Characterization of polymers by NMR

- Analysis :
  - Of monomers
  - Of copolymers (sequences)
  - Of reaction products
  - Of the microstructure (3 types of isomerism, including tacticity)
  - Of the composition of a copolymer
  - Of branching in polyethylene
  - Of relaxation mechanisms

Copolymer composition analysis

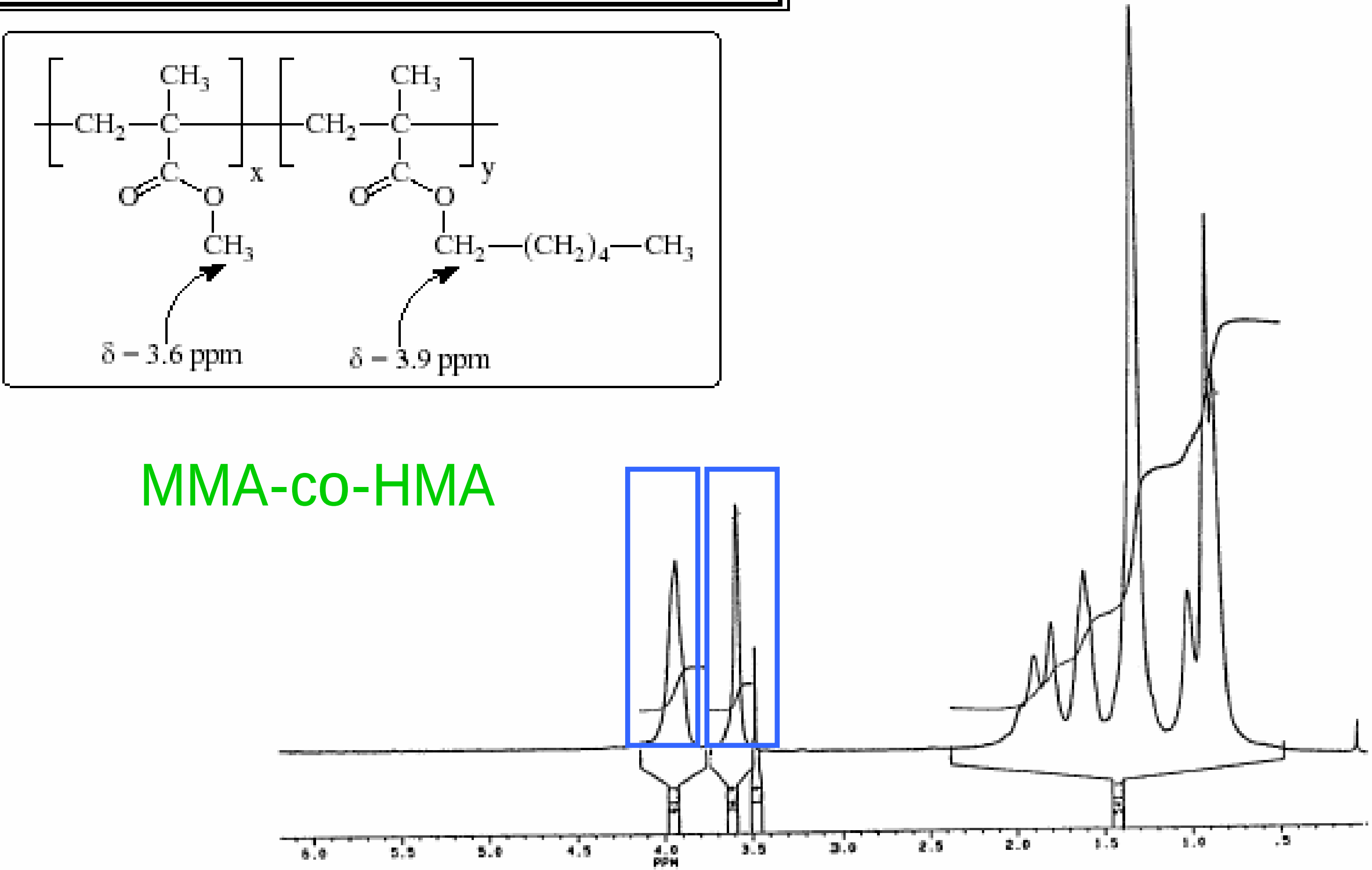
Examples in ^{1}H NMR :

1. Methyl methacrylate - co- hexyl methacrylate (MMA-co-HMA)
2. Styrene - co – vinyl phenol

Characterization of Polymers - NMR Spectroscopy

Copolymer Analysis

Example:
methyl methacrylate-co-hexyl methacrylate copolymers.



