

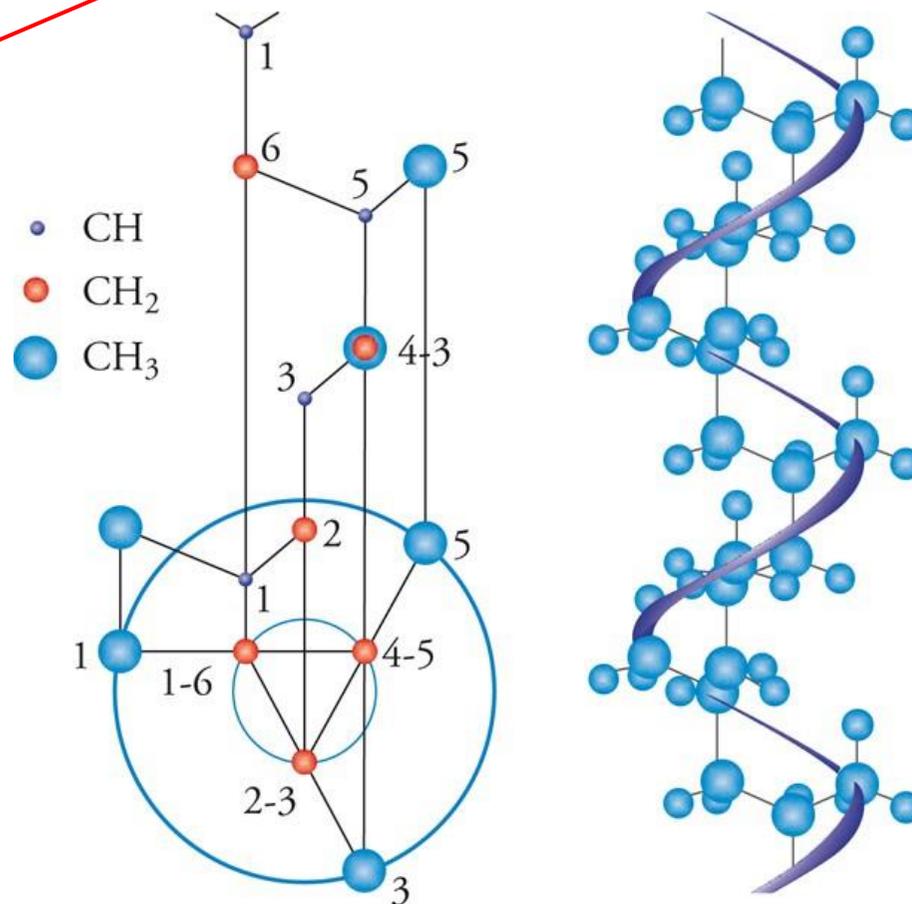
# Struttura della catena polimerica

Polipropilene isotattico: conformazione a elica  $3_1$   
3 unità monomeriche in  $1 \times 360^\circ$   
periodo di ripetizione:  $6.5 \text{ \AA}$

$m_n$

$n$

Passo dell'elica



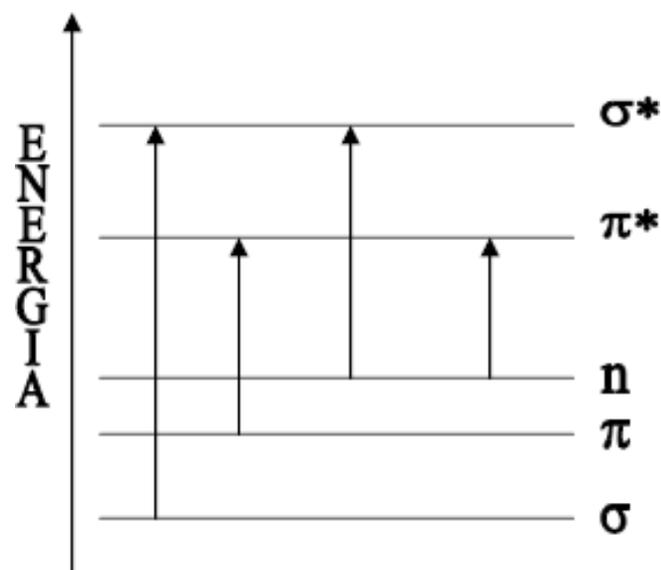
# Spettroscopie

**UV-Visibile:** transizioni elettroniche  
( $100 < \lambda < 1000 \text{ nm}$ )

**IR/Raman:** transizioni vibro-rotazionali  
( $1 \mu\text{m} < \lambda < 500 \mu\text{m}$ )

**NMR:** transizioni magnetiche  
( $1 \text{ m} < \lambda < 5 \text{ m}$ , onde radio con frequenze 300-60 Mhz)

# UV-Visibile



TIPO DI TRANSIZIONE	LUNGHEZZA D'ONDA DELLA RADIAZIONE NECESSARIA PER OTTENERE LA TRANSIZIONE	La $\lambda$ necessaria per la transizione è tanto maggiore quanto minore è il dislivello energetico
$\sigma \rightarrow \sigma^*$	110 – 135 nm	
$\pi \rightarrow \pi^*$	160 – 255 nm	
$n \rightarrow \sigma^*$		
$n \rightarrow \pi^*$	> 285 nm	

# Utilizzi UV-VISIBILE

- Rivelatore GPC
- Individuazione e quantificazione coloranti e stabilizzanti
- Gruppo carbonile =CO  
(presenza gruppo, degradazione)
- Misura della lunghezza di coniugazione (segmenti rigidi SBR)
- Isomeria cis-trans
- Polimerizzazione (stirene/polistirene)
- Composizione copolimeri

# Spettrometria infrarossa

Frequenza ( $\nu$  in Hz,  $\text{sec}^{-1}$ )

Lunghezza d'onda ( $\lambda$  in nm o in  $\mu\text{m}$ )

Numero d'onda ( $\bar{\nu} = 1/\lambda$  in  $\text{cm}^{-1}$ )

Campo spettrale della radiazione IR:

0.7 - 500  $\mu\text{m}$  (14000 - 20  $\text{cm}^{-1}$ )

0.7 - 2.5  $\mu\text{m}$  (14000 - 4000  $\text{cm}^{-1}$ ): vicino IR (NIR)

⇒ 2.5 - 25  $\mu\text{m}$  (4000 - 400  $\text{cm}^{-1}$ ): medio IR (MIR)

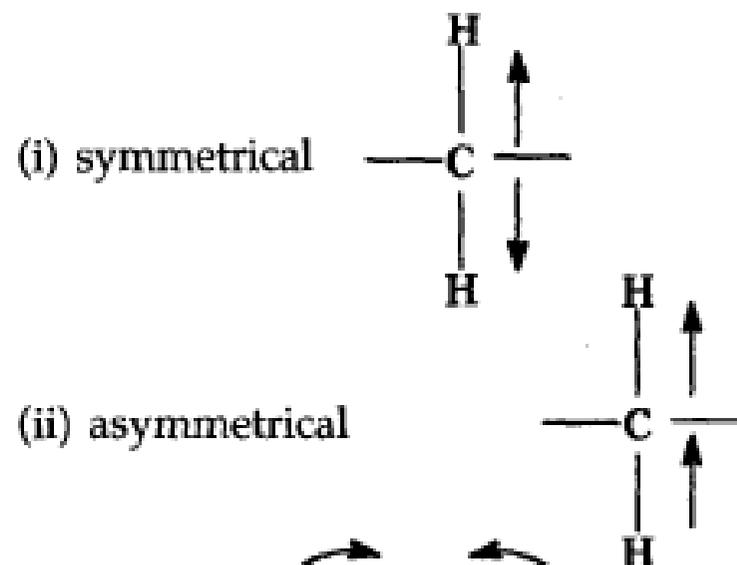
25 - 500  $\mu\text{m}$  (400 - 20  $\text{cm}^{-1}$ ): lontano IR (FIR)

# Modi di vibrazione delle molecole

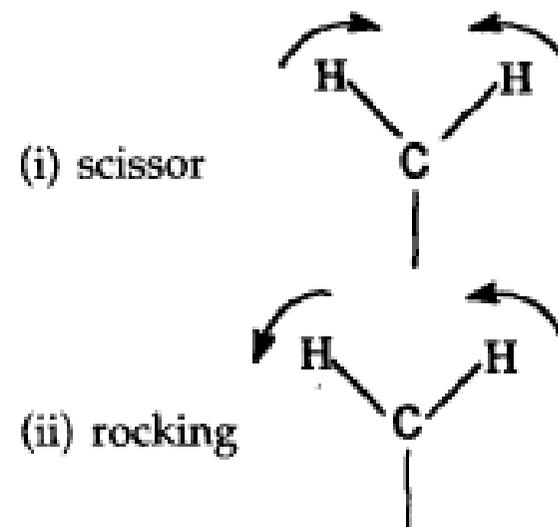
- *stretching*: modificano le lunghezze dei legami. Distinti in:
  - simmetrico
  - asimmetrico
- *bending*: modificano gli angoli tra gli atomi. Distinti in:
  - rocking
  - scissoring
  - wagging
  - twisting

# IR: modi di vibrazione

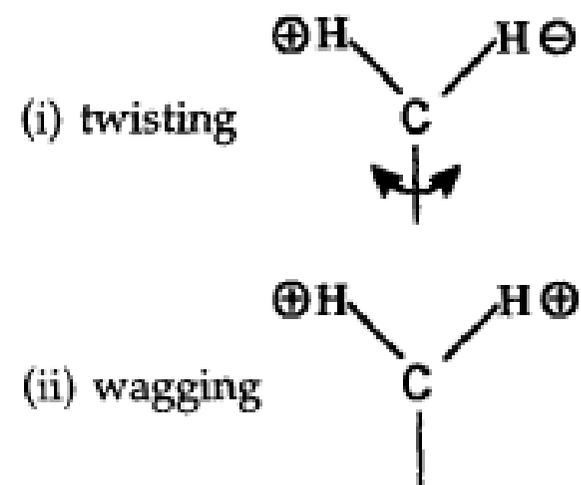
(a) stretching



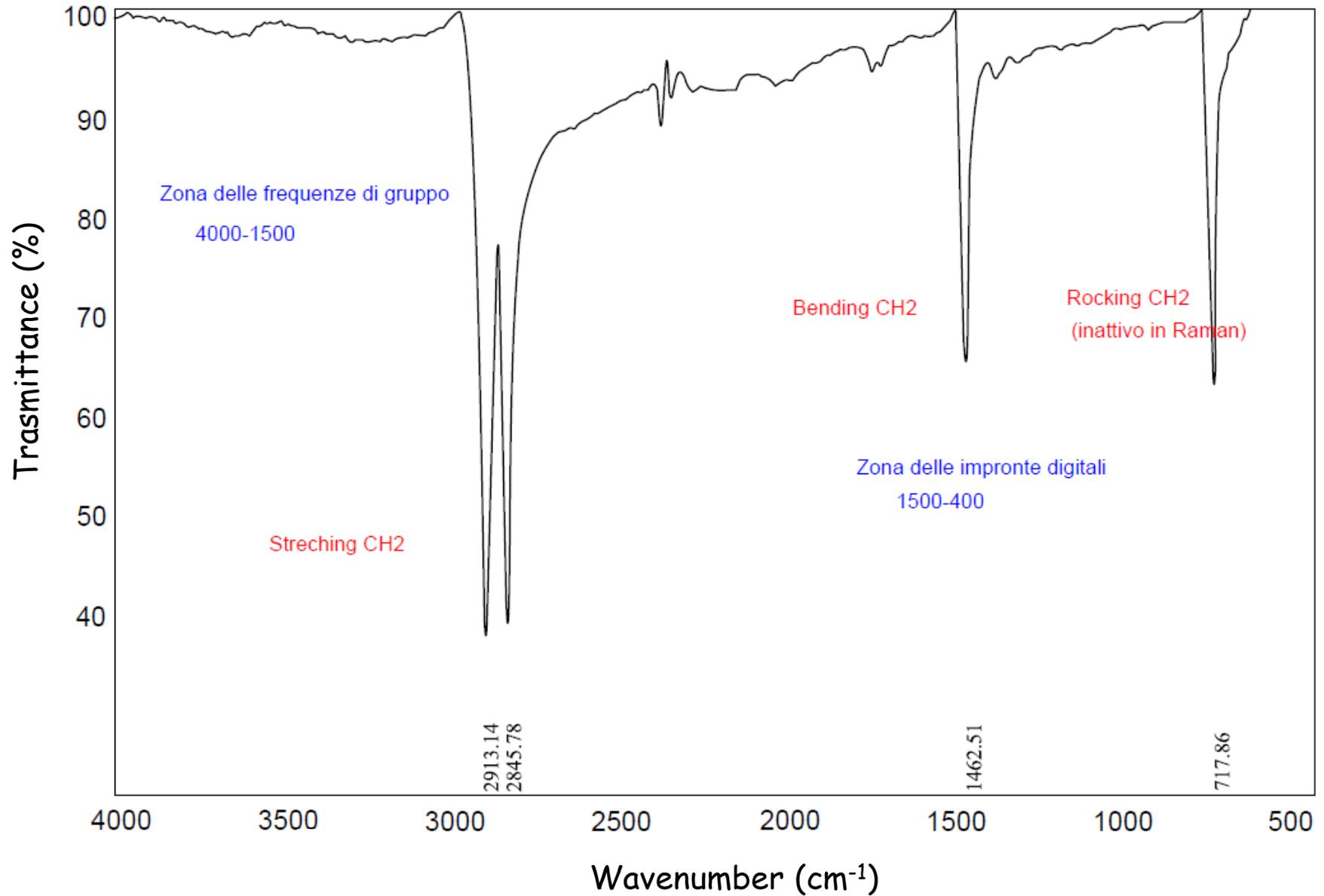
(b) in-plane bending



(c) out-of-plane bending



# Polietilene (PE)



# Spettroscopia Raman

La tecnica sfrutta un fenomeno scoperto nel 1928 dal fisico indiano C.V. Raman (premio Nobel per la fisica nel 1930).

Egli scoprì che una piccola frazione della radiazione diffusa da certe molecole aveva energia diversa da quella della radiazione incidente, e che la differenza di energia era legata alla struttura chimica delle molecole responsabili della diffusione: questo fenomeno è noto come l'effetto Raman

