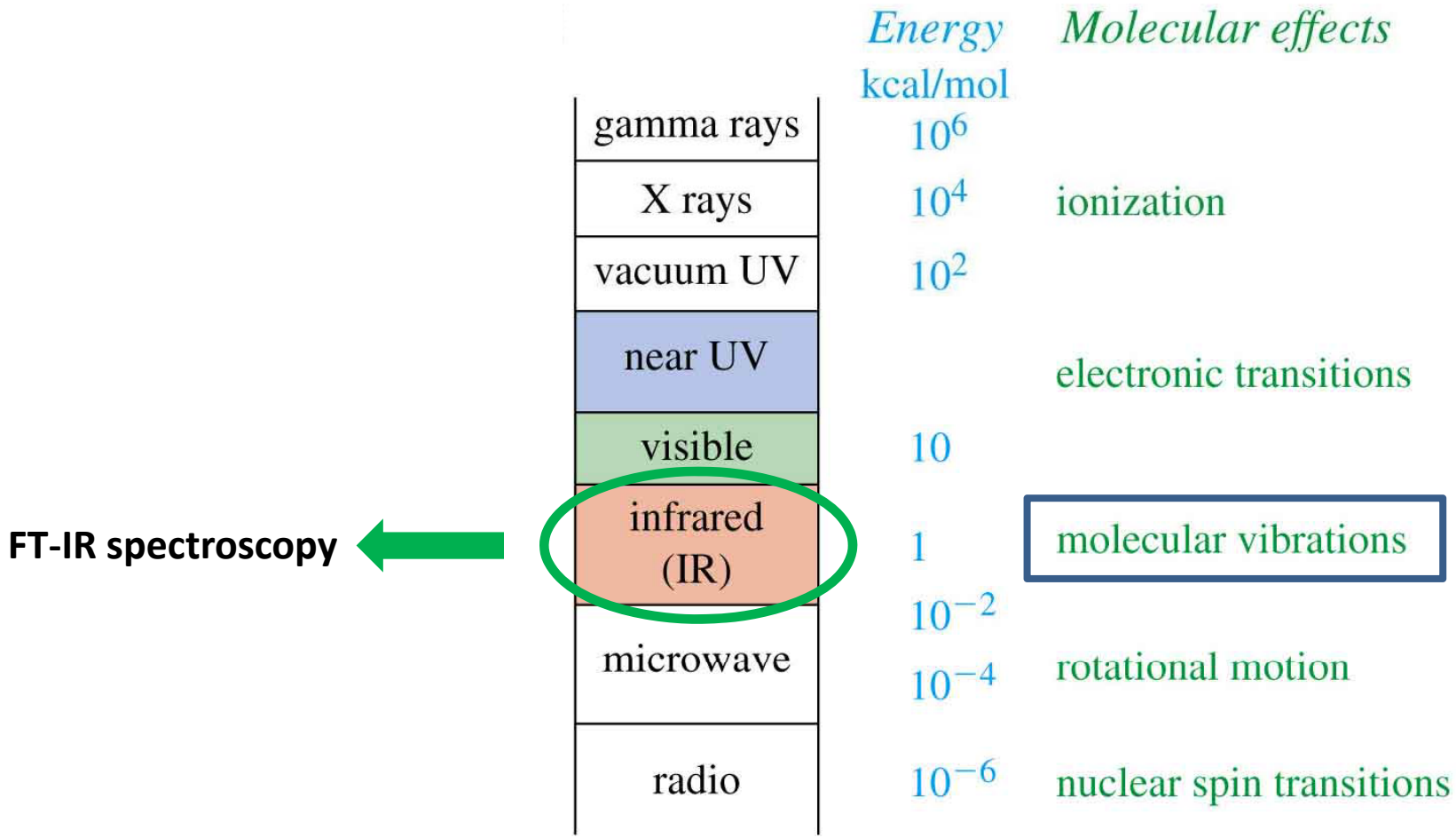
Spettroscopia infrarossa

tecnica principe per il riconoscimento di polimeri

Importante anche in fase di riciclo!


Energy
kcal/mol
Molecular effects
gamma rays
10^6
X rays
10^4
ionization
vacuum UV
10^2
near UV
electronic transitions
visible
10
infrared
(IR)
1
molecular vibrations
10^{-2}
microwave
10^{-4}
rotational motion
radio
10^{-6}
nuclear spin transitions
FT-IR spectroscopy

Classical vibrational model:

