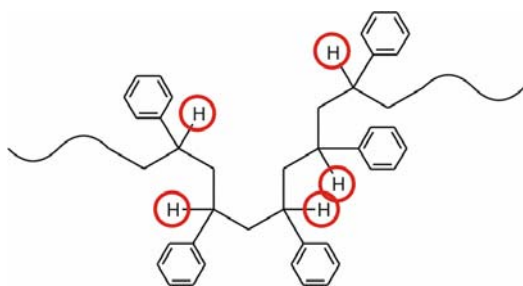


Assignment 6 Solutions, Spectral Analysis

You may have noticed 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 NMR acquisition.

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.

So which broad peak is which? There are some characteristic features of your NMR. First, all of the aromatic protons are in the $\delta = 6.5\text{--}8.5$ ppm, aromatic region of the spectrum. Each styrene monomer has five aromatic protons, and they are all represented by the huge peaks in this area. (The sharp peak at 7.26 ppm is CHCl_3 from the NMR solvent, and shouldn't have been included in the integration. But, it doesn't contribute much, so we'll ignore it.) The peaks have a relative integrated intensity of 560, as shown at the bottom of the scale. If these peaks represent five protons, then the relative number of monomer units would be

$$\text{integral intensity (aromatic region)} \times \frac{1 \text{ styrene molecule}}{5 \text{ aromatic styrene protons}} = \text{relative \# styrene molecules}$$

$$560 \times \frac{1}{5} = 112 \text{ styrenes}$$

You may have noticed that there are actually two peaks in the aromatic region with ~3:2 relative integral intensity. My guess is that the 2 is the *meta* protons, and the 3 is the (*ortho* + *para*) protons, but this doesn't really matter.

As it turns out, you could do the same math for the other styrene protons. If the spectrum contains 112 styrenes worth of protons, then somewhere else in the spectrum, there must be three other styrene (backbone) protons with relative intensity $(112 \times 3) = 336$. Sure enough, there is a 2:1 set of peaks in the $\delta = 1.6$ ppm

region that integrates to 359, which is probably a bit large because there are some smaller peaks folded in there. For precision, we'll use the aromatic peaks to calculate styrene because we absolutely know there are no other protons in this region.

It looks as though the peaks from MMA are *much* smaller than those for styrene. There are two sets of non-overlapping peaks for MMA; the pair of broad peaks at $\delta = 2.6\text{-}3.0$ ppm, and the broad peak at $\delta = 0.5$ ppm. (The sharp peaks in this region must be very well defined resonances, from initiator, terminator, or impurity species.) The 2.6-3.0 ppm resonance would be characteristic of a methoxy group, and the 0.5 ppm resonance of an alkyl methyl group. Since these both represent three protons each, their total integrals should be the same, and they are, roughly. The methyl peak is less broad, so I'll use it in my math:

$$\text{integral intensity (0.5 ppm peak)} \times \frac{1 \text{ MMA molecule}}{3 \text{ MMA methyl protons}} = \text{relative \# MMA molecules}$$
$$39 \times \frac{1}{3} = 13 \text{ MMAs}$$

So,

$$F_s = \frac{\text{moles styrene}}{\text{moles styrene} + \text{moles MMA}} = \frac{112}{112 + 13} = 0.896$$

$$F_{MMA} = \frac{\text{moles MMA}}{\text{moles styrene} + \text{moles MMA}} = \frac{13}{112 + 13} = 0.104$$

If you had used the methoxy peaks to integrate, you would have gotten slightly different numbers, but not too different.

University of Minnesota, VXR-300

Pulse Sequence: szpul1

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

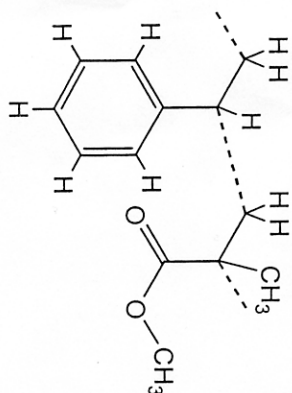
32 repetitions

OBSERVE H1, 299.8589250 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 131072



aromatic PS H's
(5 per monomer)

mostly, backbone
PS H's
(3 per monomer)

methoxy PMMA H's
(3 per monomer)

methyl PMMA H's
(3 per monomer)