- ✱ Quantitative analysis straightforward.

$$\% \text{ MMA} = \frac{A_{3.6\text{ ppm}}/3}{A_{3.6\text{ ppm}}/3 + A_{3.9\text{ ppm}}/2} \times 100$$

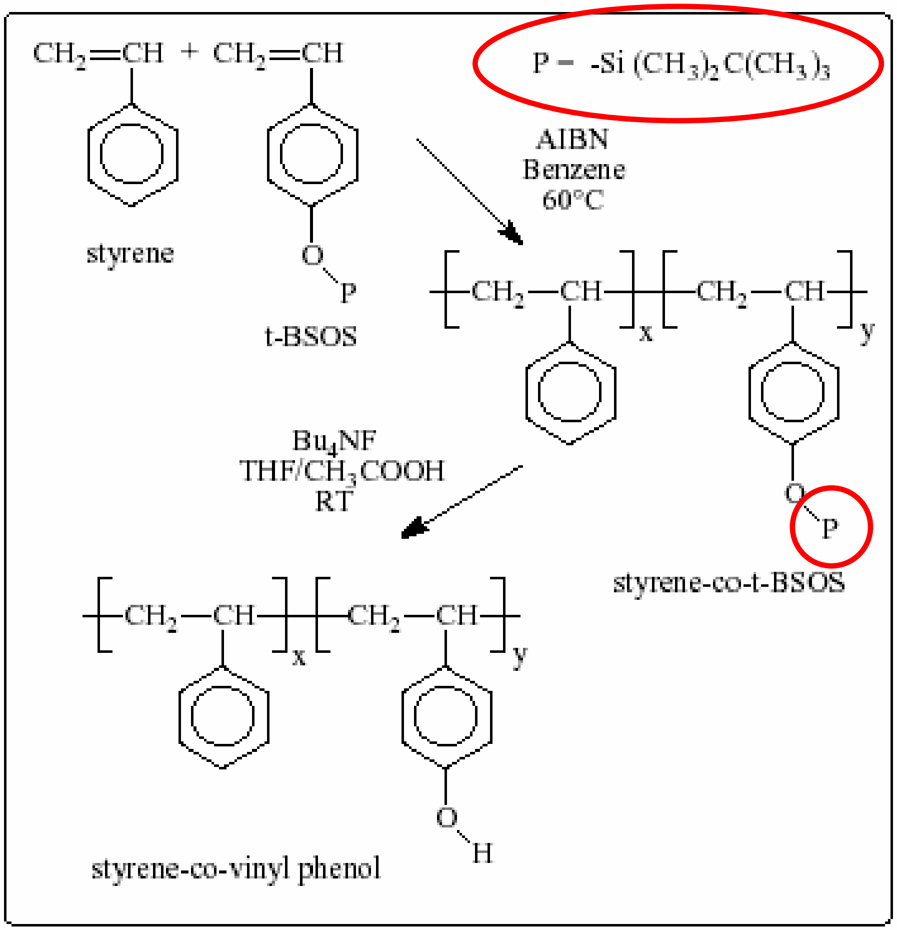
MMA-co-HMA

Proton nmr spectrum of a copolymer of methyl methacrylate and hexyl methacrylate

Characterization of Polymers - NMR Spectroscopy

Copolymer Modification and Analysis

Example: styrene-co-vinyl phenol copolymers.

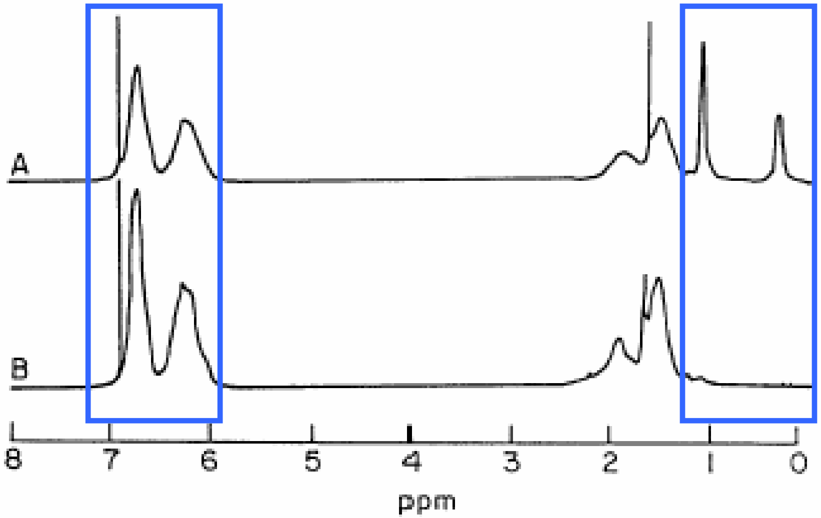


$$A^{H}_{t\text{-BSOS}} = \frac{\text{Total area of 0.16 ppm line}}{6}$$

$$= \frac{\text{Total area of 0.95 ppm line}}{9}$$

$$A^{H}_{St} = \frac{(\text{Total area of region from 6.2 to 7.2 ppm}) - 4\,A^{H}_{t\text{-BSOS}}}{5}$$

$$\%\ \text{Styrene} = \frac{A^{H}_{St}}{A^{H}_{St} + A^{H}_{t\text{-BSOS}}} \times 100$$



Proton nmr spectrum of (A) a styrene-co-t-BSOS copolymer and (B) the corresponding styrene-co-vinyl phenol copolymer after deprotection.

