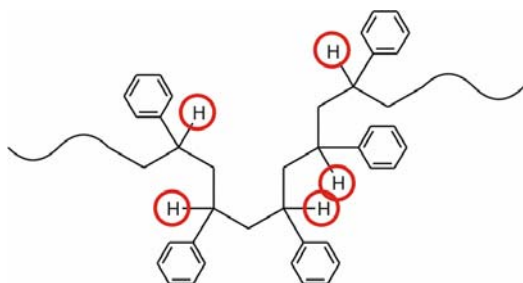


## Assignment 6

Due: *In Lab*, Thursday, February 2/Friday, February 3

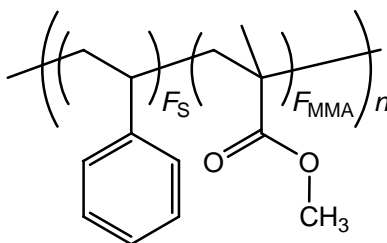
1. In the second part of Lab 2, you will be determining  $F_S$  and  $F_{MMA}$ , the fractions of styrene and methyl methacrylate incorporated in the final copolymer product, by NMR spectroscopy. The following page shows an NMR spectrum of a styrene-methylmethacrylate copolymer synthesized in a previous year. You may notice that the peaks in this spectrum look significantly broader than the sharp NMR multiplets you've analyzed previously for small organic molecules. This is because different backbone conformations along a polymer chain, combined with slow conformational mobility of the polymer chain on the NMR timescale, expose each chemically identical proton to a slightly different local environment.



*Example: Close-up view of a polystyrene chain. While the circled protons are chemically identical, they have different neighbors and environments, and thus have slightly different chemical shifts in NMR. This is only true because the speed of polymer flexing is slow compared to the timescale of NMR relaxation.*

This means that each proton has a slightly different chemical shift, and all of these many different shifts add up to a broad peak for each proton in the structure.

Which peaks/chemical shifts in the NMR spectrum on the next page correspond to which protons in the polymer structure? Based on the integral intensities for these peaks, calculate  $F_S$  and  $F_{MMA}$  for the copolymer.



(If you feel your NMR skills are rusty, you may want to consult *Proton and Carbon NMR Spectra of Polymers*, on reserve at Walter, for some help with your assignments. If you feel *really* rusty, you may want to review the chapter in your organic chemistry textbook on NMR, and particularly on chemical shifts and peak integration.)