# Diffusione della luce ed effetto Raman

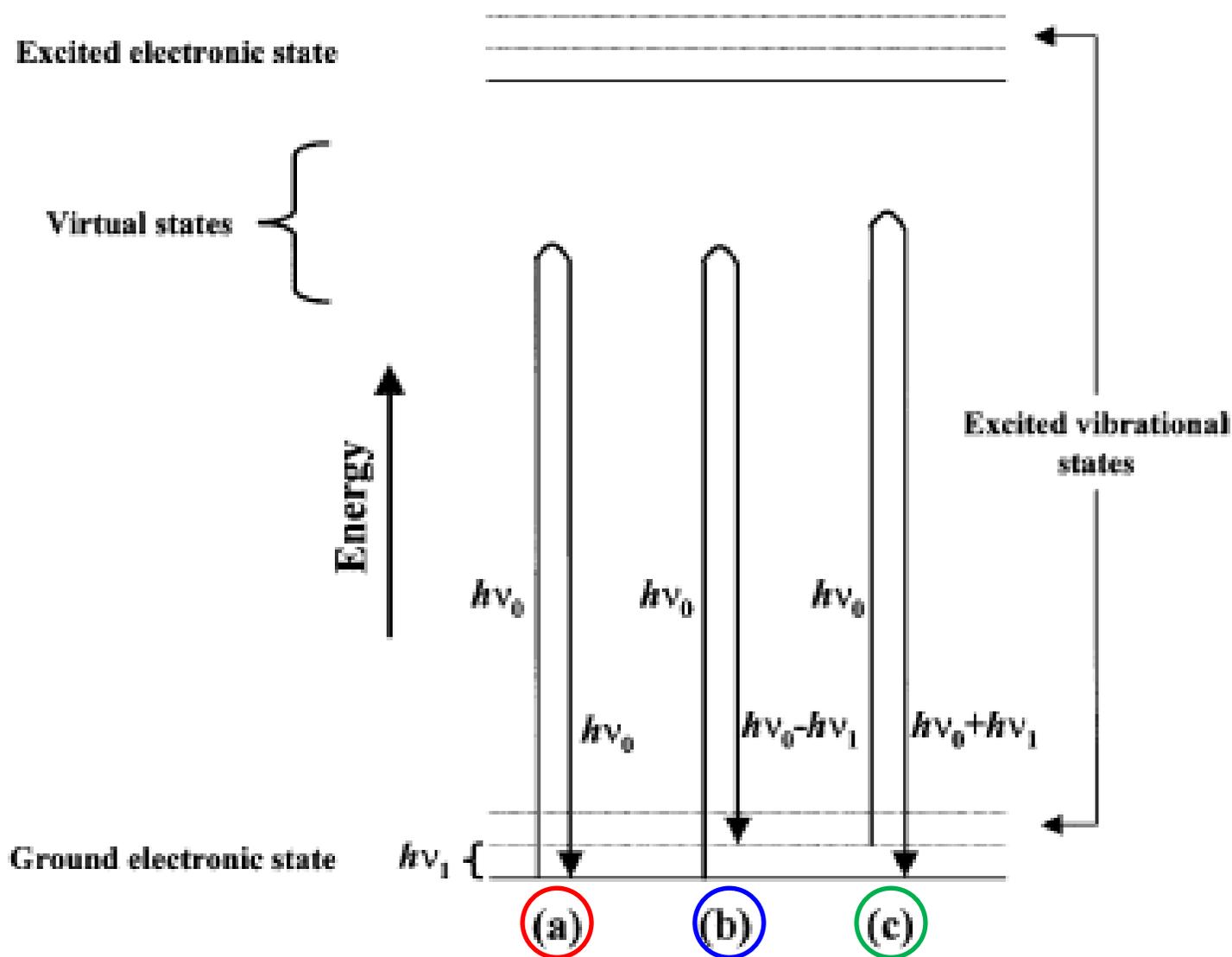
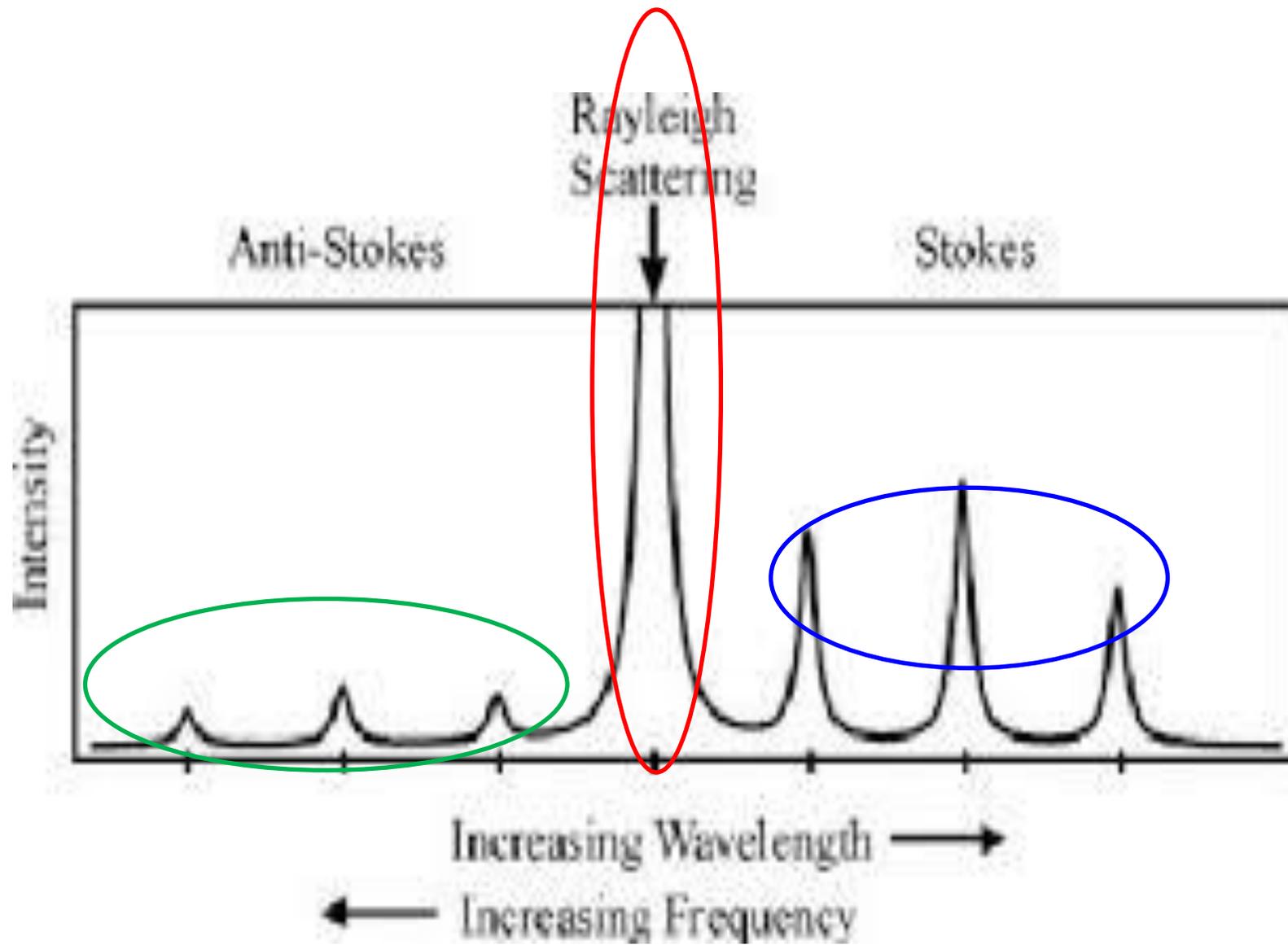
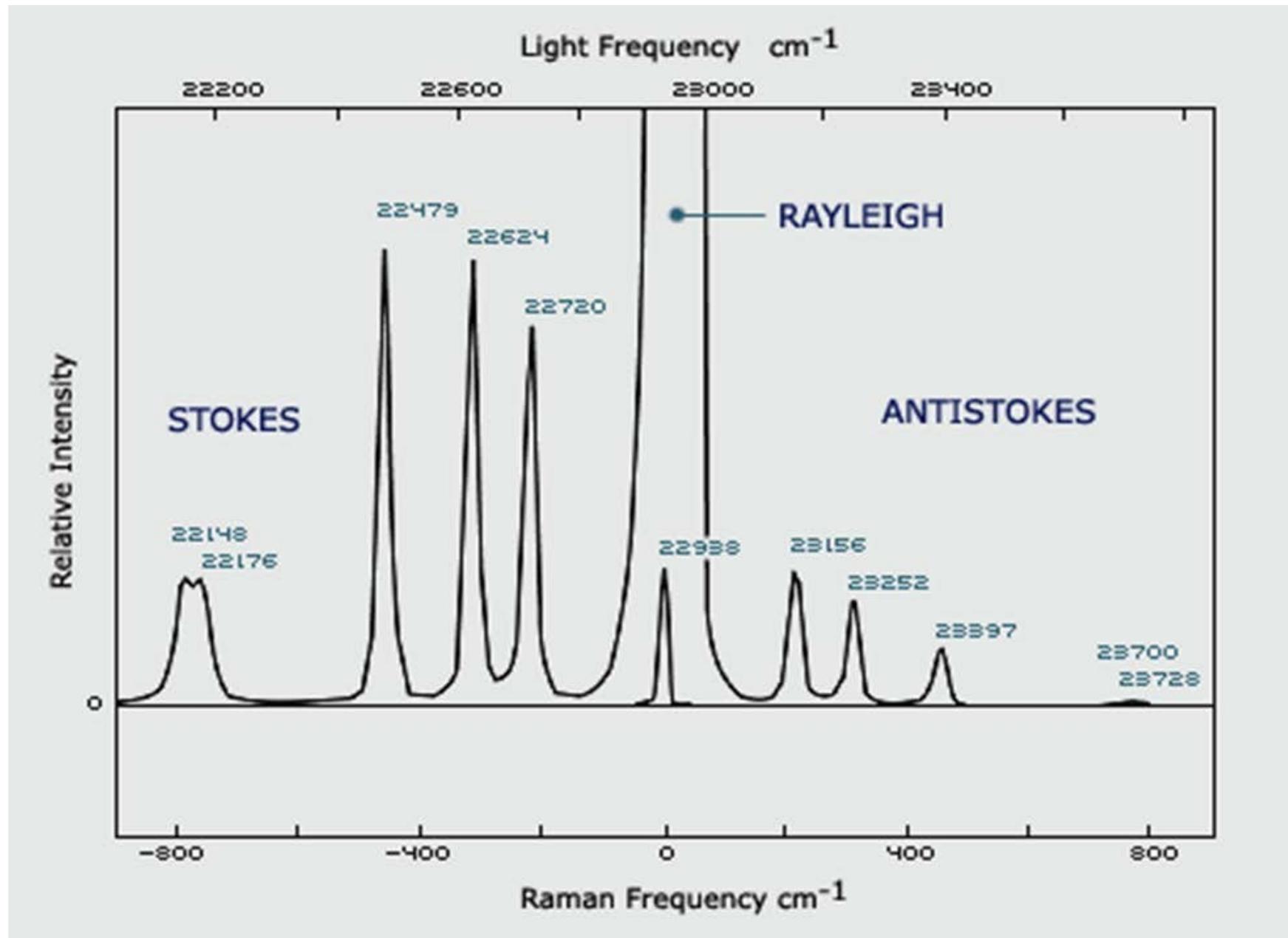


Fig. 1. Energy level diagram showing the concerted excitation-relaxation phenomena responsible for (a) Rayleigh, (b) Stokes, and (c) anti-Stokes Raman scattering.

# Spettro Raman



# Esempio di spettro Raman



**Table 5.1** Characteristic vibration modes for common groupings found in polymers

Type of vibration	Characteristic frequencies (cm <sup>-1</sup> )
O - H {stretching }	3650-3000
N - H {stretching }	3500-3300
C - H {stretching }	3200-2800
S - H {stretching }	2600-2550
C ≡ N {stretching }	2255-2220
C ≡ C {stretching }	2250-2100
C = O {stretching }	1820-1680
C = C {stretching }	1900-1500
C = N {stretching }	1680-1610
N = N {stretching } - aliphatic	1580-1550
N = N {stretching } - aromatic	1440-1410
C - NO <sub>2</sub> {stretching }	1590-1530 {asymmetric} 1380-1340 {symmetric}
C - SO <sub>2</sub> -C {stretching}	1350-1310 {asymmetric} 1160-1120 {symmetric}
C = S {stretching}	1250-1000
CH <sub>2</sub> {bending }	1470-1400
CH <sub>3</sub> {bending}	1380
C - C {aromatic - stretching}	1600, 1580, 1500, 1450, 1000
C - C {alicyclic - stretching}	1300-600
C - O - C {stretching}	1150-1060 {asymmetric} 970-800 {symmetric}
Si - O - Si {stretching}	1110-1000 {asymmetric} 550-540 {symmetric}
O - O {stretching}	900-845
S - S {stretching}	550-430
Se - Se {stretching}	330-290
C (aromatic) - S {stretching}	1100-1080
C (aliphatic) - S {stretching}	790-630
C - Cl {stretching}	800-550
C - Br {stretching }	700-500
C - I {stretching }	660-480
C - C {bending}	400-250
lattice vibrations - accordion modes	200-20

Ref: B. Schader (1995) *Infrared and Raman Spectroscopy* (ed.) B Schader, VCH Publishing, New York, p. 190.

## Utilizzi IR-Raman

- Rivelatore GPC
- Individuazione e quantificazione additivi (cariche, plastificanti, stabilizzanti)
- Identificazione gruppi funzionali e polimero
- Gruppi terminali (peso molecolare, terminazione)
- Studi conformazionali
  - ⇒ configurazione, struttura cristallina, transizioni solido-solido
- Degradazione

Zona delle frequenze di gruppo

Zona delle impronte digitali

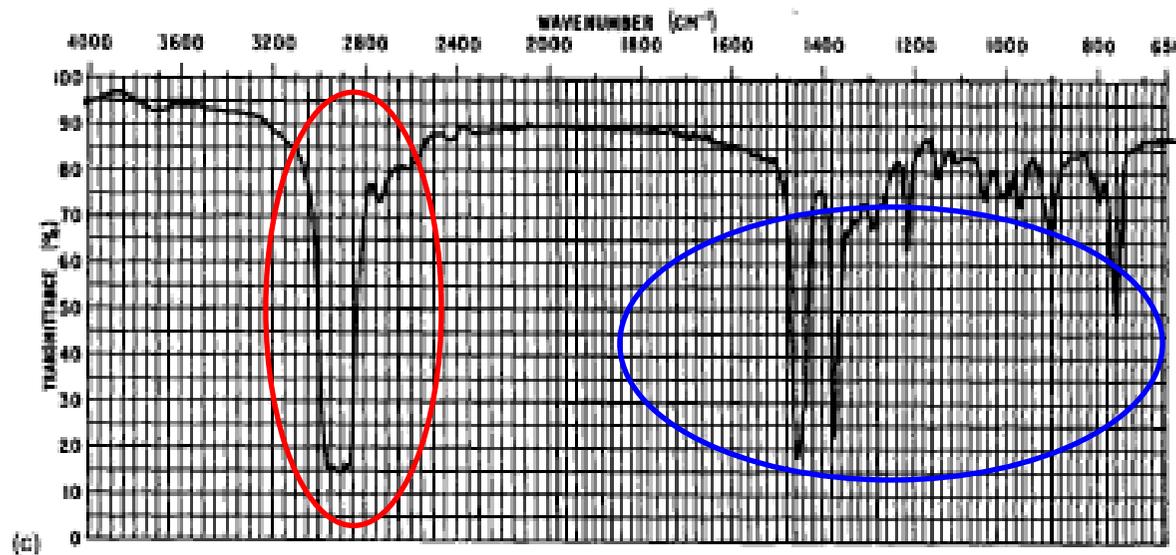
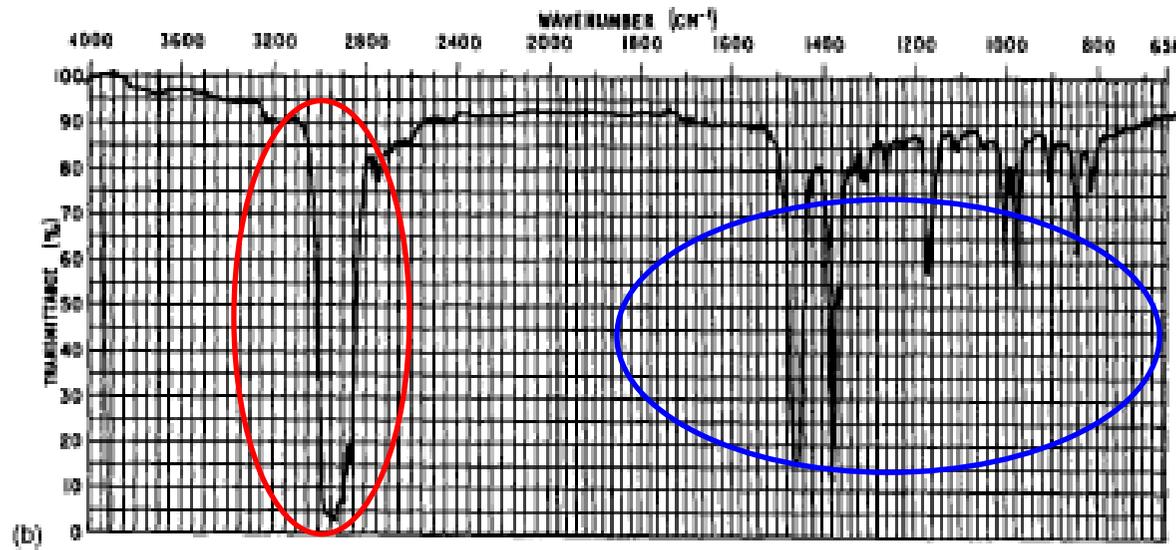
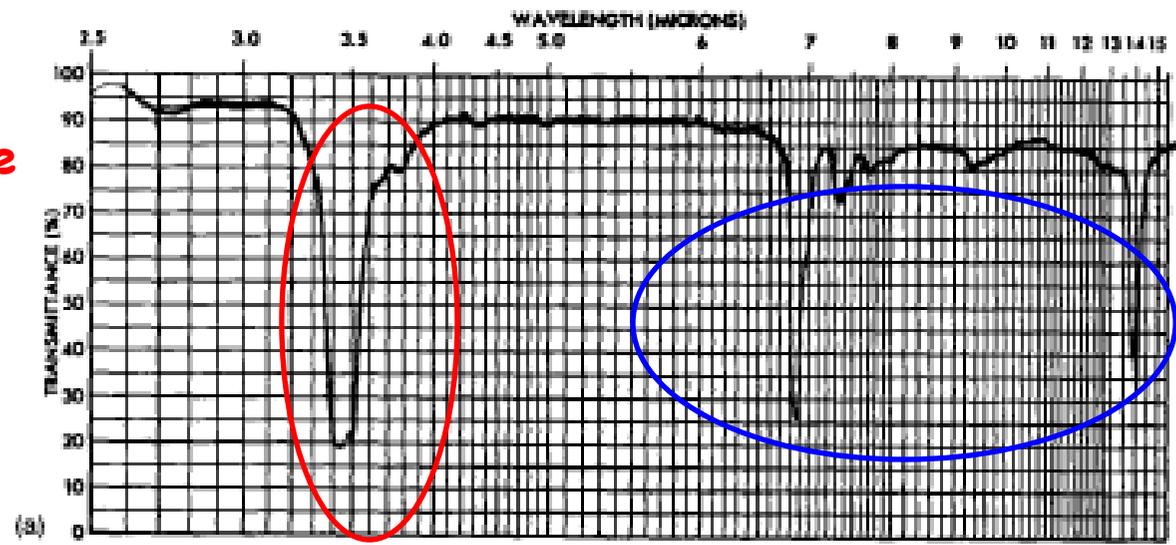
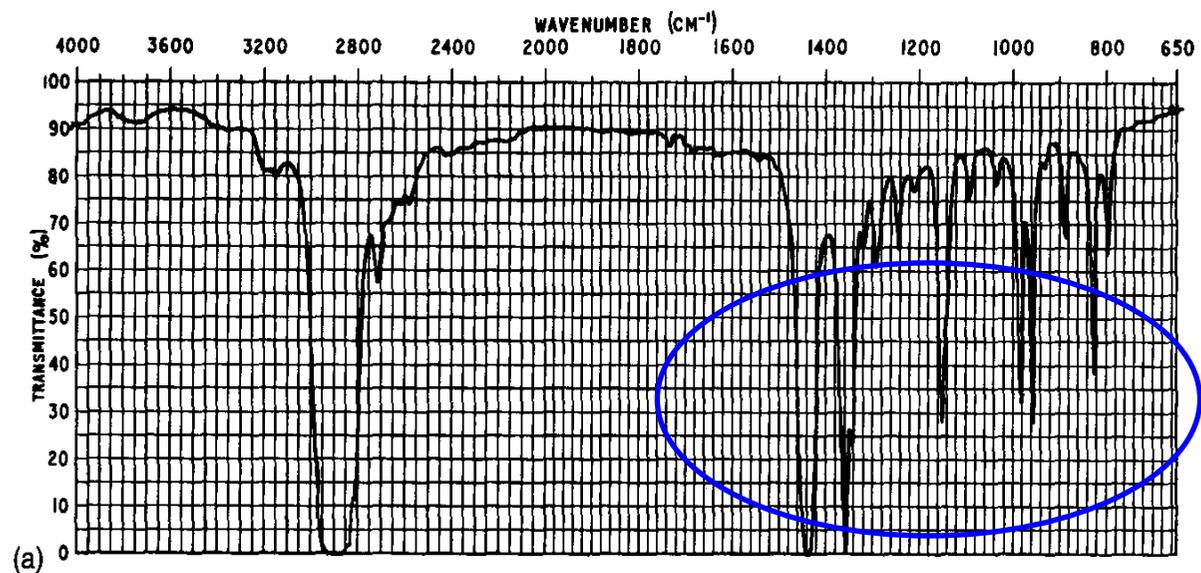
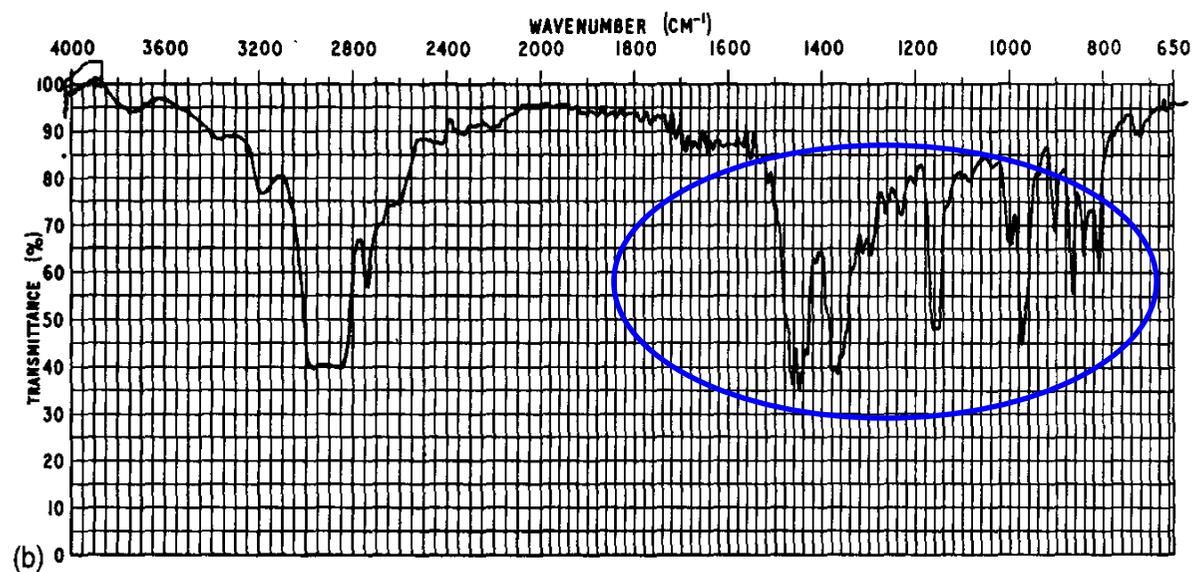


Fig. 5.7 IR spectra: (a) low density polyethylene, (b) isotactic polypropylene, (c) isotactic polybutene-1. In (a), the spectrum is plotted against wavelength for comparison.