Observation of stereoisomerism

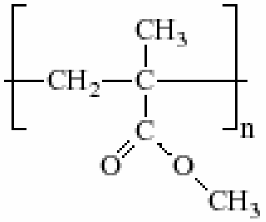
Example in ^{1}H NMR : tacticity of PMMA

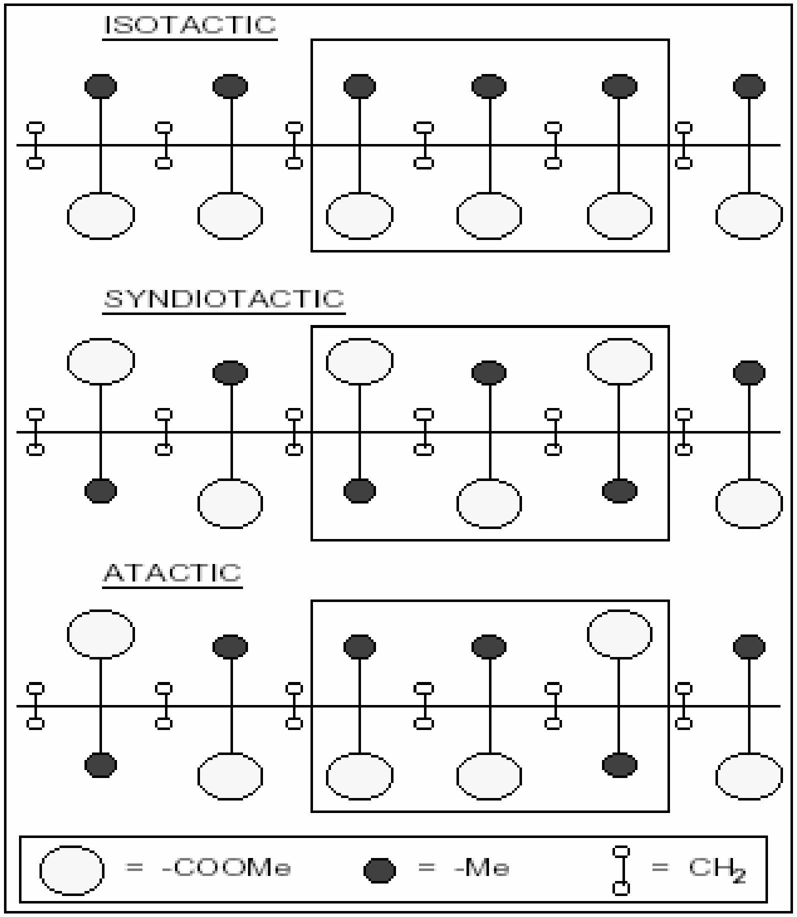
- The protons of the methylene group are not magnetically equivalent in isotactic PMMA → appearance of 4 lines
- Equivalent for syndiotactic PMMA → single line, in center of the 4 preceding ones
- Atactic → combination of the two, we cannot differentiate between a polymer blend or a copolymer
- Easier with protons of the methyl group → sensitive to triad arrangements : line appears at different locations for the three arrangements. The atactic line is between the iso and syndio lines

Characterization of Polymers - NMR Spectroscopy

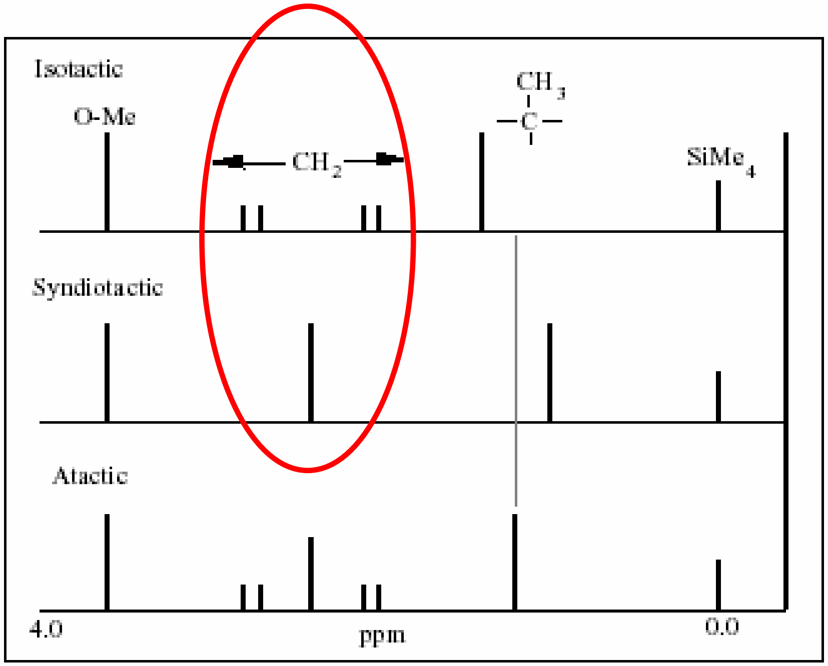
The Observation of Tacticity

Example: poly(methyl methacrylate).





