic Polymerization: Principles and Practical Applications* (H. Hsieh and R. Quirk; Marcel Dekker, New York, 1996; Available as a NetLibrary resource, <http://www.netlibrary.com/>.)

For each of these isomeric units, which protons would be most clearly distinguished from polystyrene peaks by NMR? At what chemical shifts would you expect to find these resonances, and how many would you find for each?