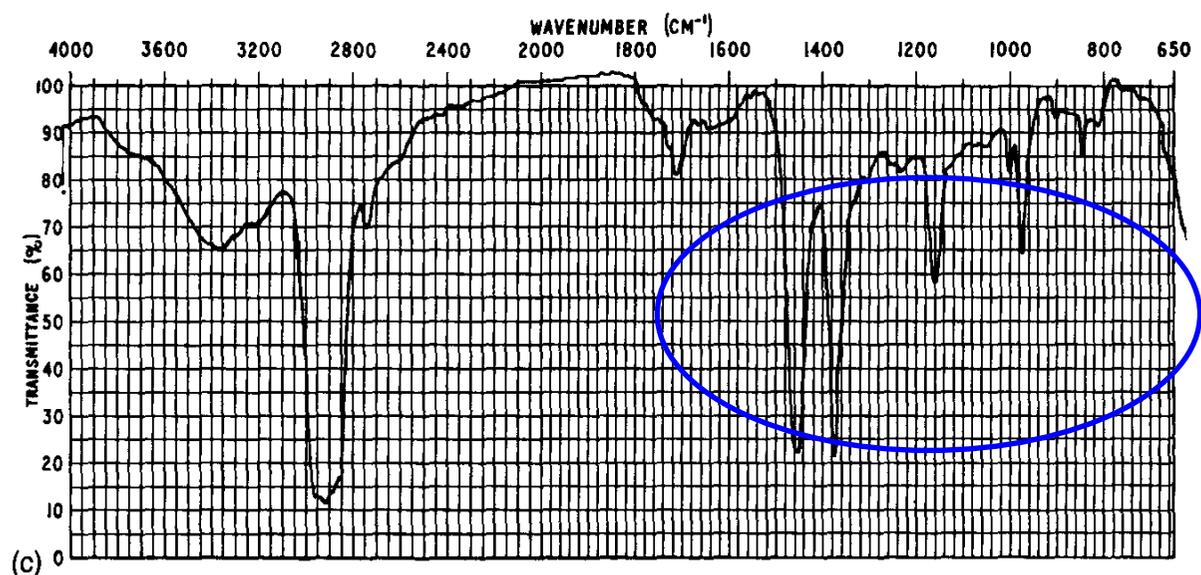
(PP isotattico)



(PP sindiotattico)



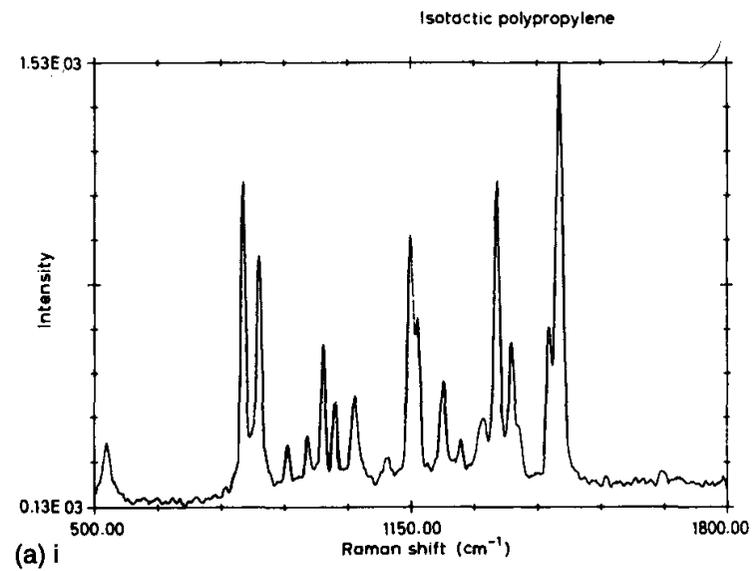
(PP atattico)



Zona delle impronte digitali

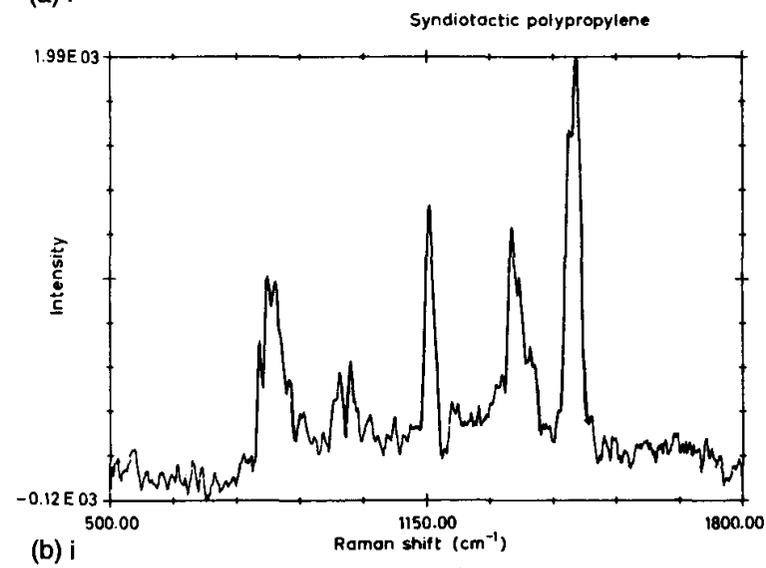
Fig. 5.12 IR spectra of different tactic forms of polypropylene (a) isotactic (b) syndiotactic, (c) atactic.

(PP isotattico)



Zona delle impronte digitali

(PP sindiotattico)



(PP atattico)

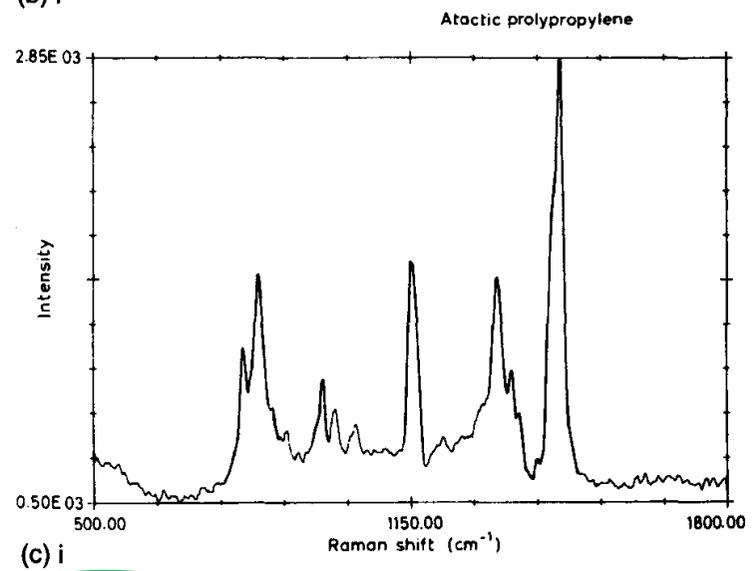
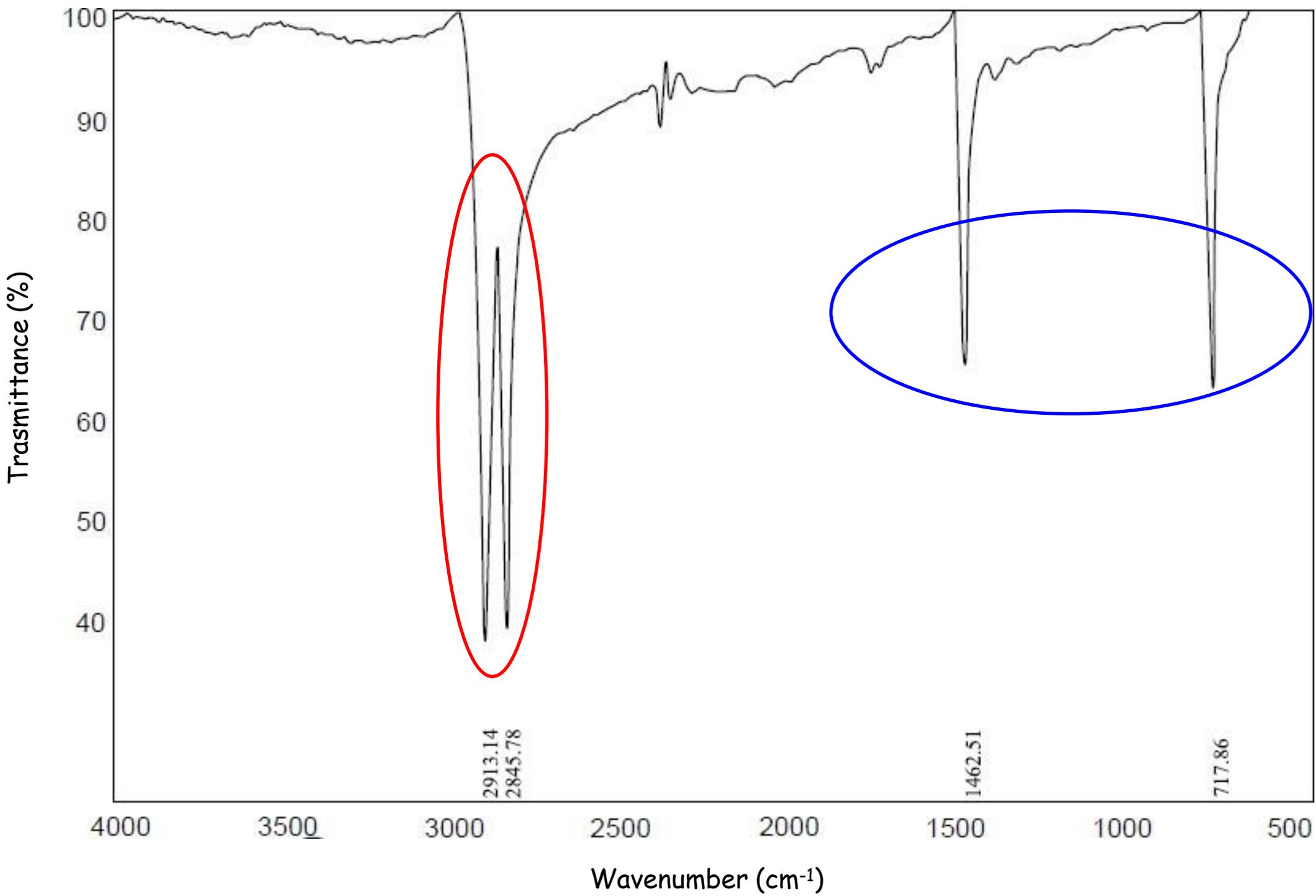


Fig. 5.18 Raman spectra of different tactic forms of polypropylene (a) isotactic) (b) syndiotactic, (c) atactic. (Courtesy D.J. Gardner.)

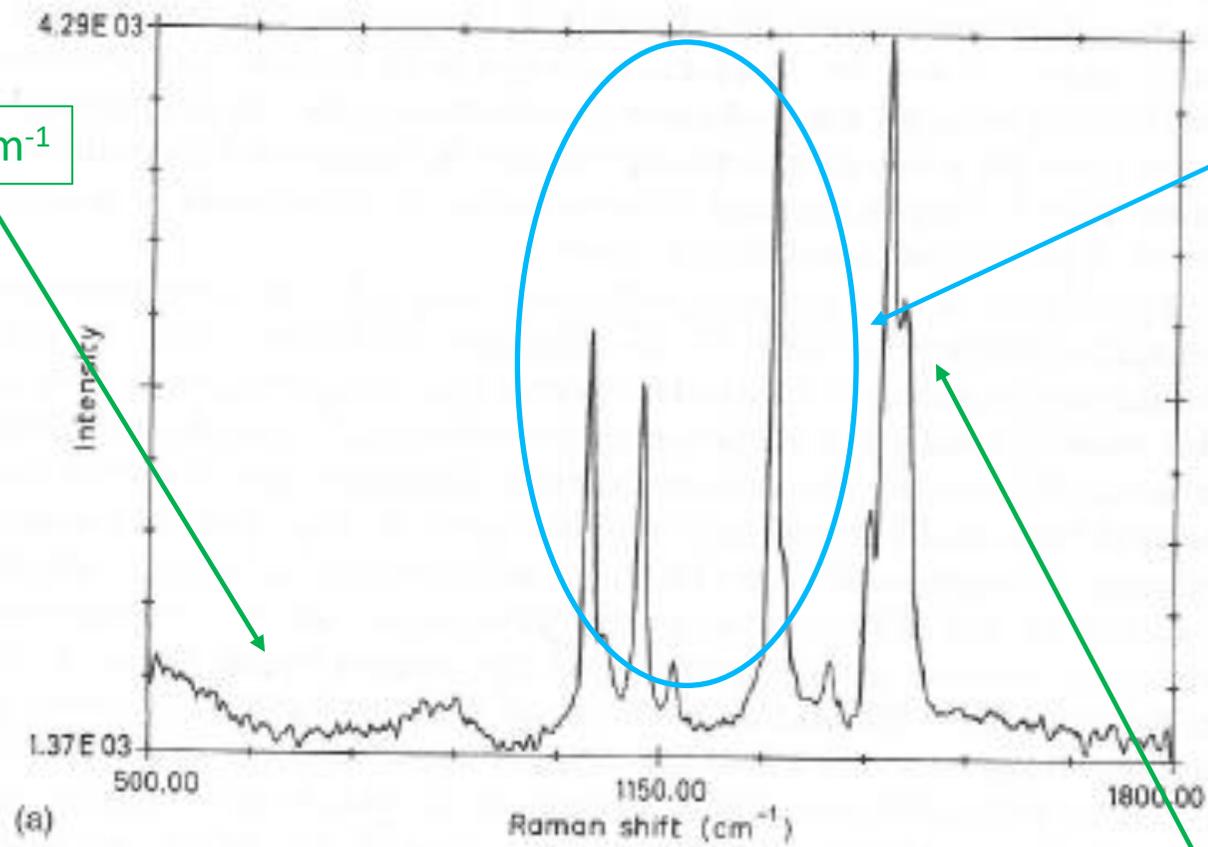
# Polietilene (PE)



Zona delle impronte digitali

700  $\text{cm}^{-1}$

1070-1300  $\text{cm}^{-1}$



1400  $\text{cm}^{-1}$

Zona delle frequenze di gruppo

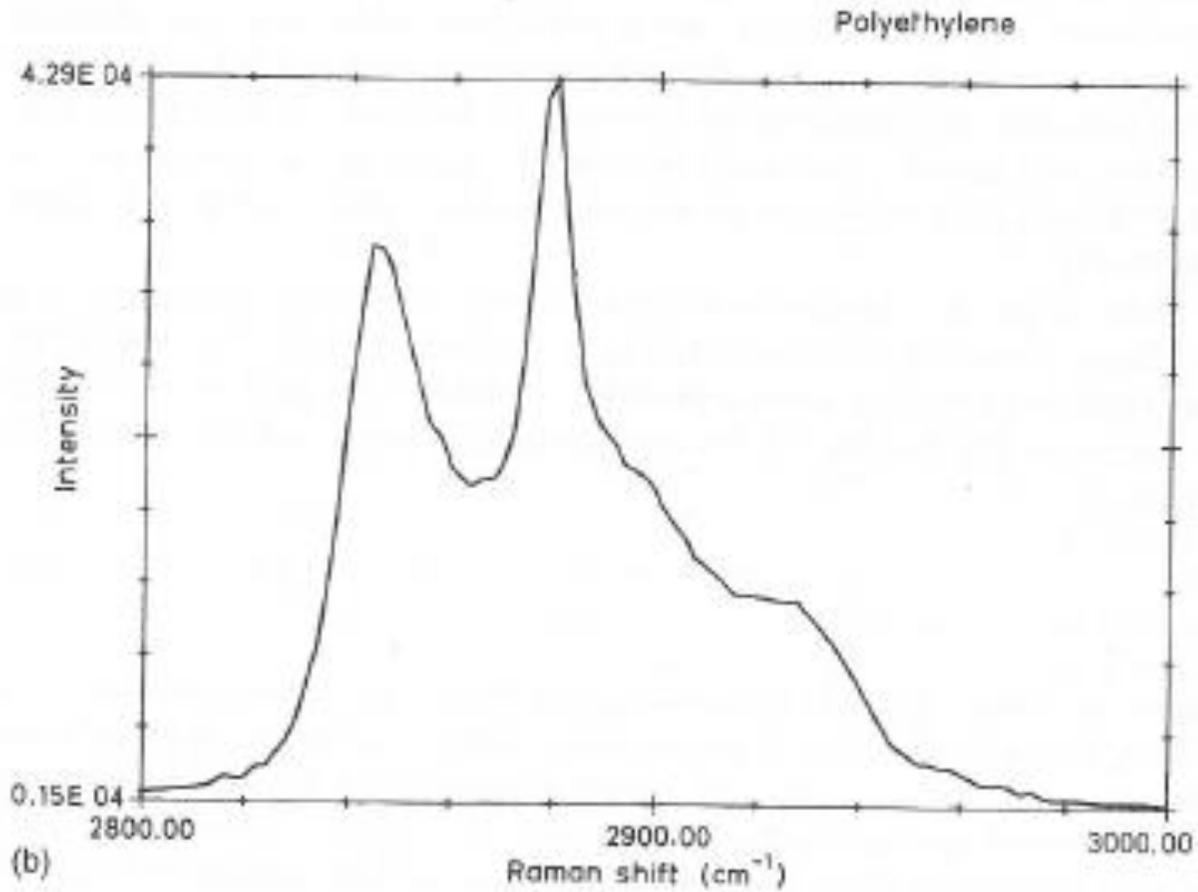
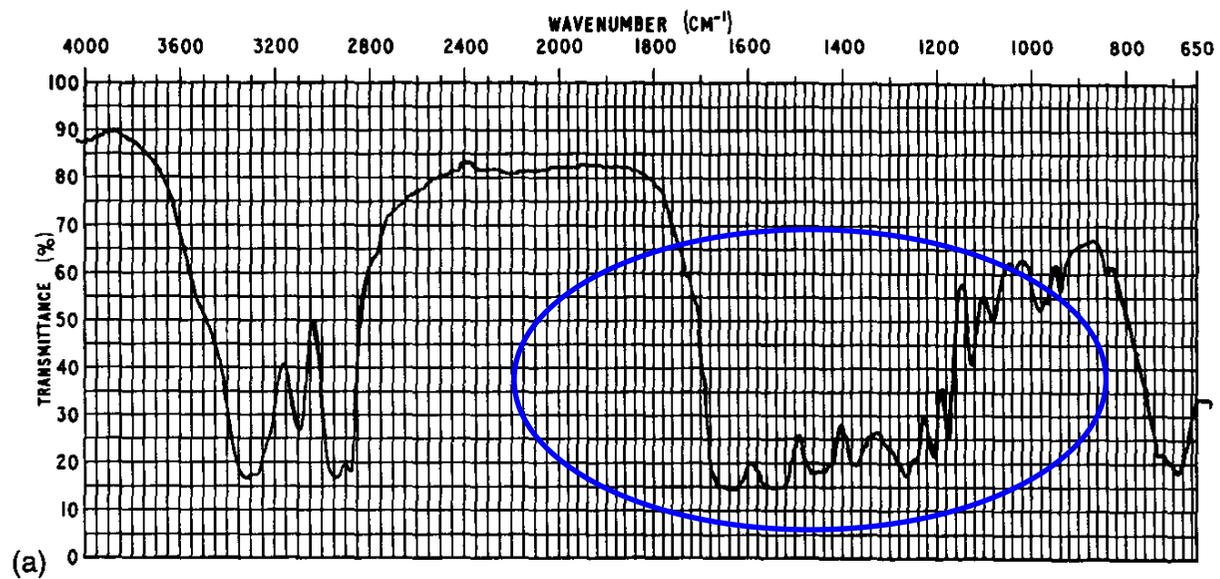
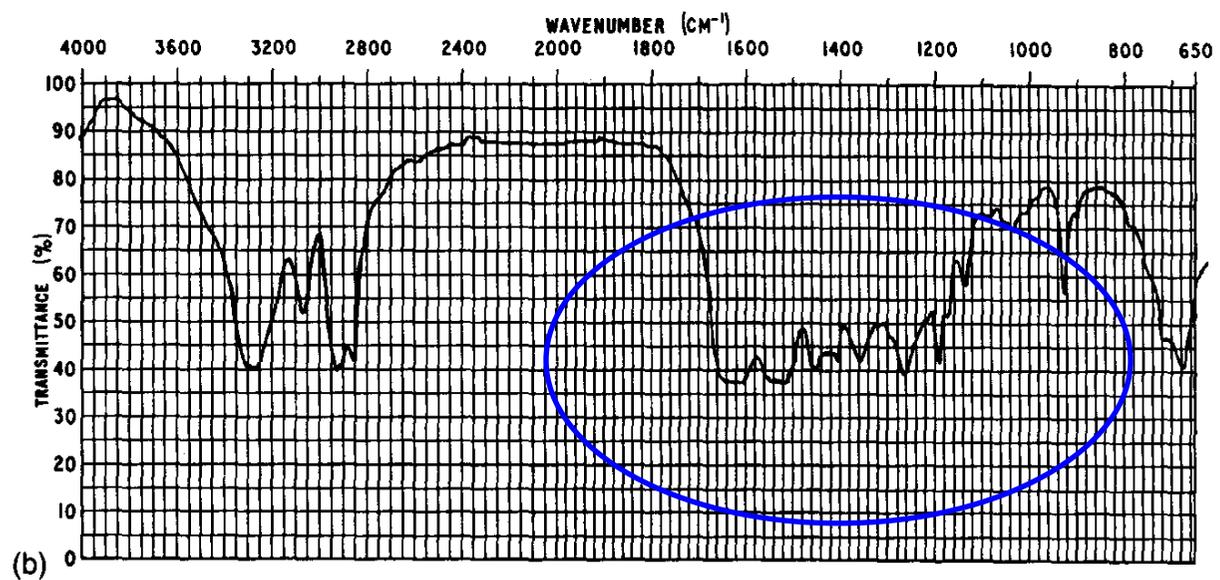


