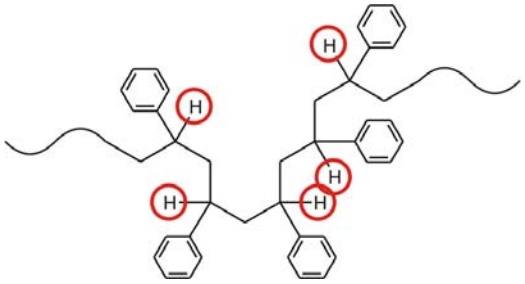
Chem/MatS/ChEn 4223W

Assignment 5
Due: *In Lab*, Tuesday, February 12/Thursday, February 14

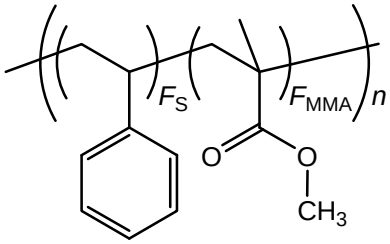
1. In the second part of Lab 2, you will be determining F_S and F_{MMA}, the fractions of styrene and methyl methacrylate incorporated in the final copolymer product, by NMR spectroscopy. The following page shows an NMR spectrum of a styrene-methylmethacrylate copolymer synthesized in a previous year. 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.)

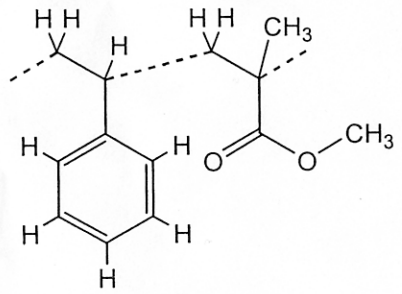
University of Minnesota, VXR-300

Pulse Sequence: s2pul

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. In Lab 3, each group will be polymerizing both styrene and methyl methacrylate at a specific volume %. You will be analyzing both polymer solutions by DLS, but only purifying one by centrifugation. Here's a chart that tells you which polymers to make:

Groups	Sample to polymerize and purify	Sample to polymerize, but don't purify
1,9	2 vol% MMA	2 vol% styrene
2,10	4 vol% MMA	4 vol% styrene
3,11	6 vol% MMA	6 vol% styrene
4,12	8 vol% MMA	8 vol% styrene
5,13	2 vol% styrene	2 vol% MMA
6,14	4 vol% styrene	4 vol% MMA
7,15	6 vol% styrene	6 vol% MMA
8,16	8 vol% styrene	8 vol% MMA

You will be using a syringe to add monomer to your polymerization emulsion. How much monomer will you need to add?

3. In Lab 3, you will be analyzing your polymer particles (latex) by dynamic light scattering (DLS). Although performing a DLS measurement is very easy—you put a cuvette into the machine and push a button—understanding the physics behind the measurement, and using that understanding to evaluate the validity of your data, is a bit more complicated. You'll find two good resources on how our Malvern NanoZS DLS works in Malvern's "Dynamic Light Scattering: An Introduction in 30 Minutes" (http://tinyurl.com/MalvernDLSIntro), or from "Size Theory" (http://tinyurl.com/ZetasizerIntro), a chapter from the instrument manual.

   It will be extremely important in this experiment to exclude large environmental particles (e.g., dust) from your sample, because they scatter light more intensely than smaller particles. How much more? How would the scattered light intensity of a 1-μm diameter dust particle compare to that of a 30-nm diameter latex particle, assuming they were made of the same material?

4. Particles suspended in a medium will only scatter light if the refractive index of the particle material is different from that of the medium. In Lab 3, your particles will be made of PS and PMMA, and the medium will be H_2O. What are the refractive indices of these materials with respect to the 633-nm wavelength light emitted by the HeNe laser in the NanoZS?