Hooke's law $F = -k \cdot y$

Energy: force*distance: $dE = -Fdy$ $E = \frac{1}{2}ky^2$

Clasisical vibrational frequency:

$$\nu_{classical} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

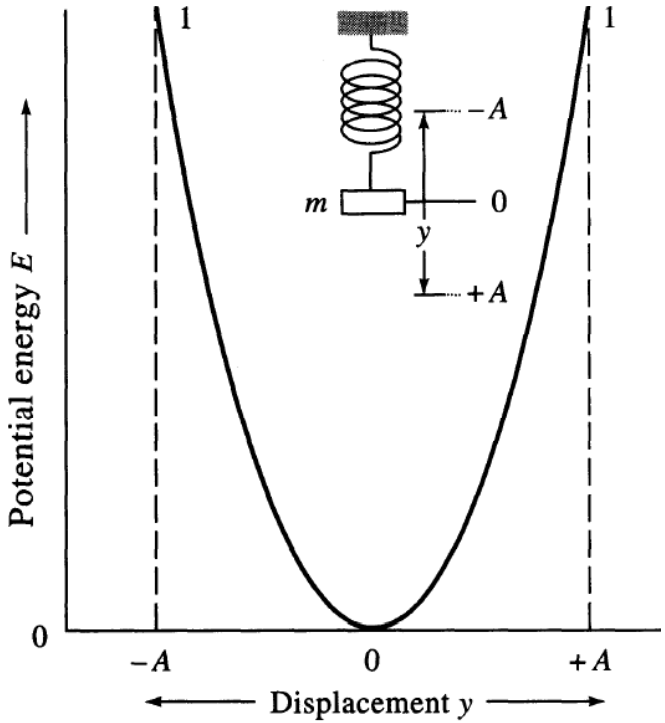
Quantum mechanics: energy is <u>quantized</u>

$$E = \left(\nu + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = \left(\nu + \frac{1}{2}\right)h \cdot \nu_{classical}$$

In any case, $\Delta E = h\nu_{classical}$

- **Mass - ATOMS**
- **Force constant - BOND**
- **Geometry**

Harmonic oscillator



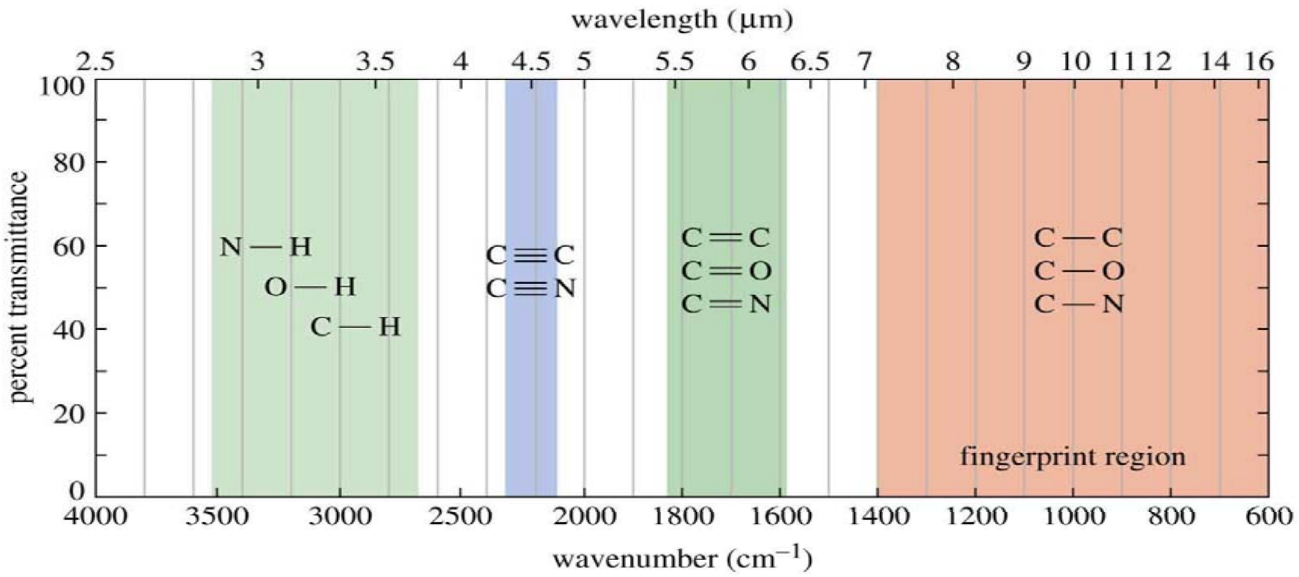
Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm^{-1})
Frequency dependence on atomic masses		
C—H	100 (420)	3000
C—D (heavier atoms)	100 (420)	2100 ($\bar{\nu}$ decreases)
C—C	83 (350)	1200
Frequency dependence on bond energies		
C—C	83 (350)	1200
C=C (stronger bond)	146 (611)	1660 ($\bar{\nu}$ increases)
C≡C	200 (840)	2200

➢**Mass**

➢**Force constant**

$$\nu_{classical} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Reduced mass = $\frac{m_1 \cdot m_2}{m_1 + m_2}$