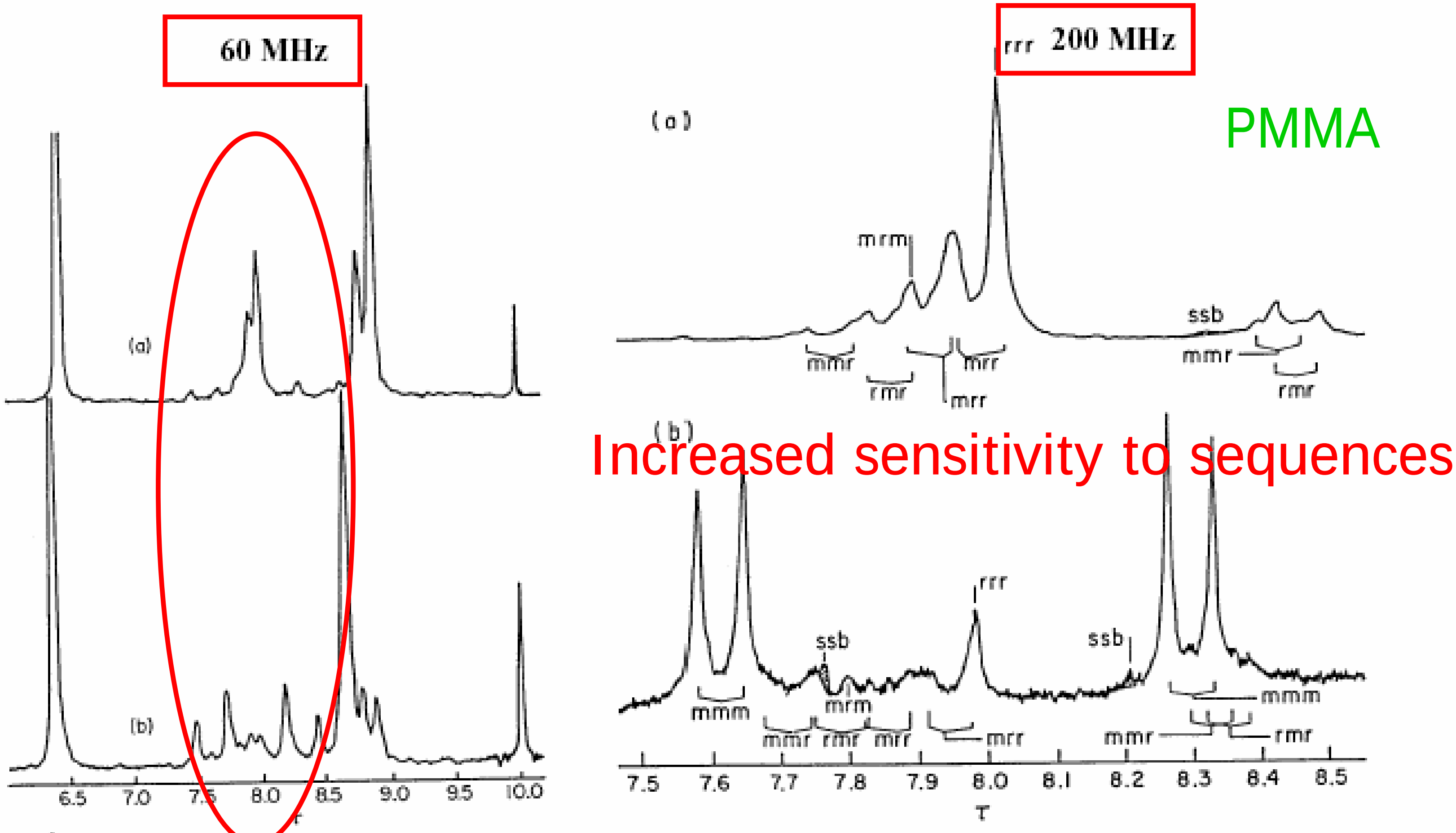
- *Isotactic* - two methylene protons are not magnetically equivalent - AB pattern.
- *Syndiotactic* - two methylene protons are magnetically equivalent - Single resonance.
- *Atactic* - combination - *diad* information.
- The three protons of the backbone methyl group are sensitive to *triad* sequences - *Isotactic*, *Syndiotactic* and *Atactic* triads are resolved at different chemical shifts.



Characterization of Polymers - ^{1}H NMR Spectroscopy

The Observation of Tacticity

F. A. Bovey, *High Resolution NMR of Macromolecules*, Academic Press (1972)



PMMA

Increased sensitivity to sequences

^{1} H nmr spectra of (a) predominantly syndiotactic PMMA and (b) predominantly isotactic PMMA.

Stereoisomerism and probability

2 adjacent monomers :