Fig 5.14 Raman spectrum of low density polyethylene. (Courtesy D.J. Gardner.)

(PA6)



(PA6,6)



(PA11)

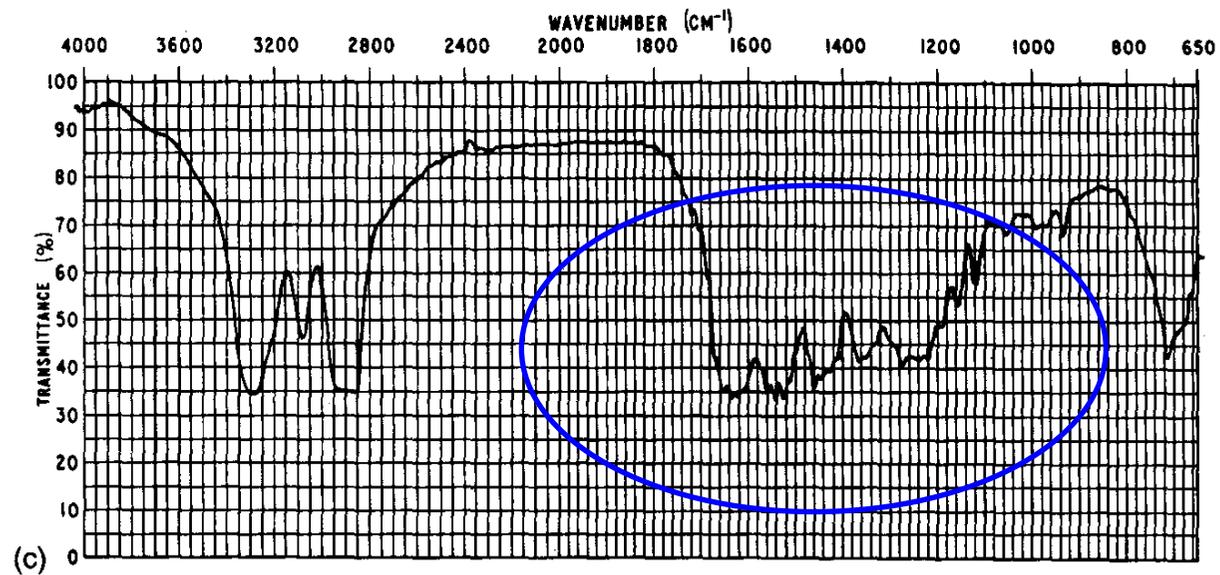
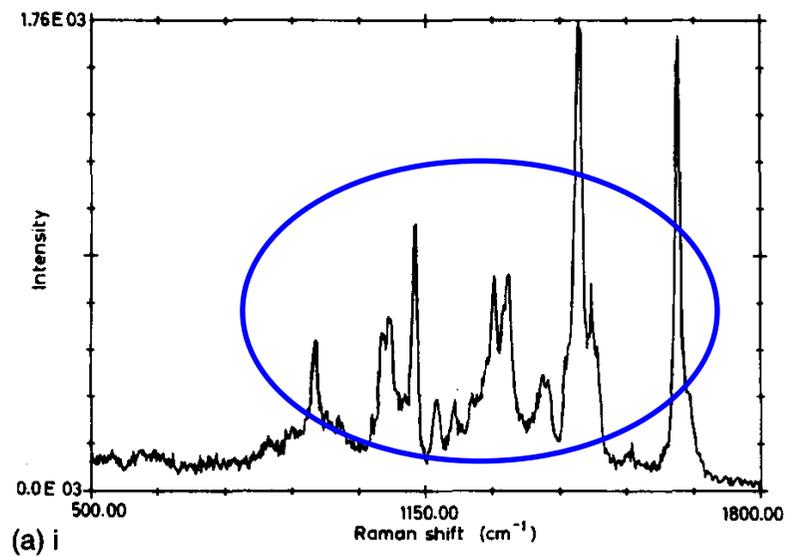
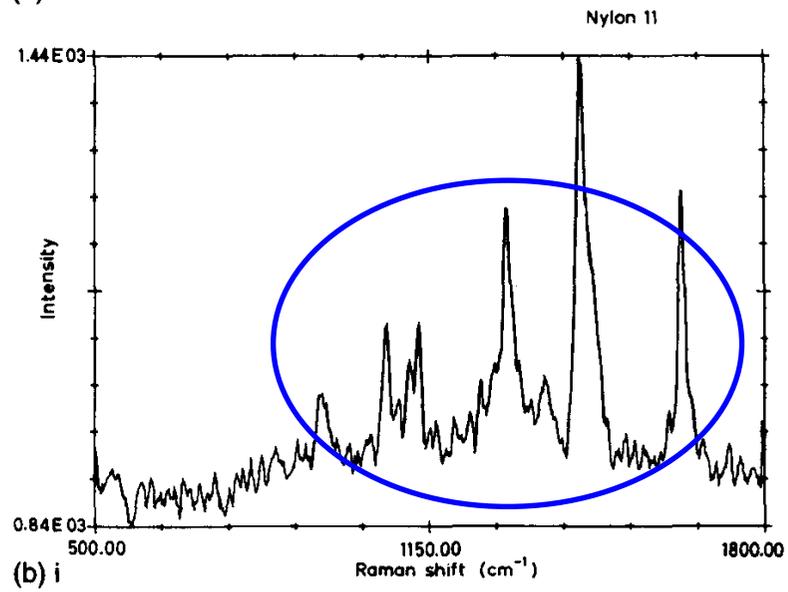


Fig. 5.16 IR spectra of different polyamides: (a) nylon 6, (b) nylon 6.6, (c) nylon 11.

(PA6)



(PA6,6)



(PA11)

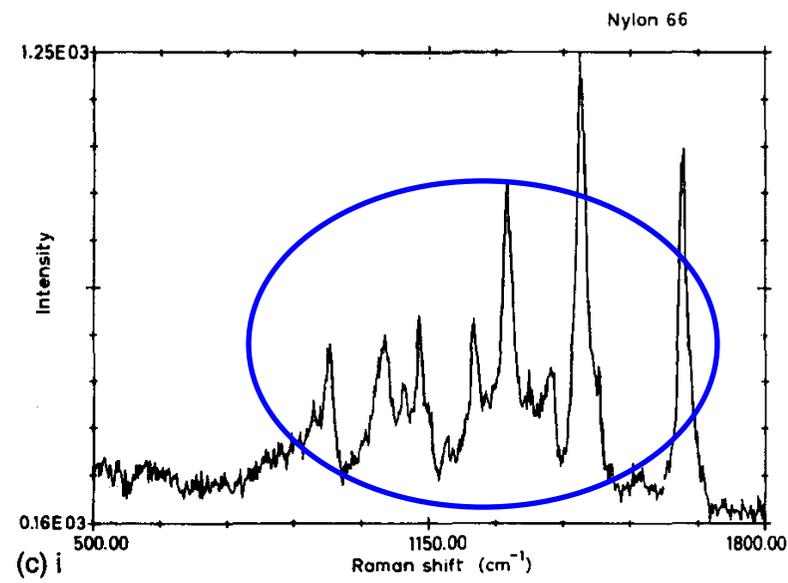


Fig. 5.17 Raman spectra of different polyamides (a) nylon 6, (b) nylon 6.6, (c) nylon 11. (See following page for spectra in higher shift range.) (Courtesy D.J. Gardner.)

# Risonanza Magnetica Nucleare (NMR)

Prerequisito essenziale: **presenza di spin nucleare**

⇒ **Numero dispari di protoni e/o neutroni**



**I= numero quantico di spin (0, intero, semi-intero)**

Se i **protoni** e i **neutroni** sono **entrambi pari**, allora il nucleo ha **numero quantico di spin zero**.

Se i **protoni** e i **neutroni** sono **gli uni pari e gli altri dispari**, allora il nucleo ha **numero quantico di spin semi intero** ( $1/2, 3/2, 5/2, \dots$ ).

Se i **protoni** e i **neutroni** sono **entrambi dispari**, allora il nucleo ha **numero quantico di spin intero** ( $1, 2, 3, \dots$ )

Nucleo	Abbondanza naturale	Protoni	Neutroni	Net Spin	$\gamma$ ( $10^7$ rad/Ts)
$^1\text{H}$	99.98	1	0	1/2	26.753
$^{13}\text{C}$	1.1	6	7	1/2	6.728
$^{14}\text{N}$	99.63	7	7	1	1.934
$^{15}\text{N}$	0.37	7	8	1/2	-2.712
$^{19}\text{F}$	100	9	10	1/2	25.179
$^{31}\text{P}$	100	15	16	1/2	10.84

Momento angolare  $\vec{P}$   $|\vec{P}| = \hbar\sqrt{\mathbf{I}(\mathbf{I} + 1)}$

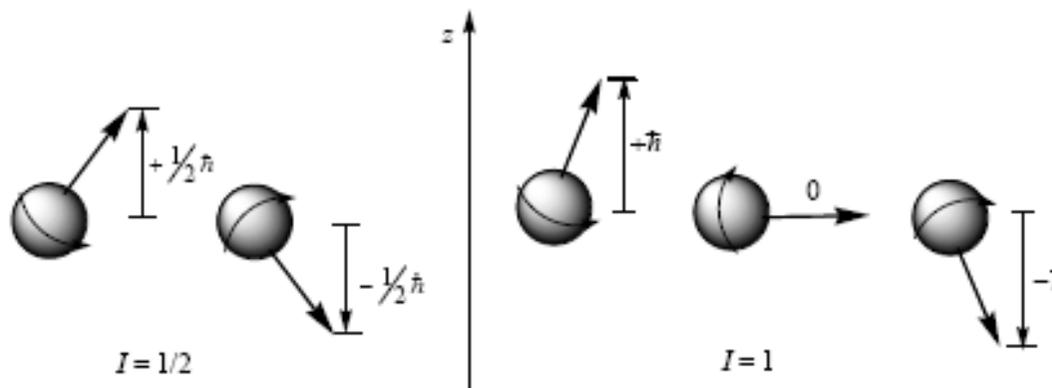
Momento magnetico  $\vec{\mu} = \gamma \vec{P}$   $\gamma$  Rapporto giromagnetico

# In presenza di un campo magnetico esterno $B_0$

$2I+1$  orientazioni permesse

Numero quantico magnetico  $m_I = I, I-1, I-2, \dots, -I$

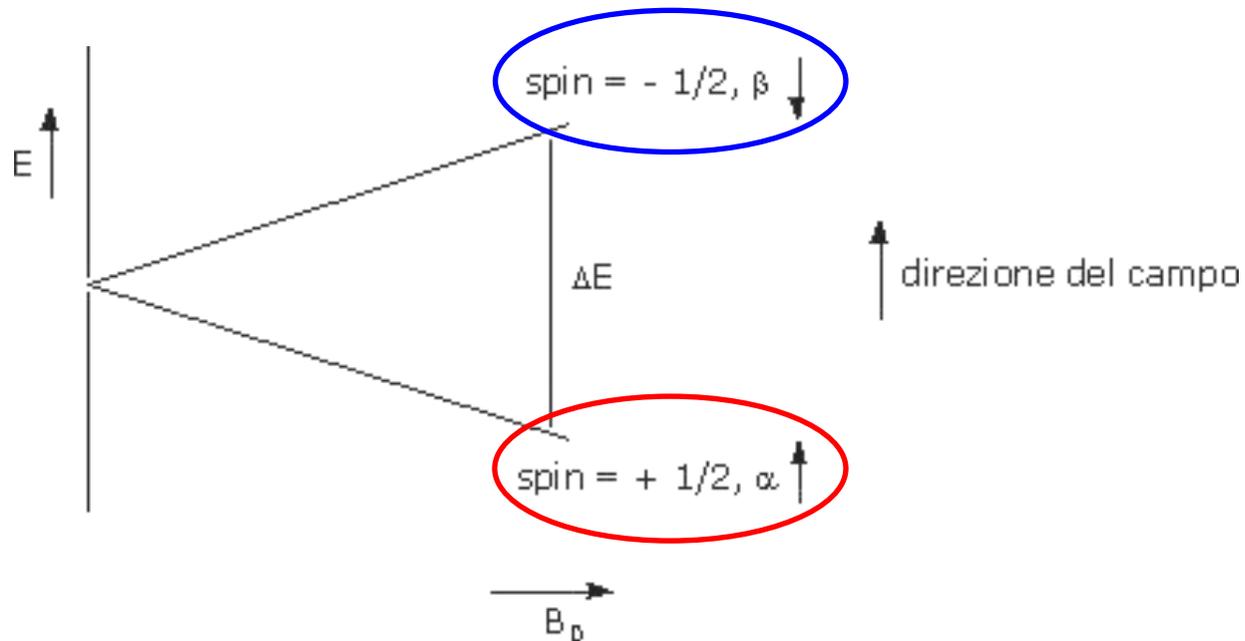
$I = 0, m = 0, P = 0$	Il nucleo non possiede momento magnetico
$I = 1, m = +1, 0, -1$	Sono possibili tre orientazioni: parallela, perpendicolare, antiparallela
$I = 1/2, m = +1/2, -1/2$	Sono possibili due orientazioni: parallela e antiparallela



In direzione  $z$   $P_z = m_I \hbar \Rightarrow \mu = \gamma m_I \hbar$

Se  $I=1/2$  allora  $m_I = \pm 1/2 \Rightarrow \mu = \pm \frac{1}{2} \gamma \hbar$

$$E = -\mu B_0 = -\gamma m_I \hbar B_0 = \pm \frac{1}{2} \gamma \hbar B_0 \quad \Rightarrow \quad \Delta E = \gamma \hbar B_0$$