University of Minnesota, VXR-300

Pulse Sequence: szpul

User: vnmr

Date: Feb. 18, 2002

Solvent: CDCl3

File: F2copolymer

Starting Time: 15:05:12

Total acq. time 11 minutes

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 20.000 sec

Pulse 90.0 degrees

Acq. time 2.000 sec

Width 5999.7 Hz

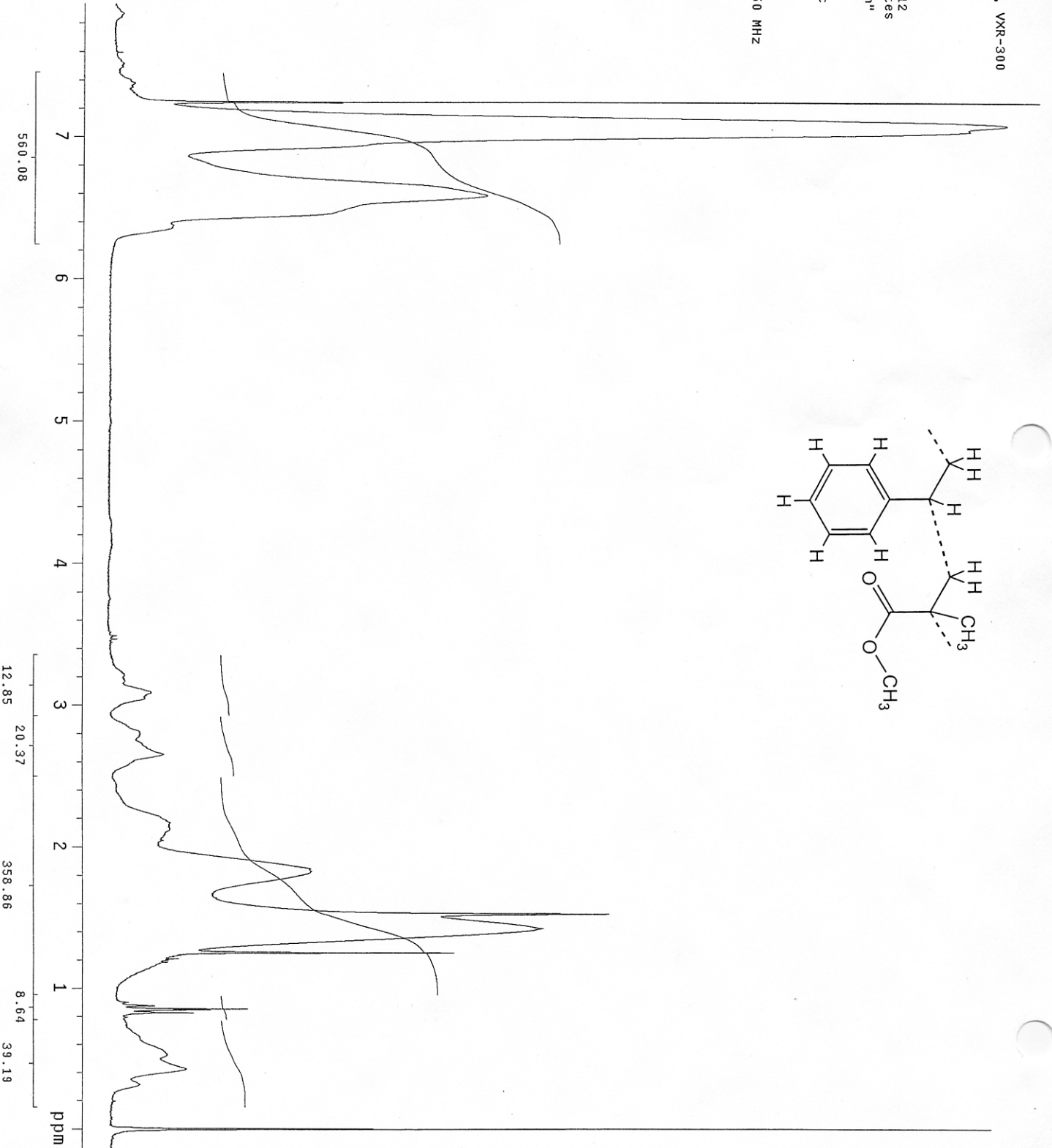
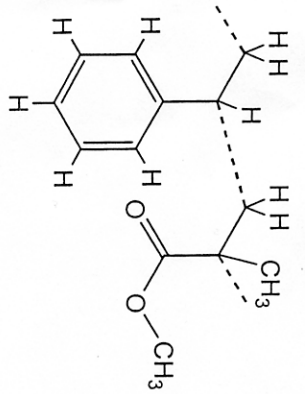
32 repetitions

OBSERVE H1, 299.8589250 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 131072



2. Some students will be performing Lab 3 in groups of four rather than pairs. Run your emulsion polymerization with an added quantity of chain-transfer agent. Use the quantity of dodecanethiol listed below:

<b>Pair</b>	<b>dodecanethiol (mL)</b>
(1+2)	0
(3+4), 9	0.3
(5+6)	0.6
(7+8), 10	0.9
11	1.2

The mechanism of emulsion polymerization is somewhat complicated, and our chalkboard discussion in class may not do it justice. Although it's aimed at an audience less educated in polymer science than you are, the Macrogalleria (<http://www.pslc.ws/macrogcss/emulsion.html>) description of the mechanism and advantages of emulsion polymerization are good reading for this lab.

Historically, the development of emulsion polymerization was critical for mass production of polyisoprene rubber. Most polymers cannot be synthesized to high molecular weights using bulk free-radical polymerization, but they can be using emulsion polymerization. In terms of rate constants, why is the molecular weight of bulk-polymerized polyisoprene so low?