- Meso diad (dd or ll) → m
- Racemic diad (dl or ld) → r

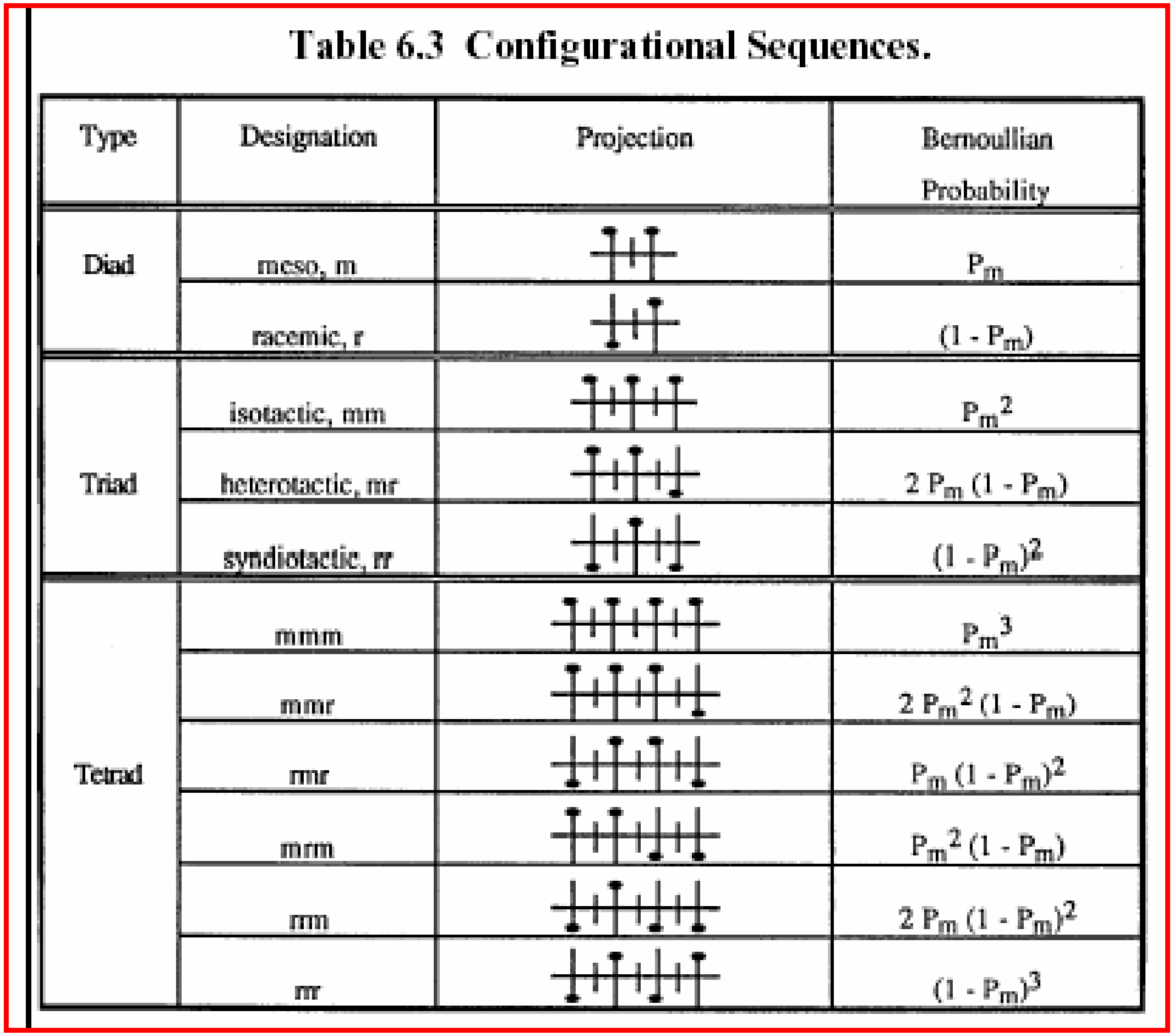


Table 6.3 Configurational Sequences.

Type	Designation	Projection	Bernoullian Probability
Diad	meso, m		P_m
	racemic, r		$(1 - P_m)$
Triad	isotactic, mm		P_m^2
	heterotactic, mr		$2\ P_m\ (1 - P_m)$
	syndiotactic, rr		$(1 - P_m)^2$
Tetrad	mmm		P_m^3
	mmr		$2\ P_m^2\ (1 - P_m)$
	rmr		$P_m\ (1 - P_m)^2$
	mrm		$P_m^2\ (1 - P_m)$
	rrm		$2\ P_m\ (1 - P_m)^2$
	rrr		$(1 - P_m)^3$

Observation of sequence isomerization

Example :

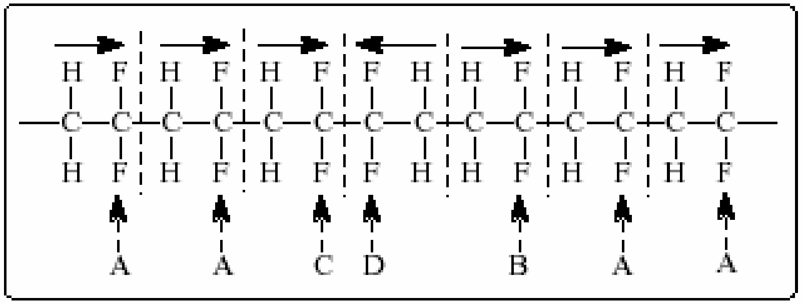
Polyvinylidine fluoride (PVDF) in ^{19}F NMR

No possible tacticity, the difference between NMR spectra is due to sequence isomerization