La frequenza di risonanza  $\nu = \frac{\Delta E}{h} = \frac{\gamma}{2\pi} B_0$

**Rilassamento spin-reticolo (longitudinale)**

$$\Rightarrow \text{Intensità} \propto 1/T_1$$

**Rilassamento spin-spin (trasversale)**

$$\Rightarrow \text{Ampiezza riga} \propto 1/T_2$$

# Chemical shift

Campo effettivo  $B_{\text{eff}} = B_0(1-\sigma)$

Con  $\sigma$  costante di schermo

$$\Rightarrow \nu_{\text{ris}} = \frac{\gamma}{2\pi} B_0(1-\sigma)$$

Definiamo Chemical shift

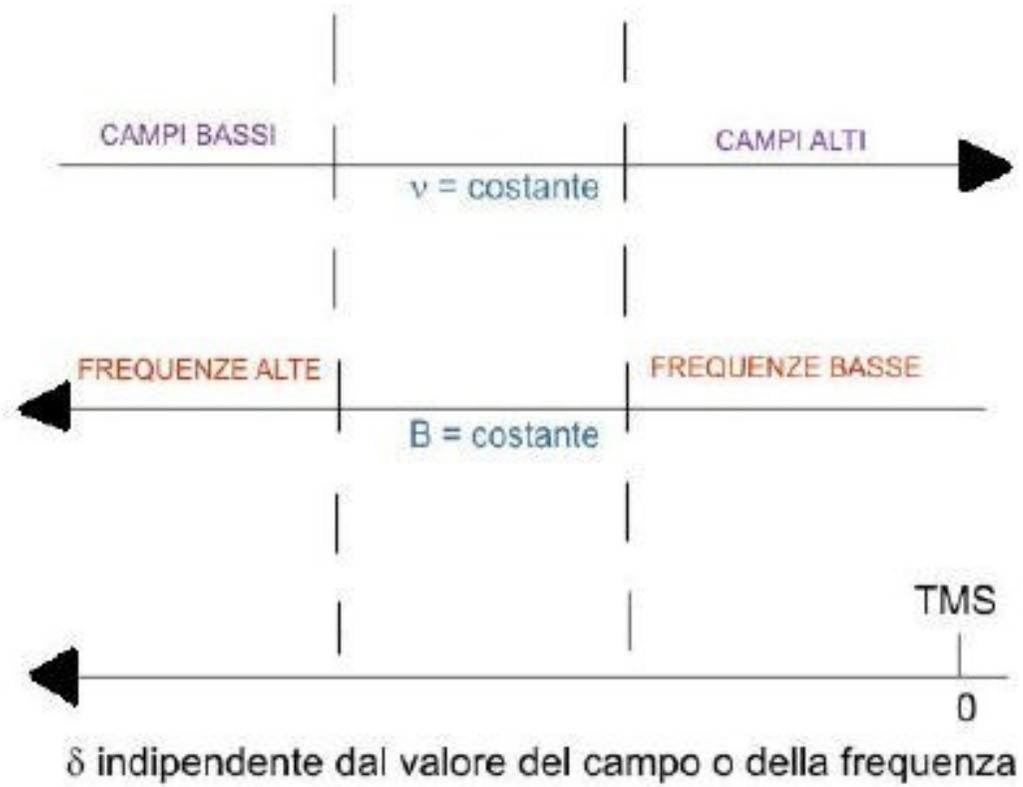
$$\delta = \frac{\nu_s - \nu_r}{\nu_r} \times 10^6 \text{ ppm}$$

r = reference      s = sample

come riferimento si usa il TMS

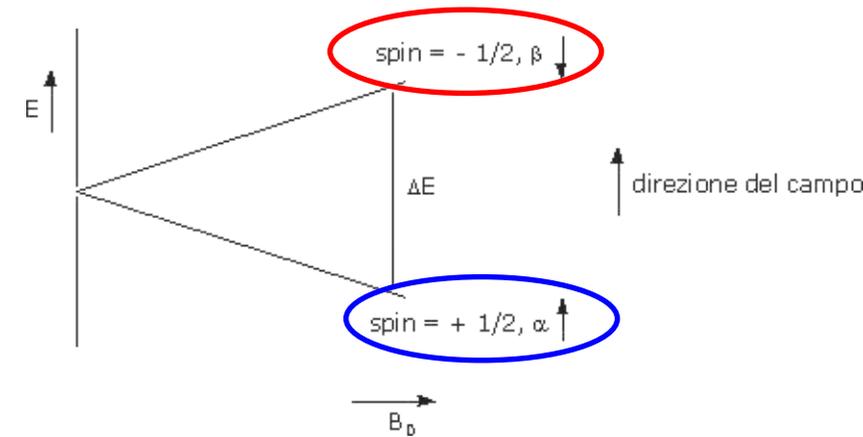
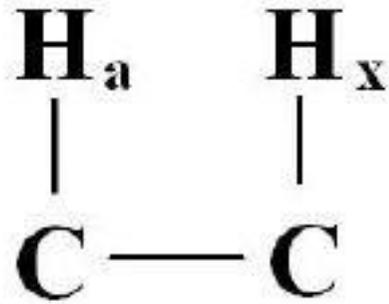


- ◆ è chimicamente inerte
- ◆ è simmetrico
- ◆ è volatile
- ◆ è solubile nella maggior parte dei solventi
- ◆ produce un singolo picco di assorbimento intenso e sottile (singoletto)
- ◆ i suoi protoni sono più schermati di quasi tutti i composti organici



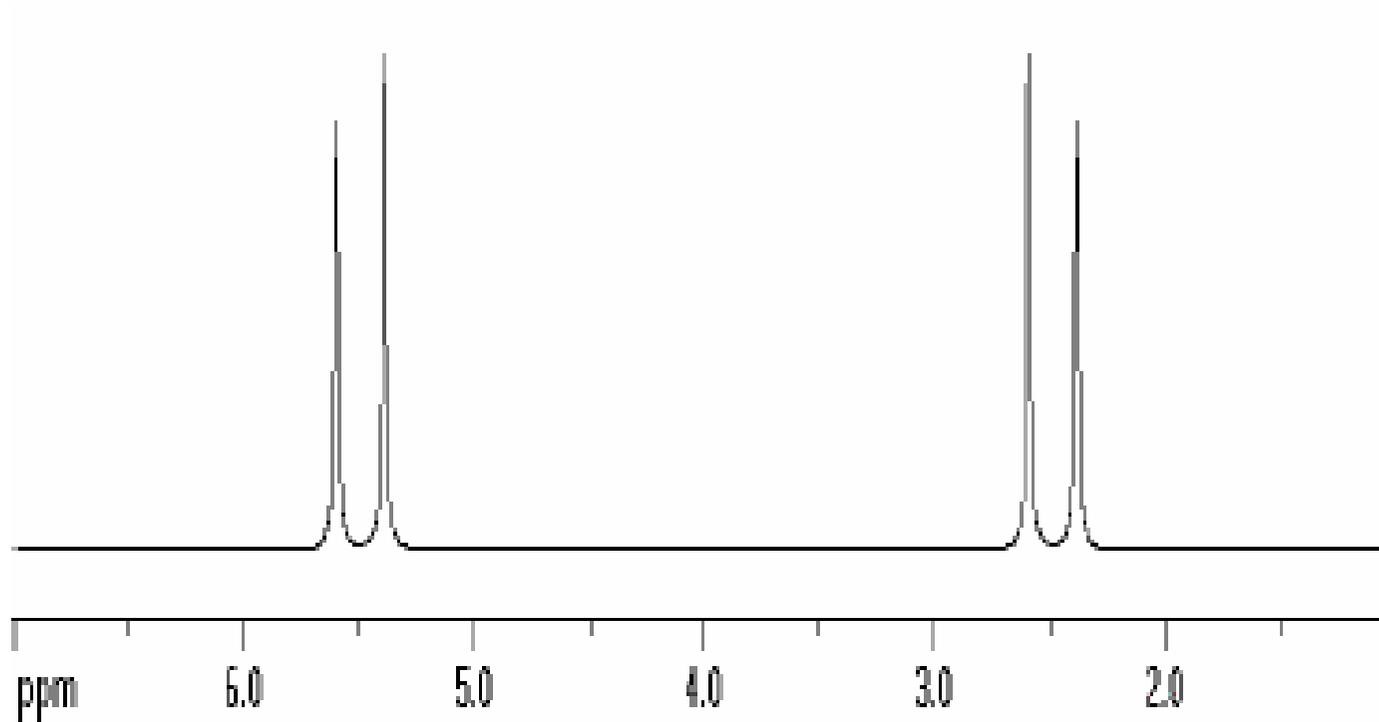
# Accoppiamento spin-spin

Consideriamo due protoni  $H_a$  e  $H_x$



Il protone  $H_a$  può trovarsi negli stati di spin  $\alpha$  o  $\beta$  con probabilità quasi uguale e influenza in maniera opposta  $H_x$

⇒ i segnali subiscono uno **split** ⇒ **doppietto**



La distanza tra i due segnali del doppietto (in Hz) è la

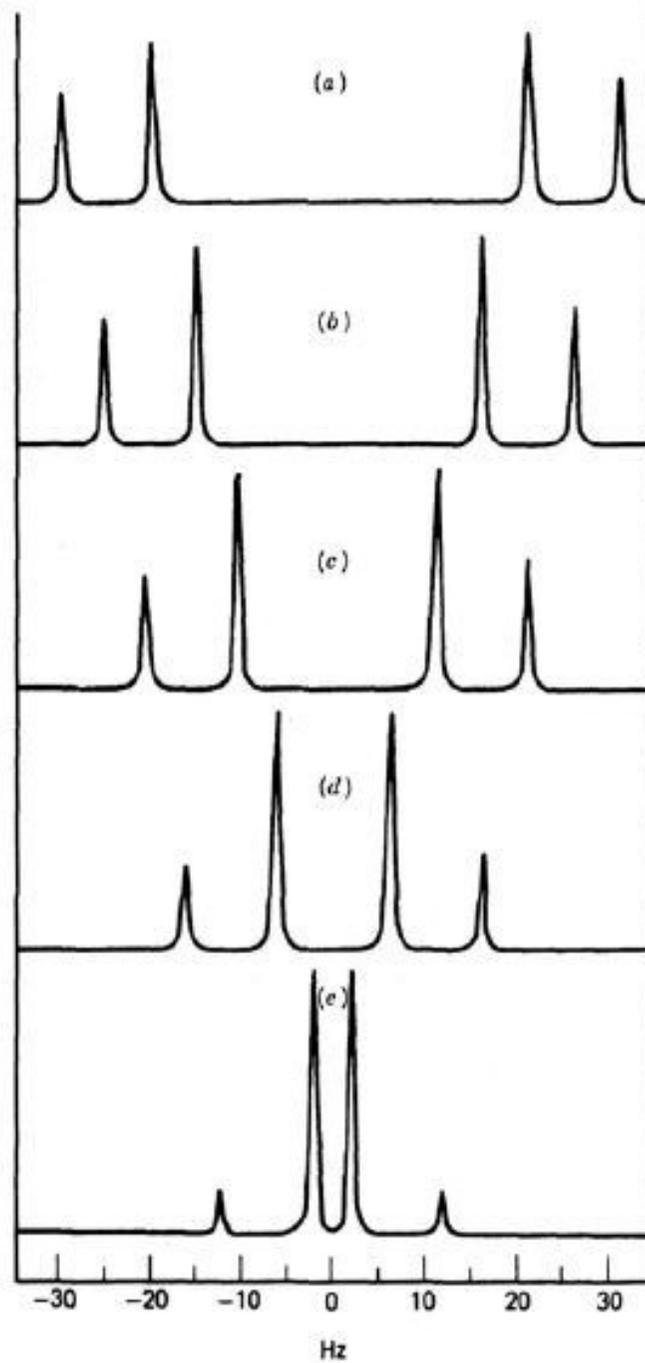
**J = costante di accoppiamento**

Se il Chemical shift di due nuclei è molto diverso:  $\frac{\Delta\nu}{J} > 10$

⇒ sistema di **primo ordine**

Se il Chemical shift di due nuclei non è molto diverso:  $\frac{\Delta\nu}{J} < 10$

⇒ sistema di **secondo ordine**



# Molteplicità e previsione di intensità

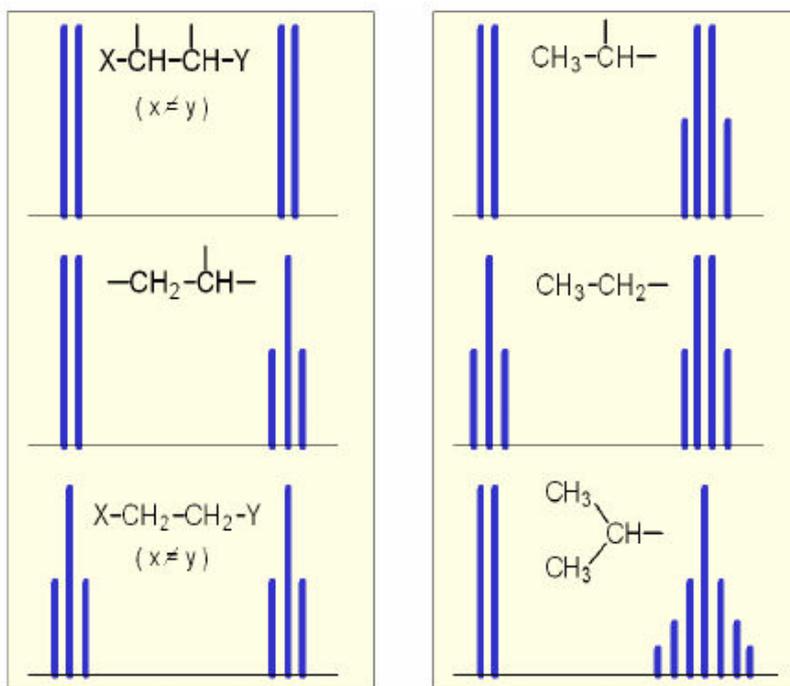
**Regola N+1**  $\Rightarrow$  **molteplicità**

Un nucleo adiacente a **N** idrogeni equivalenti si separa in

**N+1** picchi

**Triangolo di Pascal**  $\Rightarrow$  **intensità relativa**

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1



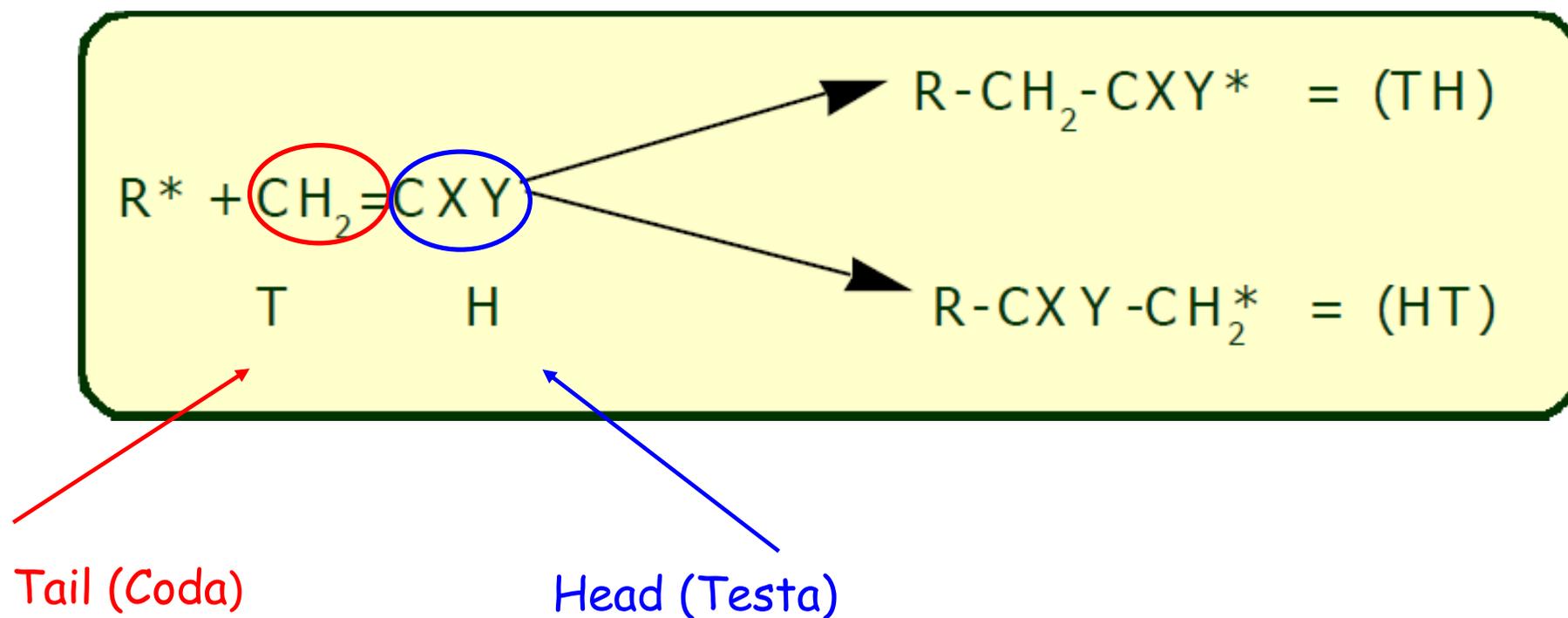
# Utilizzi NMR

- Modo di addizione (testa-coda)
- Studi configurazionali
  - ⇒ isomerie, tatticità
- Ramificazioni
- Gruppi terminali (peso molecolare, terminazione)
- Composizione copolimeri
- Meccanismi di reazione

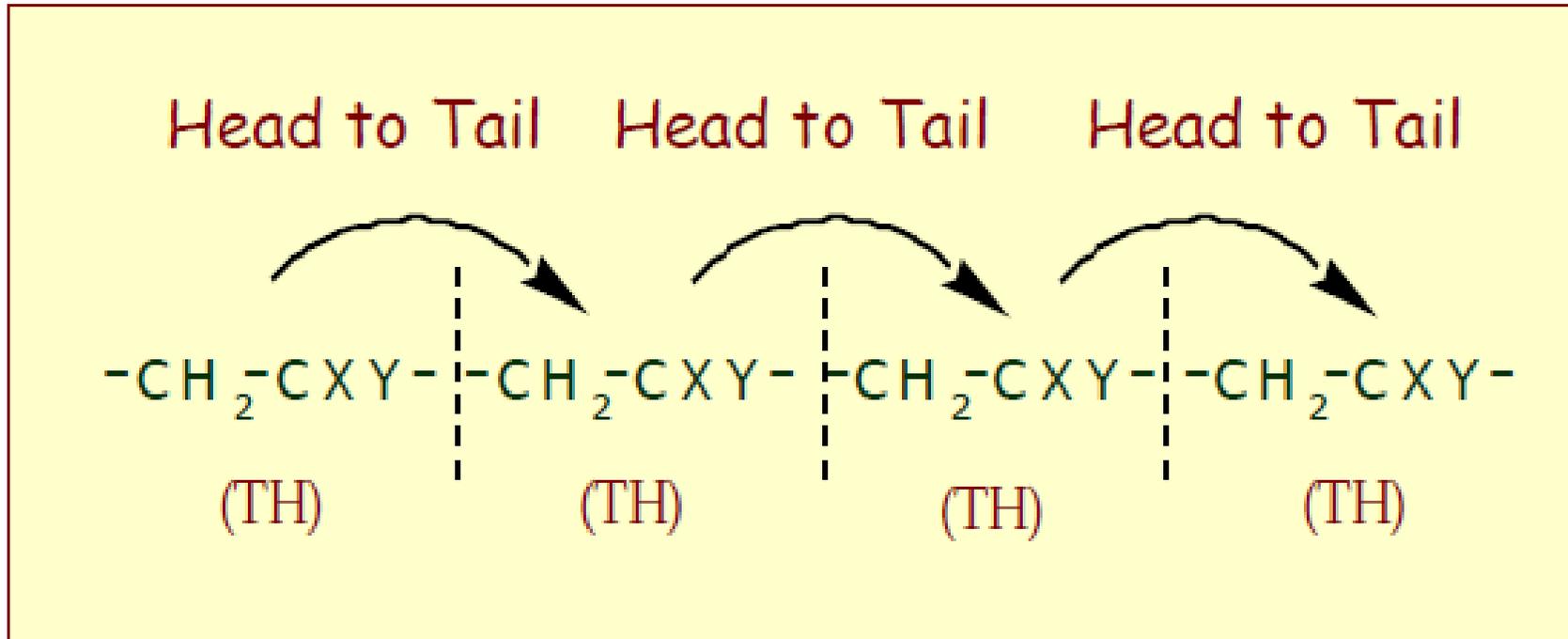
# Isomerie nei polimeri

1. Isomeria di sequenza
2. Isomeria strutturale (polimeri dienici)
3. Stereoisomeria (polimeri vinilici)

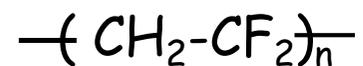
# Isomeria di sequenza



# Isomeria di sequenza

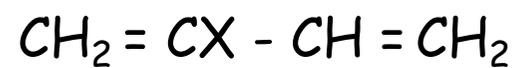


Esempio di polimero in cui è probabile la presenza di addizioni testa-testa o coda-coda : Polivinilidenfluoruro (PVDF)



