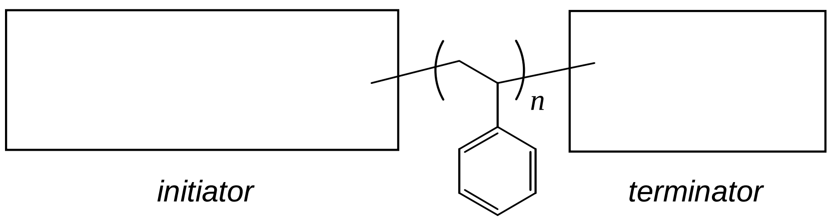
Chem/MatS/ChEn 4223W

Assignment 12
Due: *In Lecture*, Monday, March 11

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

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

where N_M/N_I is the ratio of monomer units to initiator (or terminator) units in a polymer and MW(M) is the monomer molecular weight. Because N_M/N_I can be measured by NMR integration, NMR is often 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

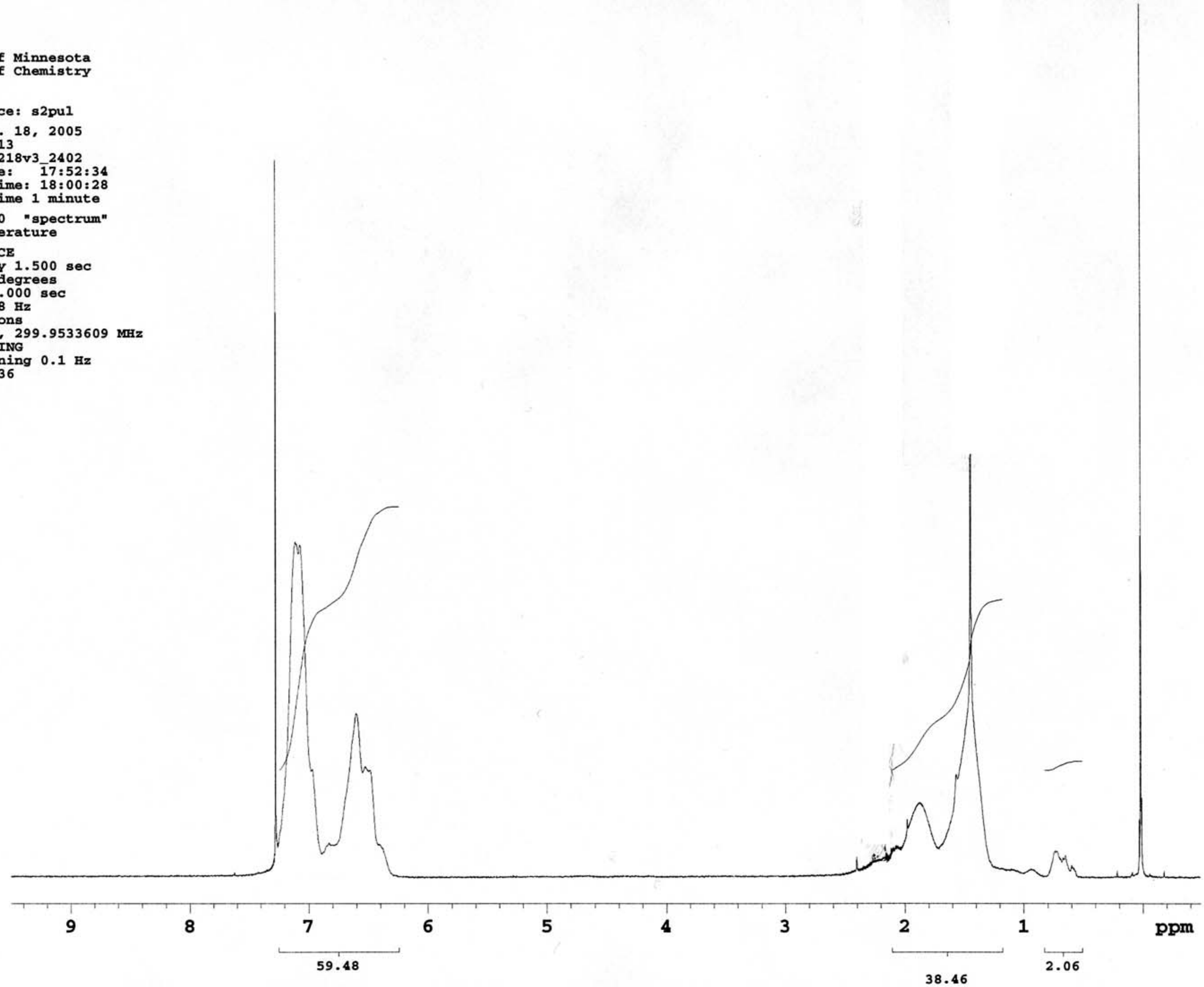
University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

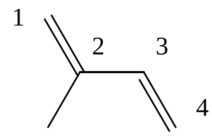
Date: Feb. 18, 2005
Solvent: $CDCl_3$
File: 050218v3_2402
Starting Time: 17:52:34
Completion Time: 18:00:28
Total acq. time 1 minute

UNITYplus-500 "spectrum"
Ambient temperature

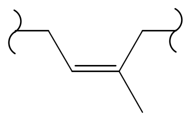
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 5998.8 Hz
16 repetitions
OBSERVE H1, 299.9533609 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536

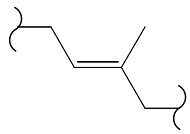


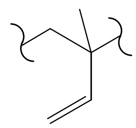
3. Last week you also synthesized polymers containing polyisoprene blocks. The connectivity of every styrene unit in polystyrene is the same—C_α of one styrene is connected C_β of the next, and so on. However, isoprene can be incorporated into a growing polyisoprene chain in a number of regiochemically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

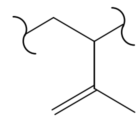


isoprene









cis-(1,4) *trans*-(1,4) (1,2) (3,4)

Which regiochemistry predominates in a particular polymerization depends sensitively on solvent(s), counterion (lithium in this case), 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 online at* http://tinyurl.com/anionpoly.) This review points out that, while isoprene polymerizations carried out with alkyllithium initiators and alkane solvents yield almost exclusively 1,4-polyisoprene (Table 9.3 in the book), using pure THF as solvent yields mostly 3,4-polyisoprene (Table 9.6). In Lab 4 you will form the polyisoprene block in a mixture of cyclohexane and THF, so you'll probably end up between these two extremes.

The ratio of 1,4- to 3,4-polyisoprene can be determined by ^{1}H NMR, because distinct alkene C_{sp2}-H protons from the isoprene units appear at distinct chemical shifts.[1] How many C_{sp2}-H protons from each alkene regioisomer contributes to the NMR, and at what chemical shift would each appear?

[1] Sato, H.; Tanaka, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3551.

4. In Lab 4, in the characterization of PS-*b*-PI, why wouldn't you be able to integrate polyisoprene's distinct *alkyl* (C_{sp3}-H) protons instead?