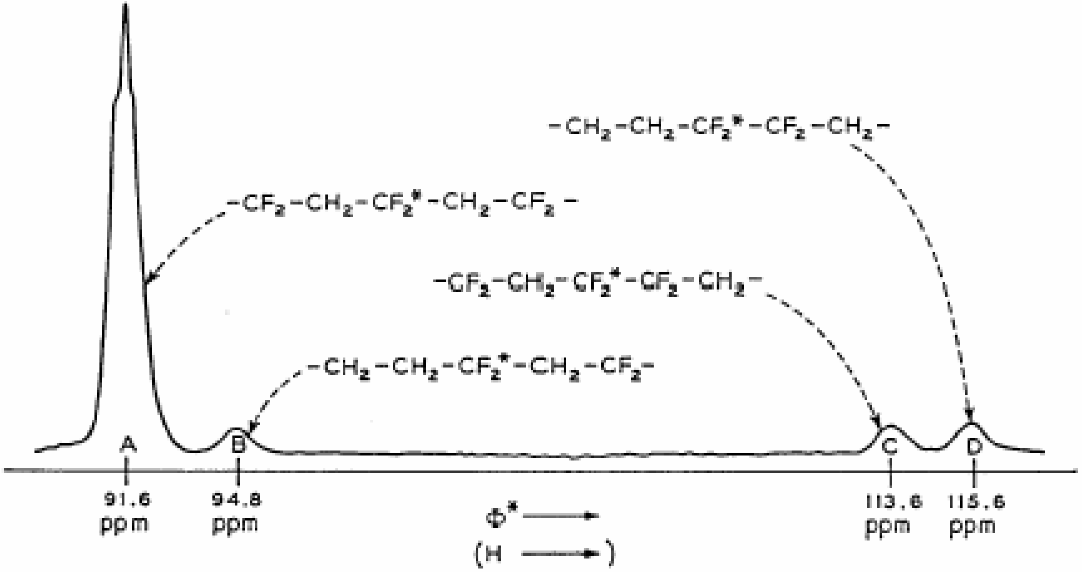
Characterization of Polymers - ^{19}F NMR Spectroscopy

The Observation of Sequence Isomerization - Poly(vinylidine fluoride)

C. W. Wilson III and E. R. Santee, Jr., *J. Polym. Sci. Part C*, 8, 97 (1965)



PVDF



Observation of structural isomerization

As effective as Raman spectroscopy, and much more sensitive to distribution of sequences.

^{1}H NMR spectroscopy is not very sensitive to structural isomerization, better in ^{13}C NMR.

Examples in ^{13}C NMR :

Polybutadiene (PBd)

Characterization of Polymers - ^{13}C NMR Spectroscopy

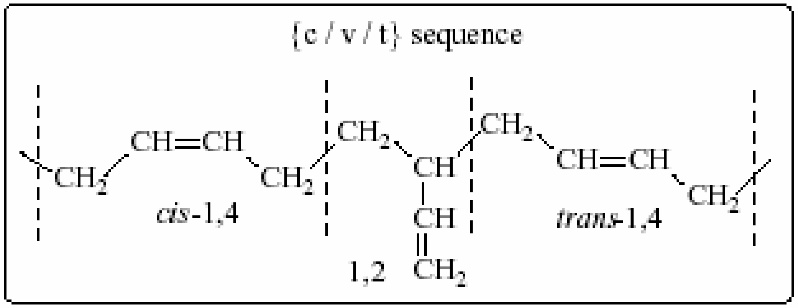
Observation of Structural Isomerization - Polybutadiene

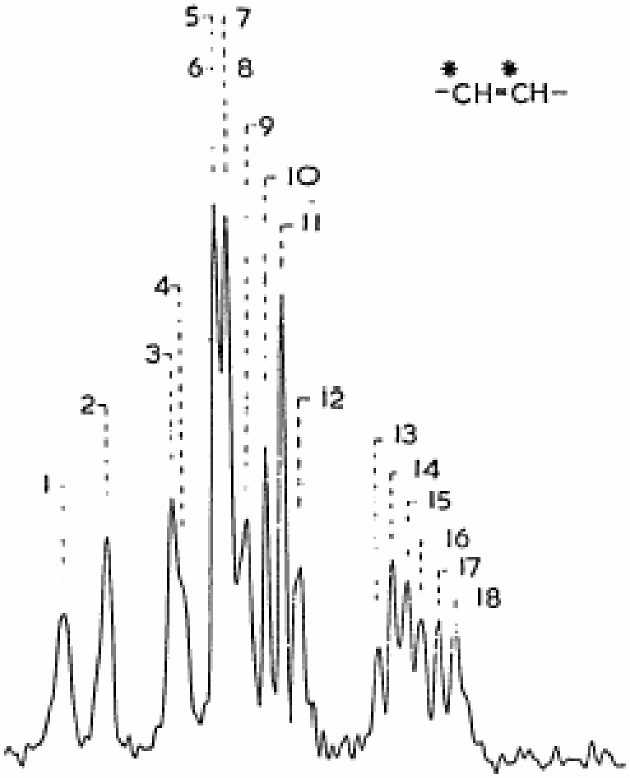
K-F Elgert, G. Quack and B. Stutzel, *Polymer*, 16, 154, (1975).

PBd

- Each resonance has been assigned to a specific triad sequence of trans-1,4-; cis-1,4- and1,2- placements.

Example:





^{13}C nmr spectrum of polybutadiene containing 34% *trans*-1,4-; 24% *cis*-1,4- and 42% 1,2- placements.