# Isomeria strutturale (polimeri dieni)

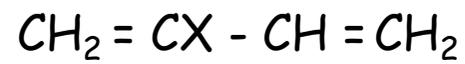
I monomeri sono dieni coniugati



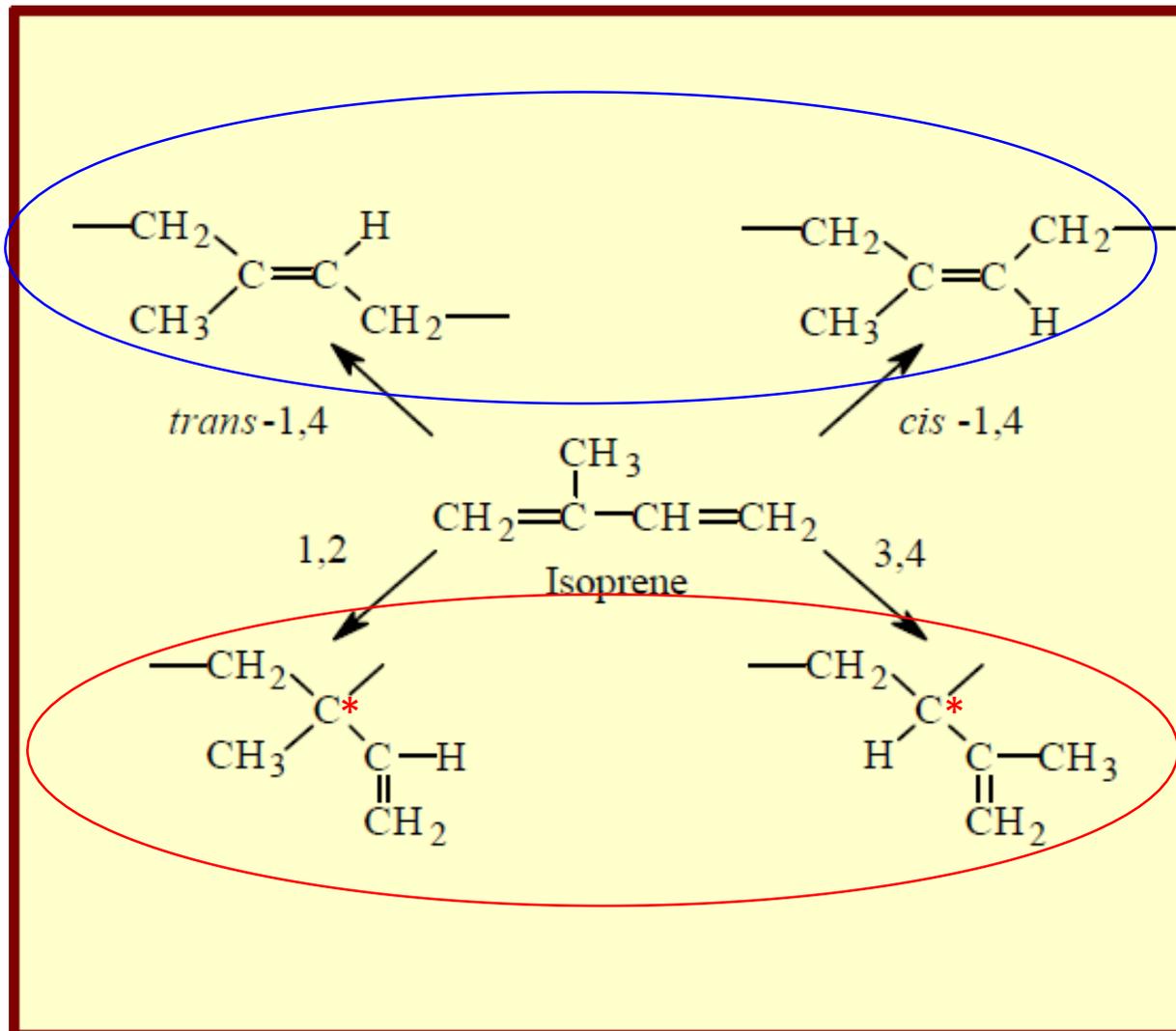
se

- |                    |   |                |
|--------------------|---|----------------|
| X= H               | → | Polibutadiene  |
| X= CH <sub>3</sub> | → | Poliisoprene   |
| X= Cl              | → | Policloroprene |

# Isomeria strutturale (polimeri dienici)



1    2    3    4

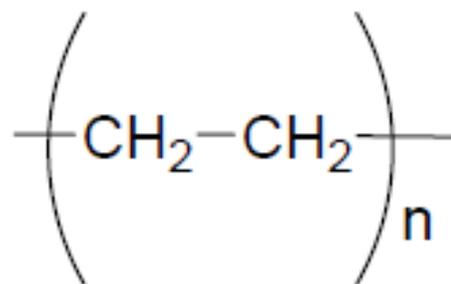


Isomeria geometrica

Stereoisomeria

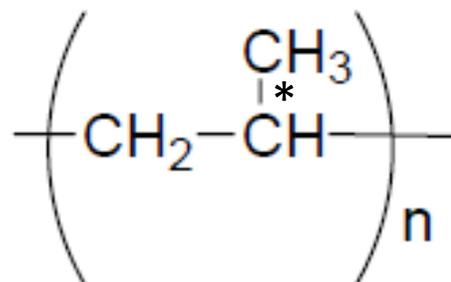
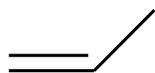
# Stereoisomeria

n



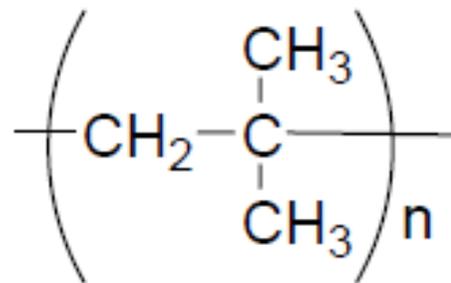
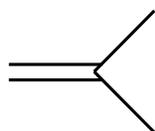
PE

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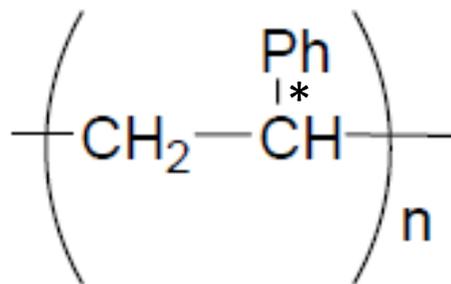
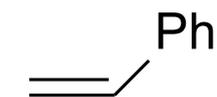
PP

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Poliisobutilene

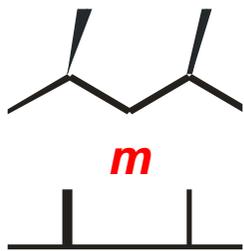
n



PS

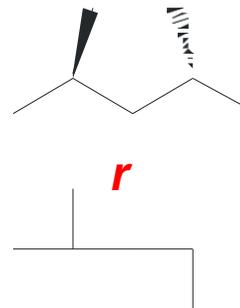
# Diadi, triadi, tetradi ...

Proiezione a zig-zag  
planare

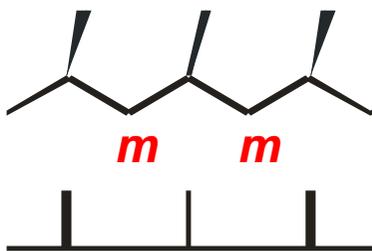


*m*

diadi

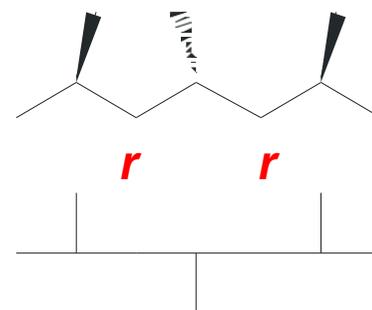


*r*



*m m*

triadi

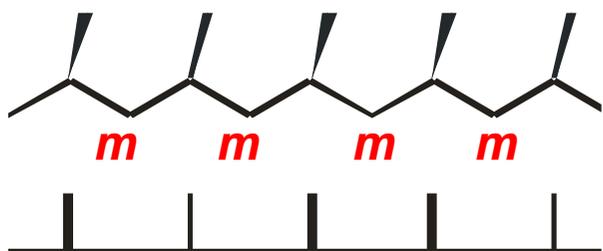


*r r*

tetradi

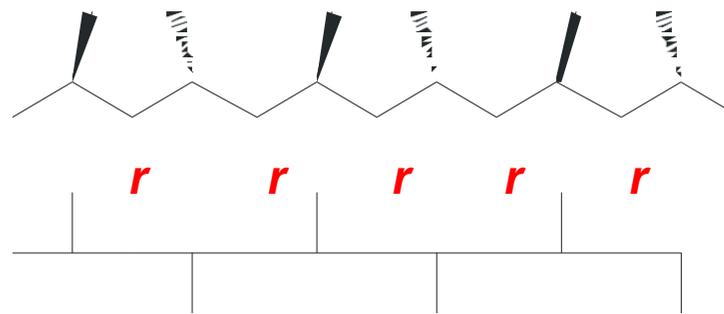
.....

.....



*m m m m*

pentadi



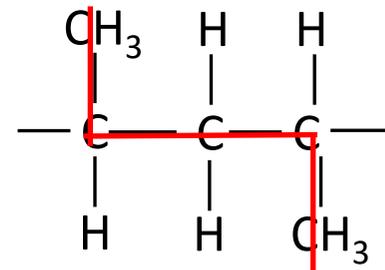
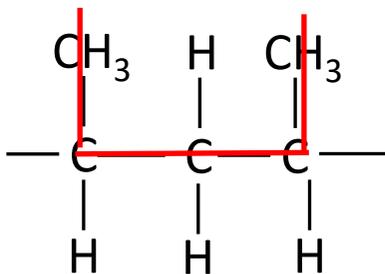
*r r r r r*

meso

racemo

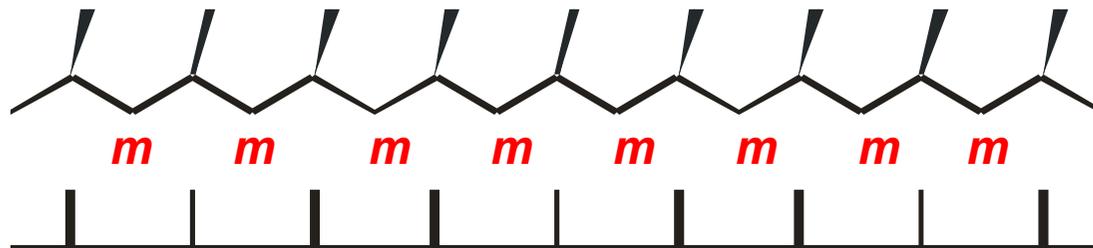
Proiezione di Fischer

*m*

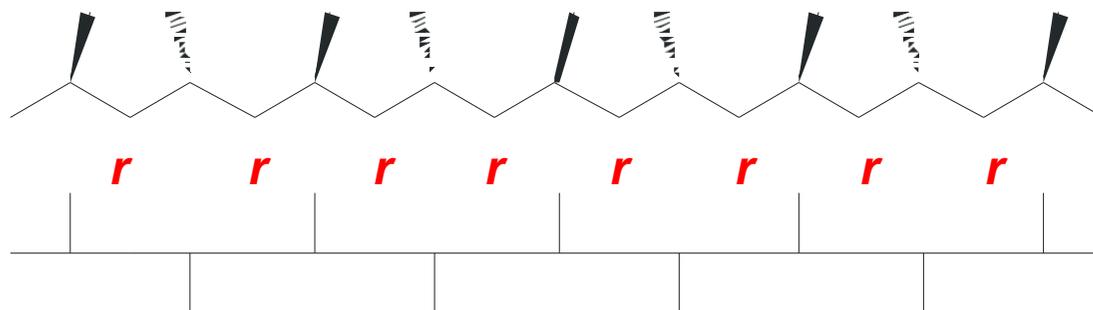


*r*

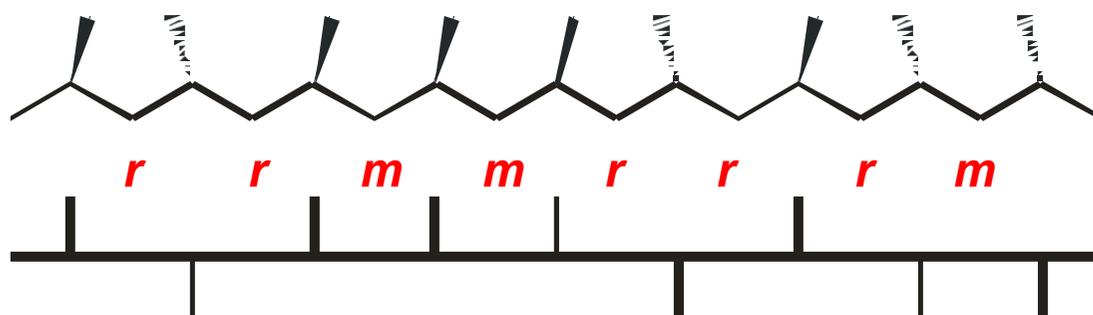
# Polimeri stereoregolari



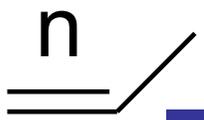
PP  
isotattico



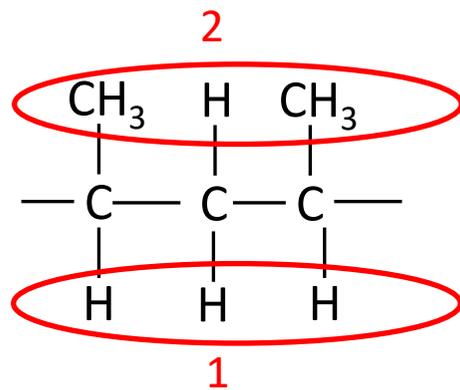
PP  
sindiotattico



PP  
atattico



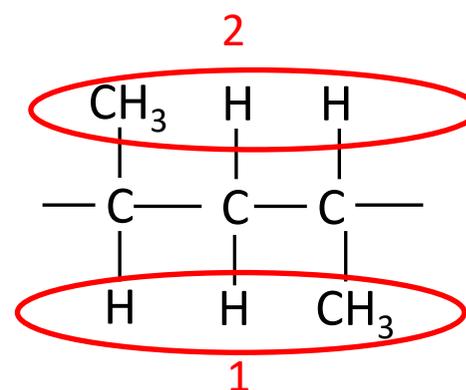
# Tassia e tatticità



Diade Meso (m)



Diverso intorno chimico di H<sub>1</sub>  
e H<sub>2</sub> (protoni **non equivalenti**)



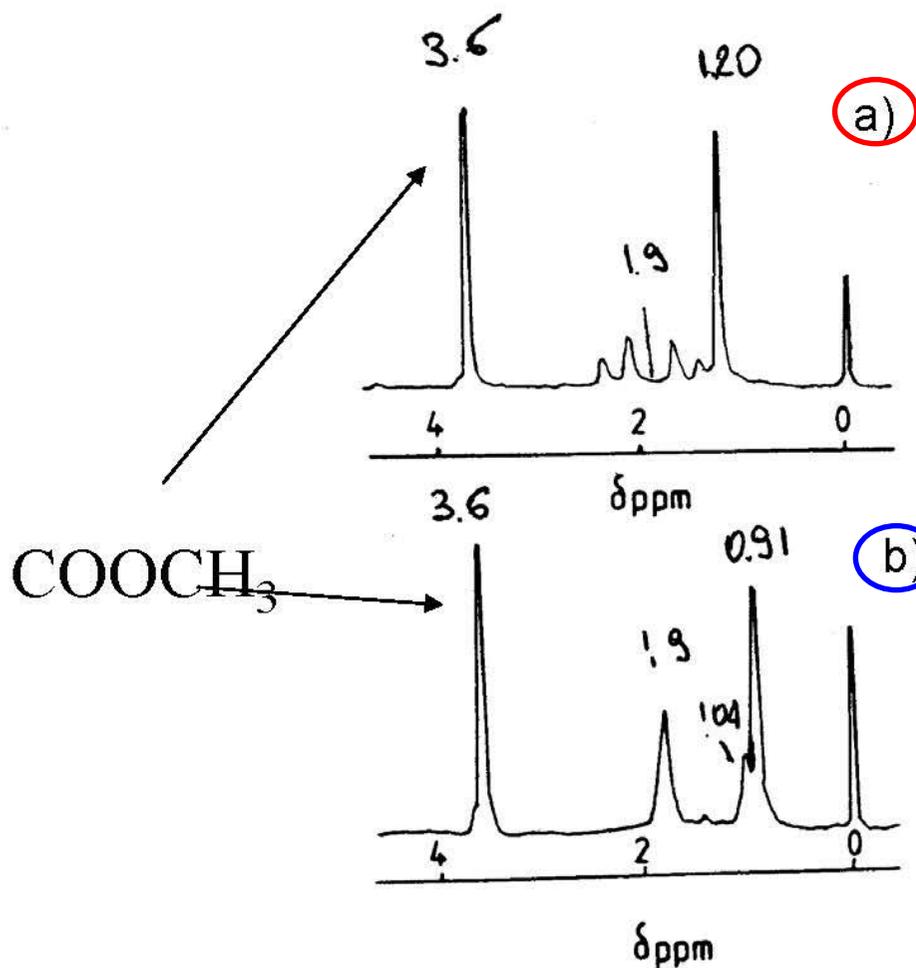
Diade Racemo(r)



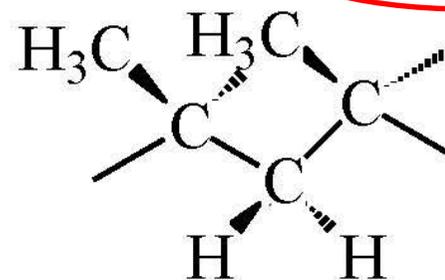
Intorno chimico di H<sub>1</sub> e H<sub>2</sub> non  
distinguibile (protoni **equivalenti**)