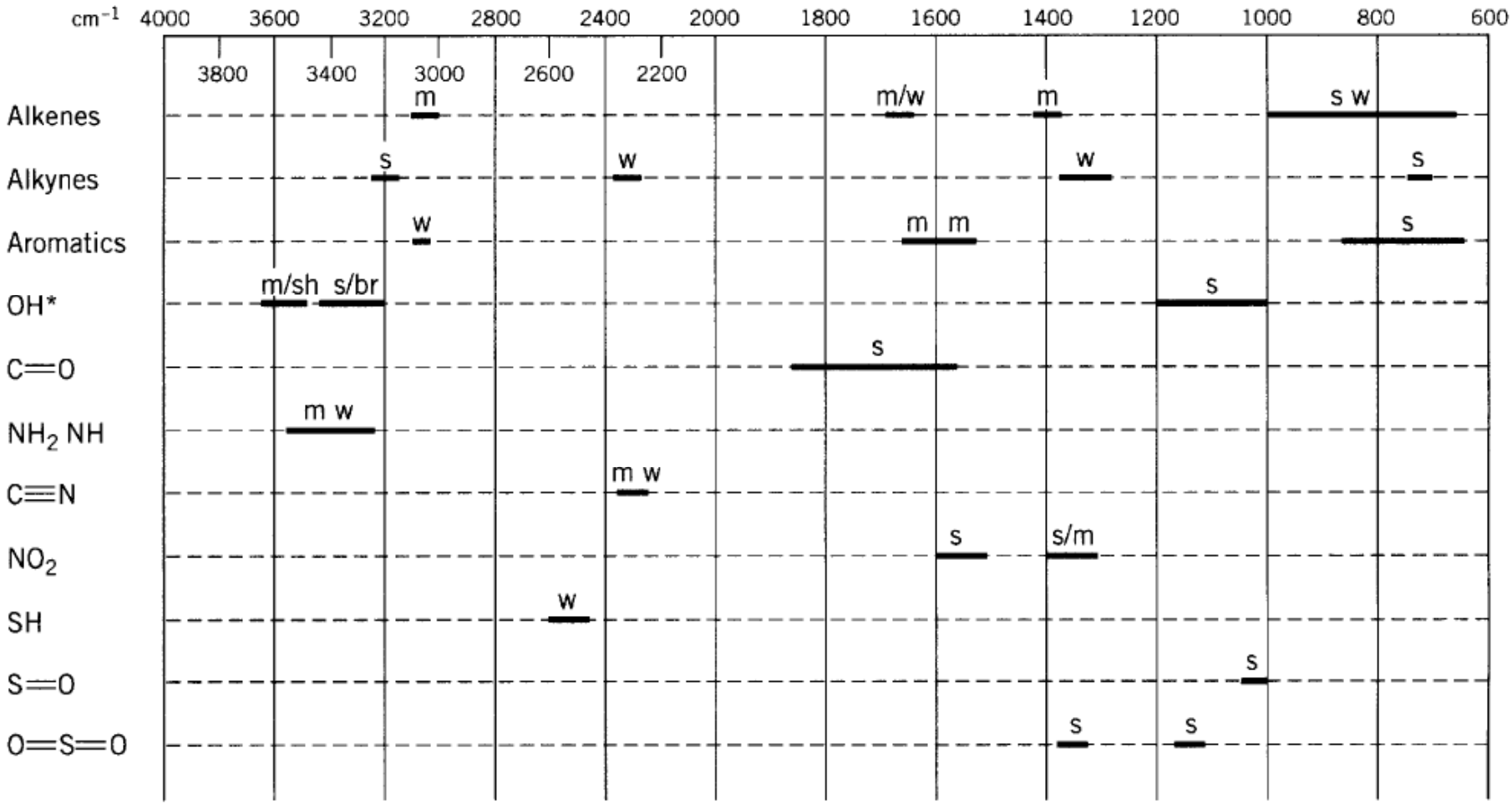
Group frequency region
Identify functional groups