Distributions of sequences for copolymers

Example in ^{1}H NMR:

Vinylidine chloride - co -isobutylene (VDC-co-IB)

Characterization of Polymers - ^{13}C NMR Spectroscopy

Copolymer Sequence Distributions - Vinylidine chloride-co-Isobutylene

F. A. Bovey, *High Resolution NMR of Macromolecules*, Academic Press (1972)

Distinguishable sequences, N(n) of length n are given by:

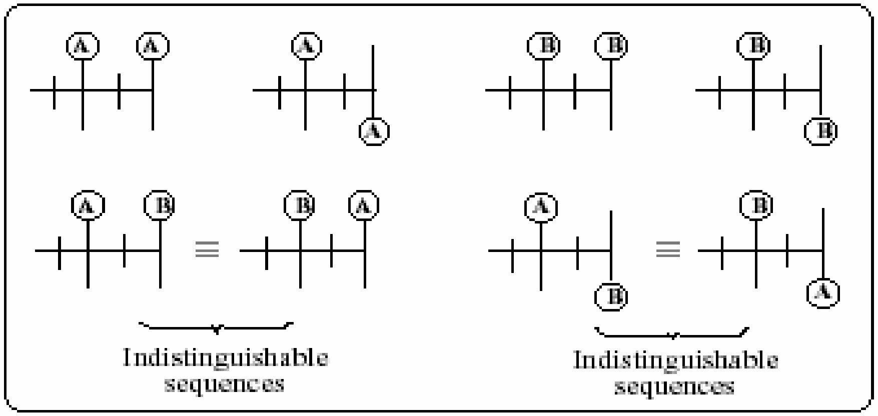
For CH_2-CX_2 and CH_2-CY_2

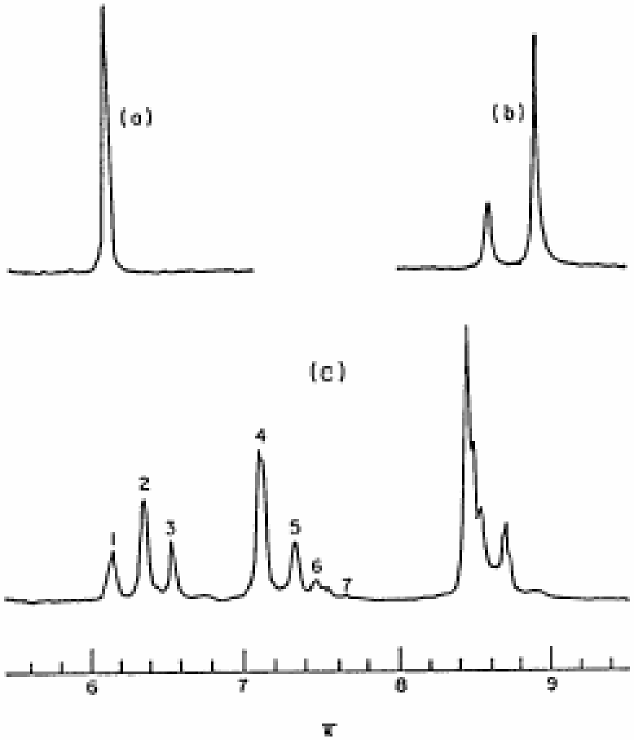
n –	2	3	4	5	6
N(n) –	3	6	10	20	36

But its a nightmare:

For CH_2-CXY and CH_2-CRZ

n –	2	3	4	5	6
N(n) –	6	20	72	272	1056





^{1}H nmr spectra of (a) PVDC homopolymer, (b) PIB homopolymer and (c) a copolymer of vinylidine chloride and isobutylene.

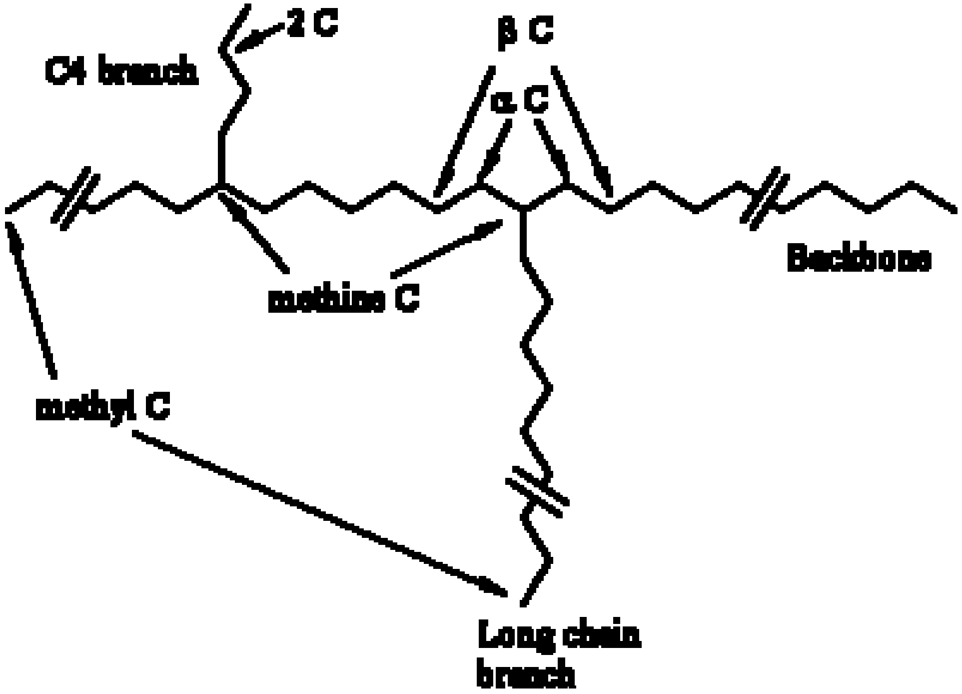
1 – VDC-VDC-VDC-VDC
2 – VDC-VDC-VDC-IB
3 – IB-VDC-VDC-IB
4 – VDC-VDC-IB-VDC
5 – IB-VDC-IB-VDC
6 – VDC-VDC-IB-IB
7 – IB-VDC-IB-IB