# Diadi

## $^1\text{H}$ NMR di PMMA

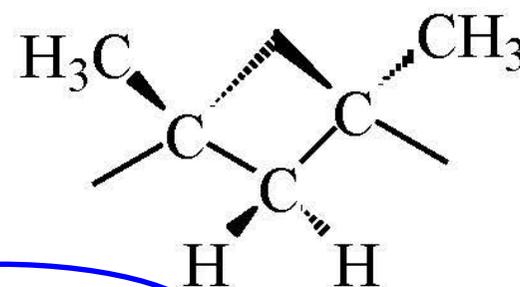


1.20 ppm isotattico (a)



1.9 ppm (quartetto)

0.91 ppm

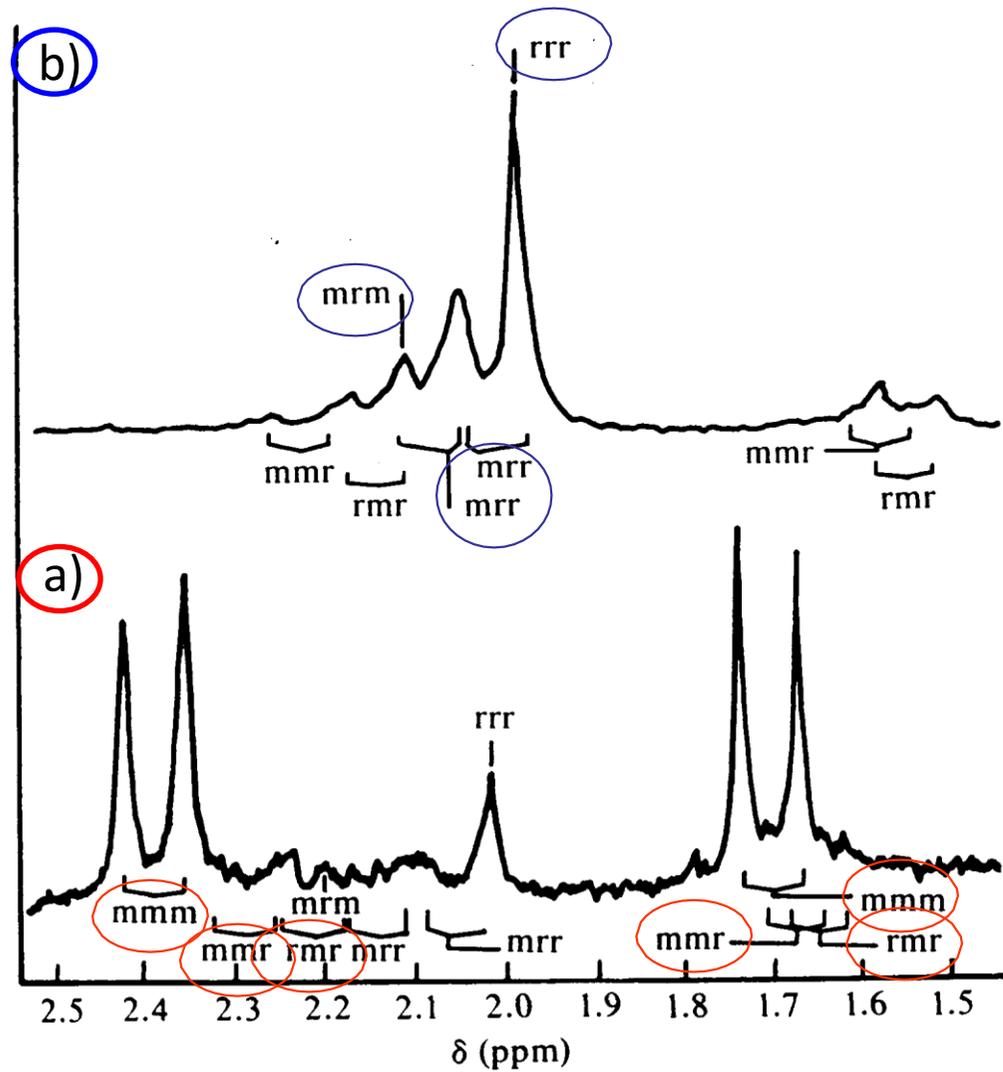


sindiotattico (b) 1.9 ppm (singoletto)

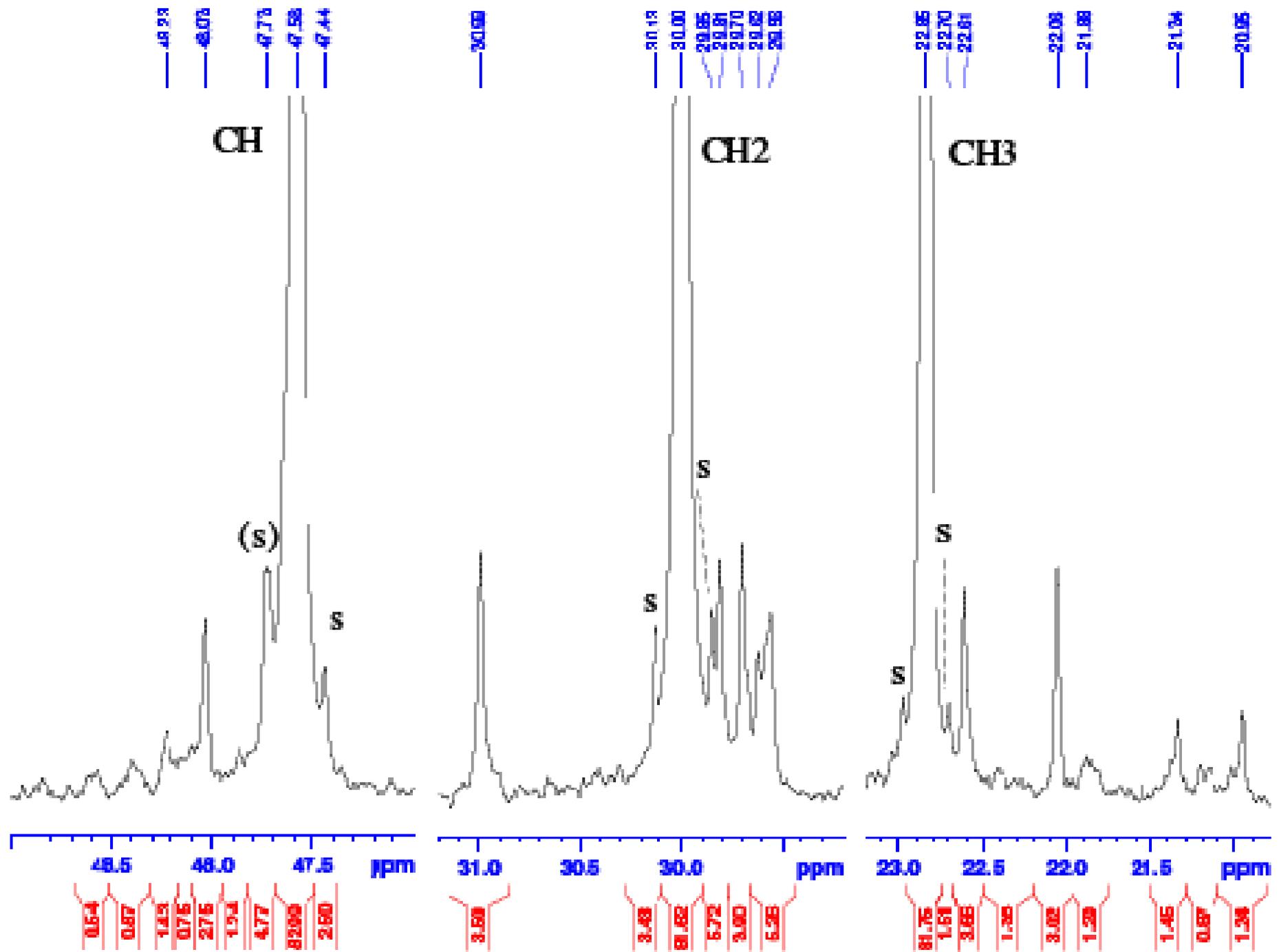
FIGURE 6.6 60 MHz proton NMR spectra of different tactic forms of poly(methylmethacrylate): (a) isotactic, (b) syndiotactic (from Johnsen, U. (1961) *Kolloid. Z* 178, 161).

# Caratterizzazione NMR di omopolimeri

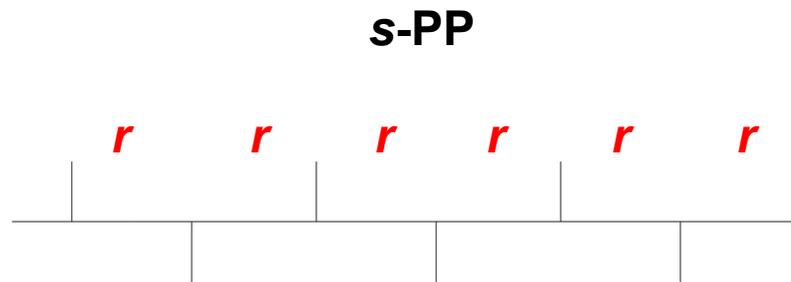
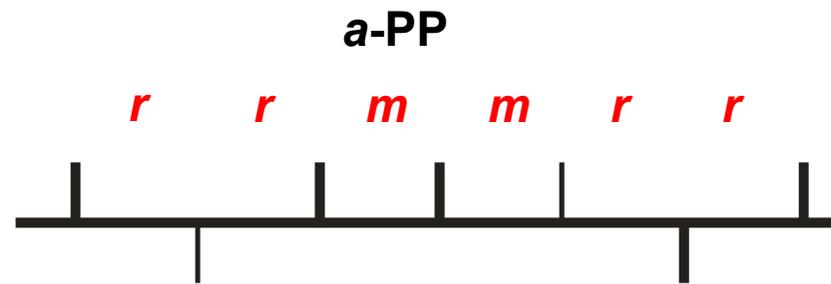
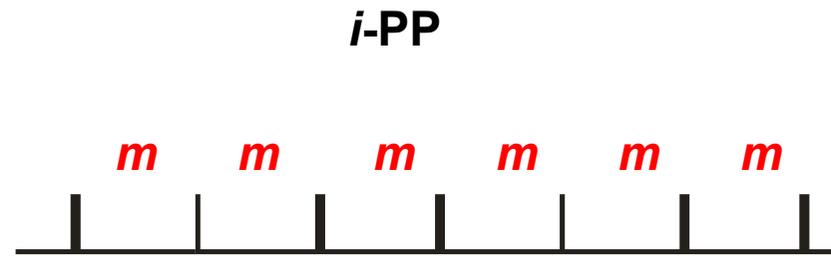
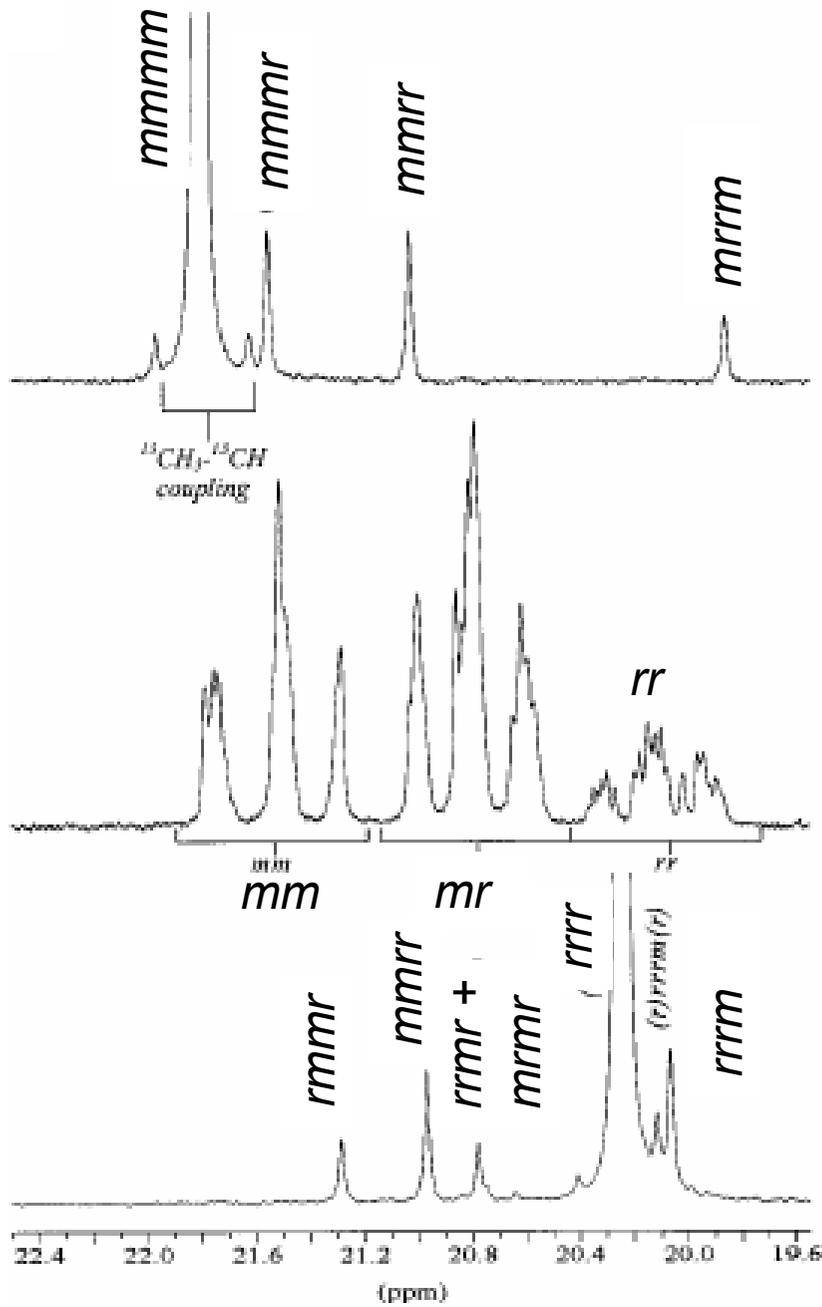
⇒ **Tetradi** nella zona dei metileni di PMMA (spettro  $^1\text{H}$  NMR)



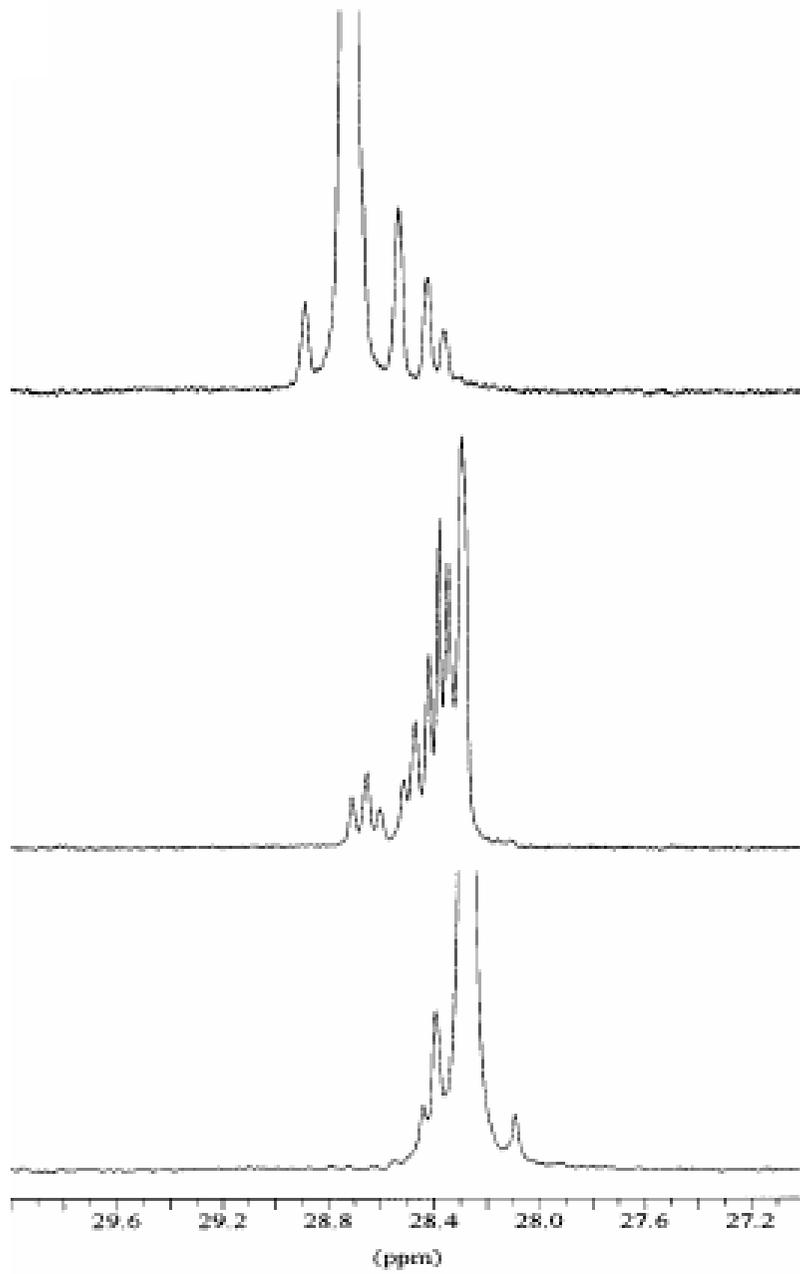
# NMR Polipropilene Isotattico



# Spettri $^{13}\text{C}$ -NMR zona del $\text{CH}_3$



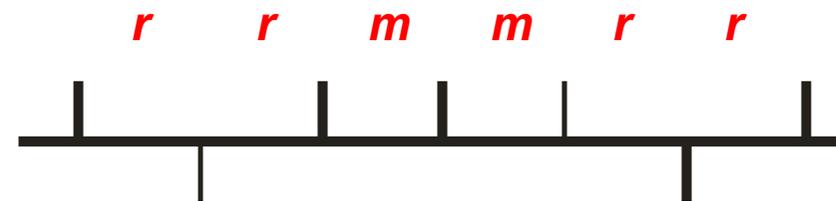
# Spettri $^{13}\text{C}$ -NMR zona del $\text{CH}_2$



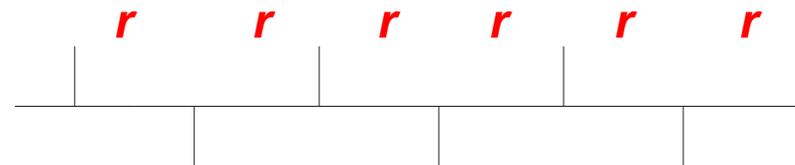
*i*-PP



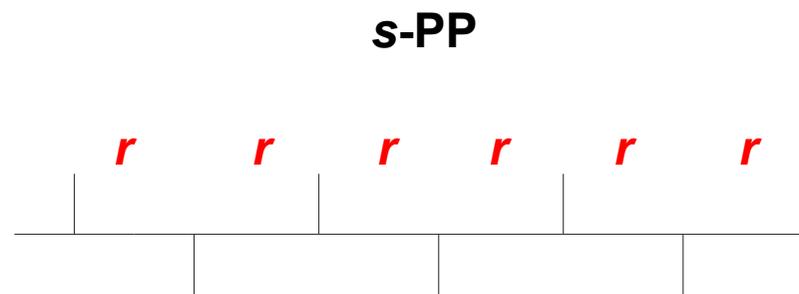
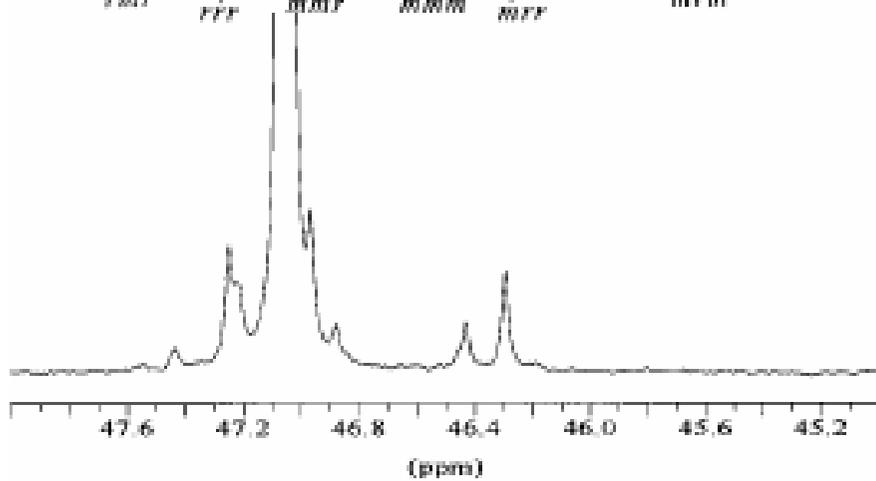
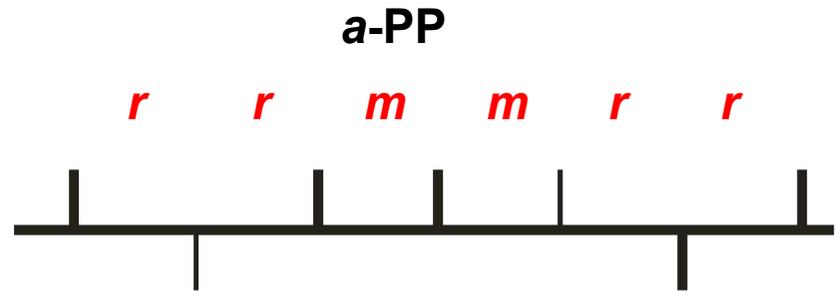
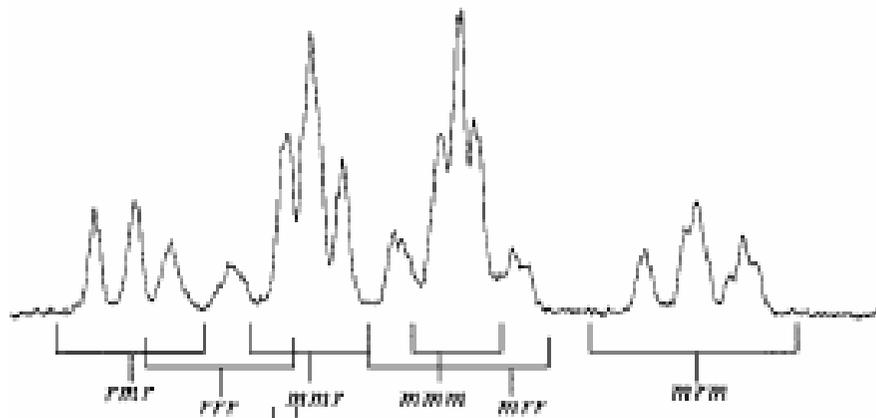
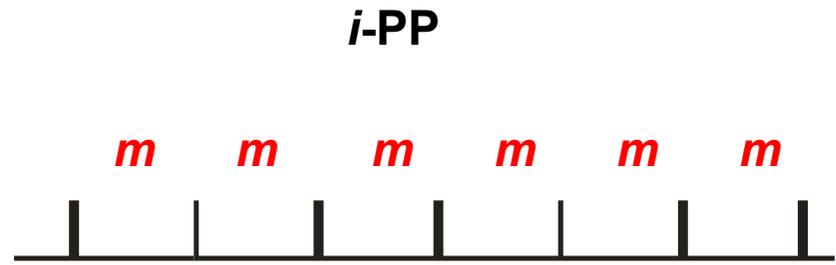
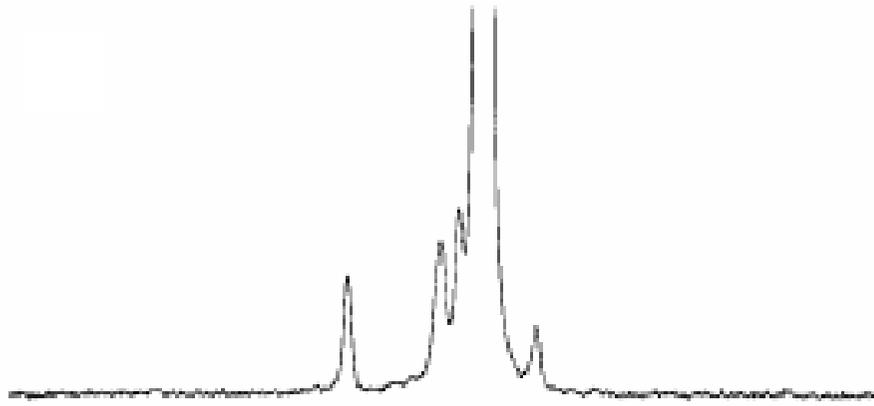
*a*-PP



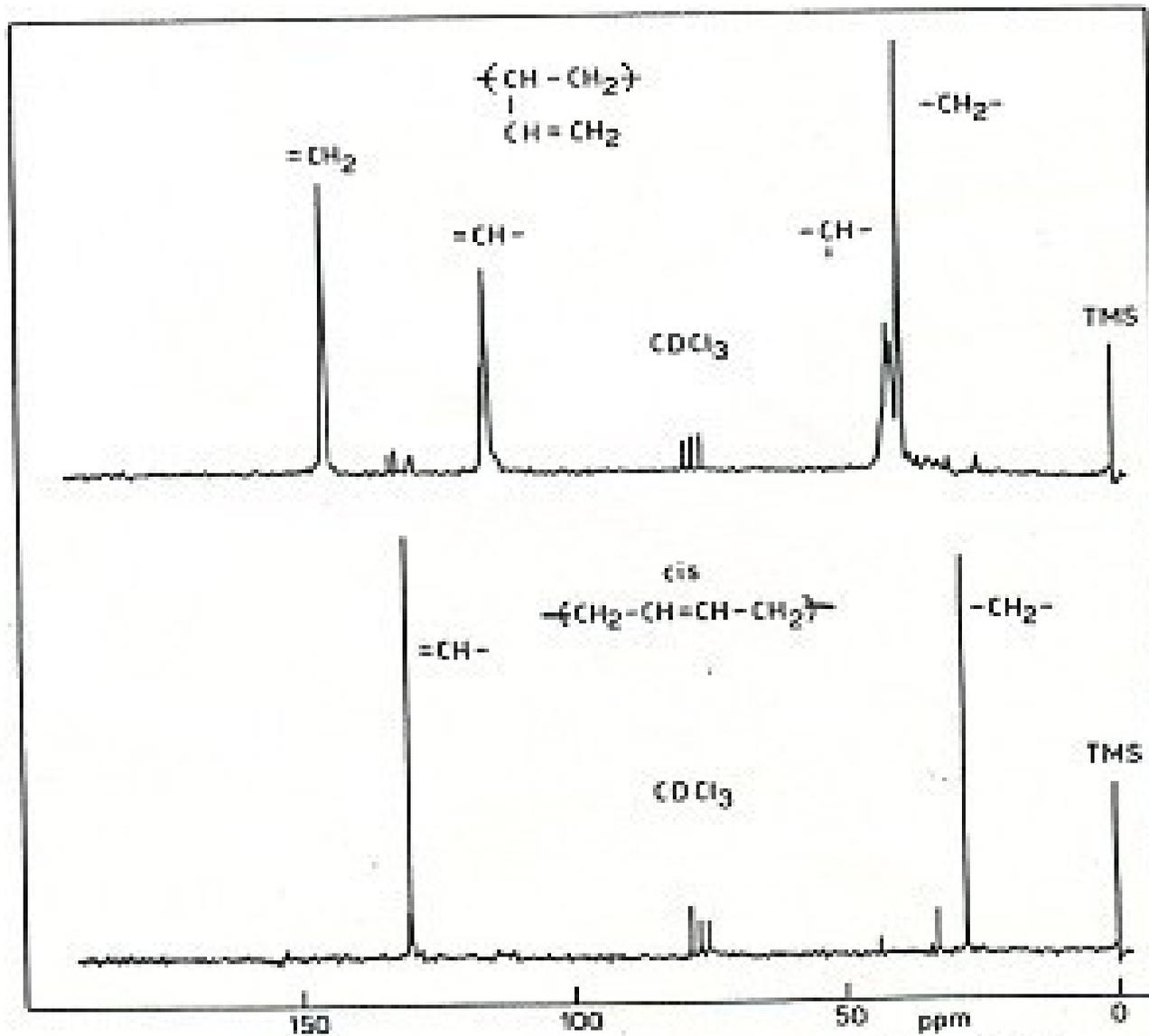
*s*-PP



# Spettri $^{13}\text{C}$ -NMR zona del CH



# Caratterizzazione NMR di omopolimeri



Polibutadiene 1,2

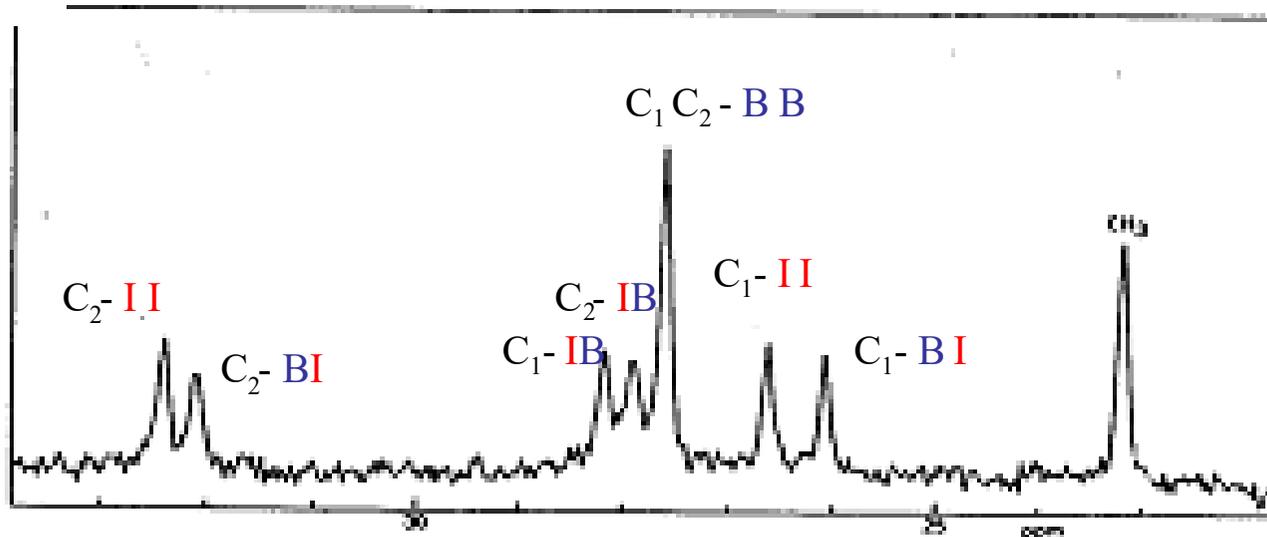
(4 C non-equivalenti)

Polibutadiene 1,4 cis

(2 C non-equivalenti)

Fig. 2.3.10 — Confronto fra gli spettri  $^{13}\text{C}$ -RMN del polibutadiene vinilico e cis 1,4.

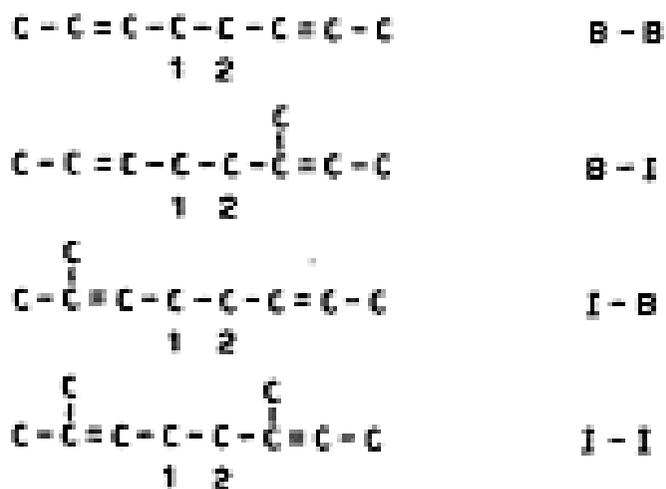
# Caratterizzazione NMR di copolimeri



Zona dei carboni saturi

Fig. 2.3.11. — Spettro  $^{13}\text{C}$ -RMN del copolimero butadiene-isoprene regione dei C saturi.

Tab. 2.3.3. - Diadi testa-coda del copolimero butadiene-isoprene.



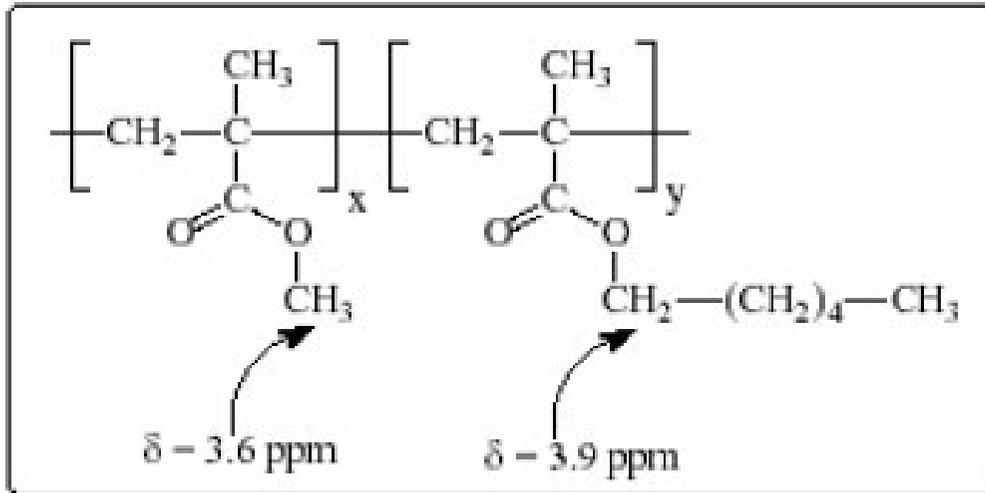
Picchi prevalenti per  
differenti Copolimeri

A blocchi      BB    ed    II

Alternati      BI    ed    IB

# Caratterizzazione NMR di copolimeri

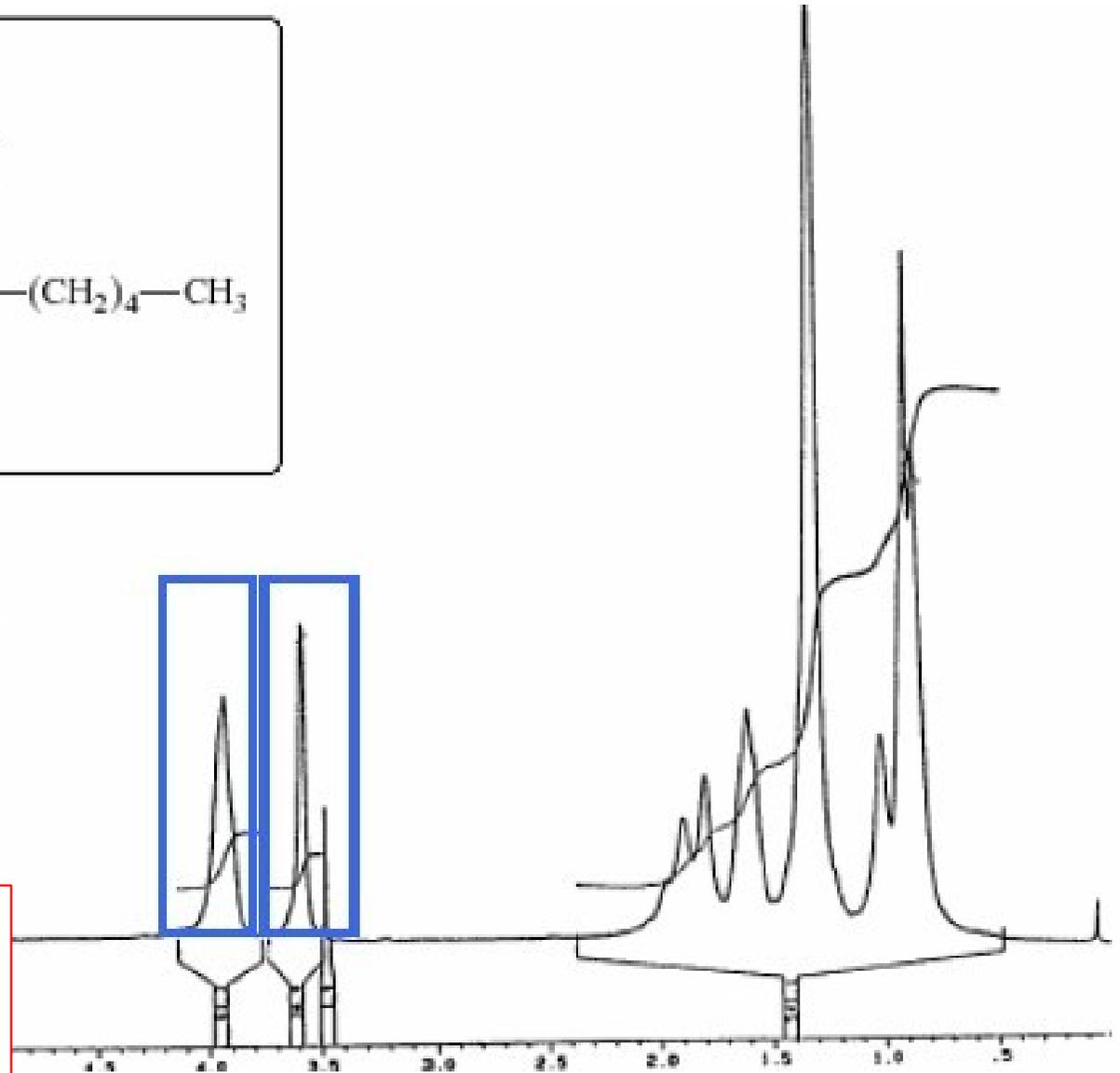
## Determinazione quantitativa della composizione media



MMA-co-HMA

metilmetacrilato-CO-esilmetacrilato

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



# NMR Polietilene (LDPE): ramificazioni