Branching in Polyethylene

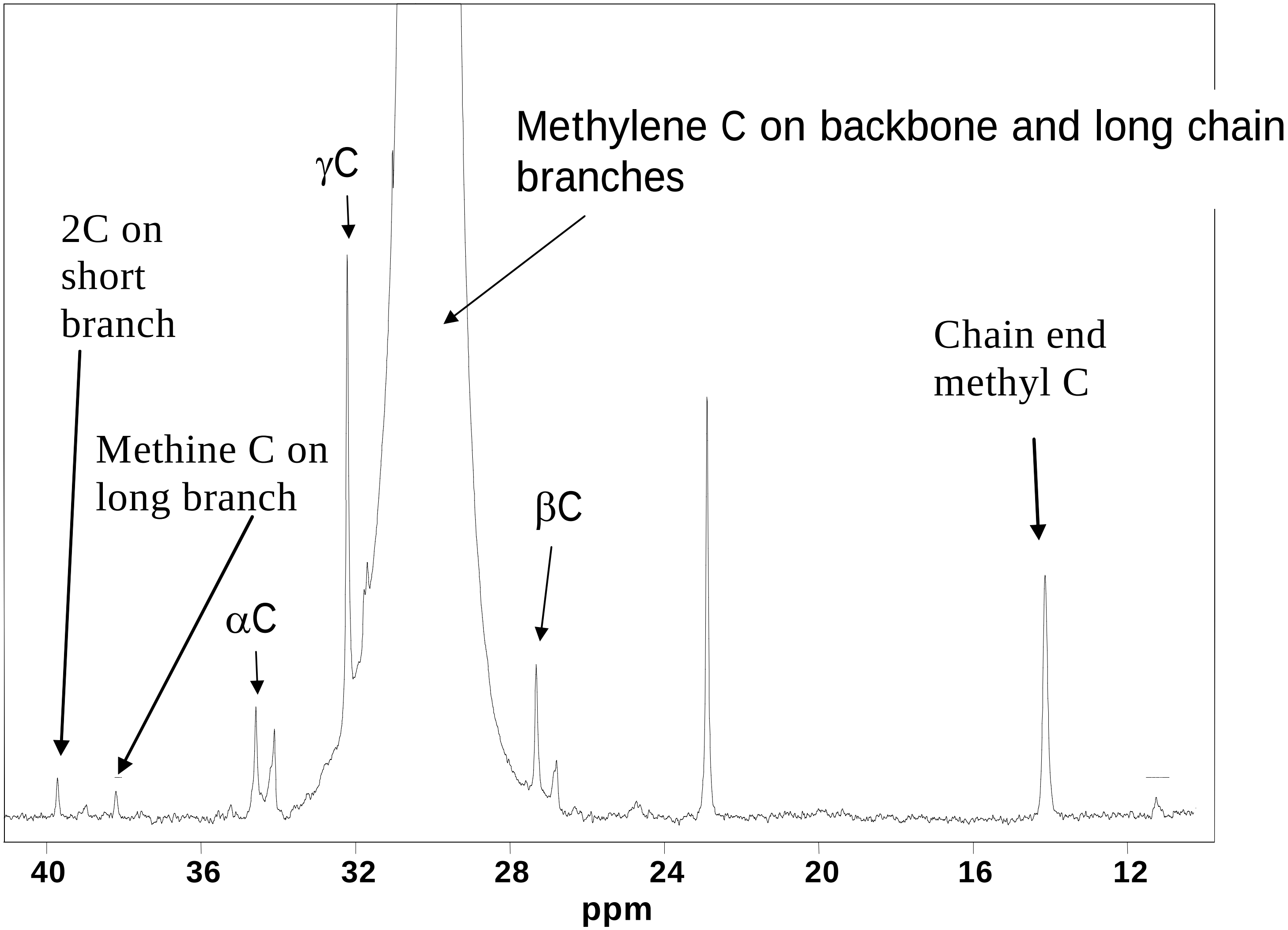
- Branching in polyethylene occurs in 2 forms:
  - Short chain branching which results from copolymerization with another olefin (i.e. butene or octene) Affects mostly solid state properties.
  - Long chain branching where the length of the branches is on the same scale as that of the backbone. Affects melt state properties (and solid state properties if high enough degree)
- Can use 13C-NMR to detect and quantify these different types of branching
- This technique is based upon the chemical shifts of the carbon atoms on the backbone chain attached to the branch.
- The chemical shift depends on the length of the branch for branches up to 6 carbons in length. It is the same for all branches 6 carbons and longer.

Classification of carbons on a branched PE chain

- Methylene carbon: C atom that is bonded to 2 other C atoms
- Methine carbon: C atom that is bonded to 3 other C atoms
- αC: Carbon atom immediately adjacent to a methine C
- βC: Carbon atom immediately adjacent to an αC
- γ C: Carbon atom immediately adjacent to a βC
- 2C: second carbon atom from an end of a short branch



^{13}C NMR spectrum of a LCB PE



More examples of applications of spectroscopic techniques to polymers are available in Chapter 2 of Sperling.