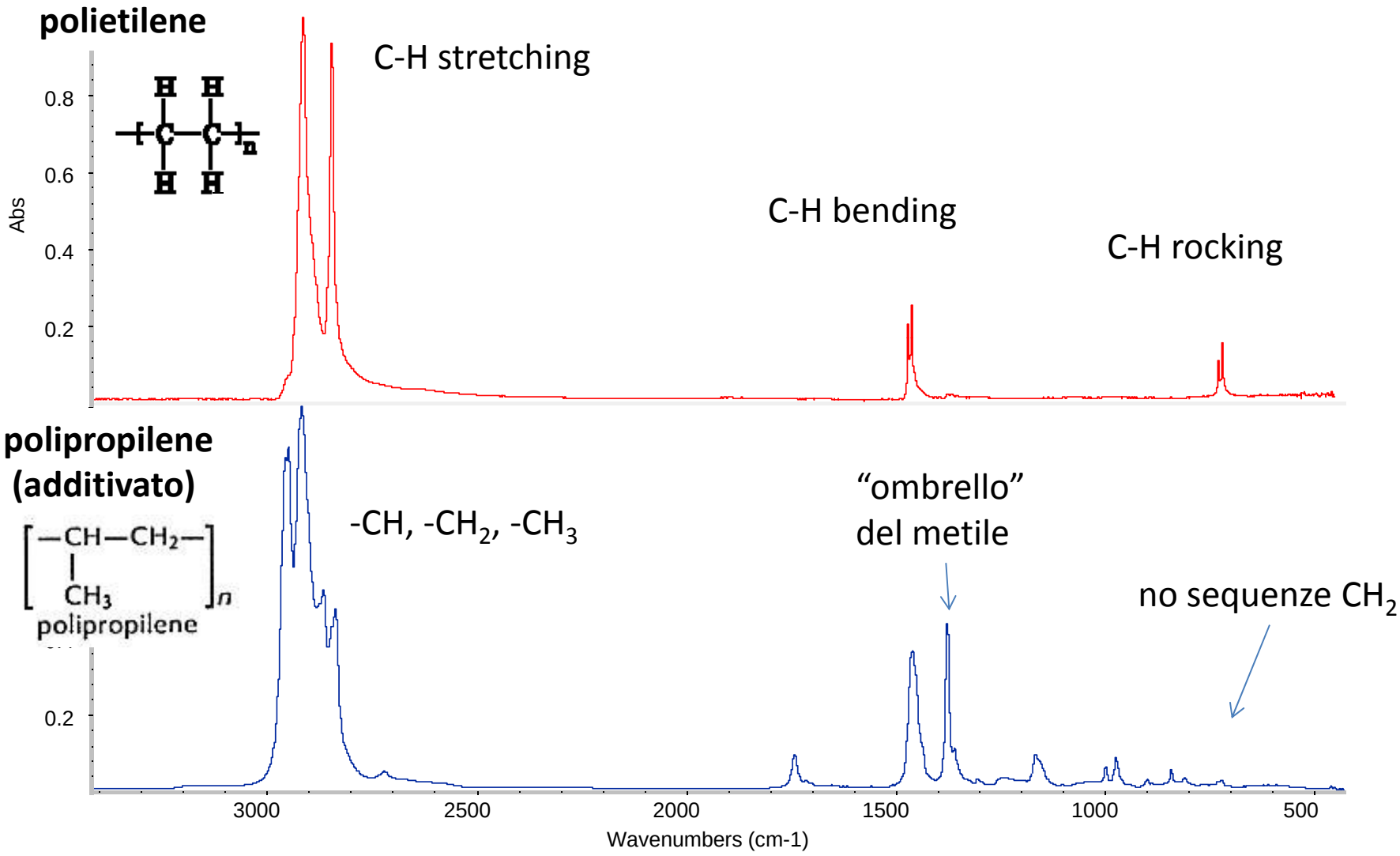
Fingerprint region
Compare with known spectra

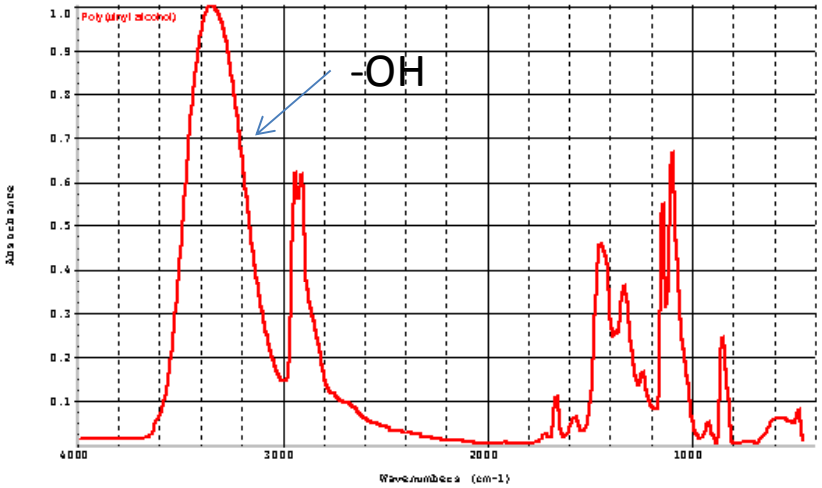
➡ No two molecules will give exactly the same IR spectrum (except enantiomers)

Qualitative analysis

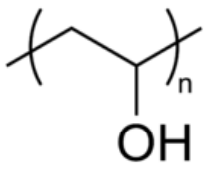
- spectra superimposition is evidence of identity
- recognition of specific chemical groups

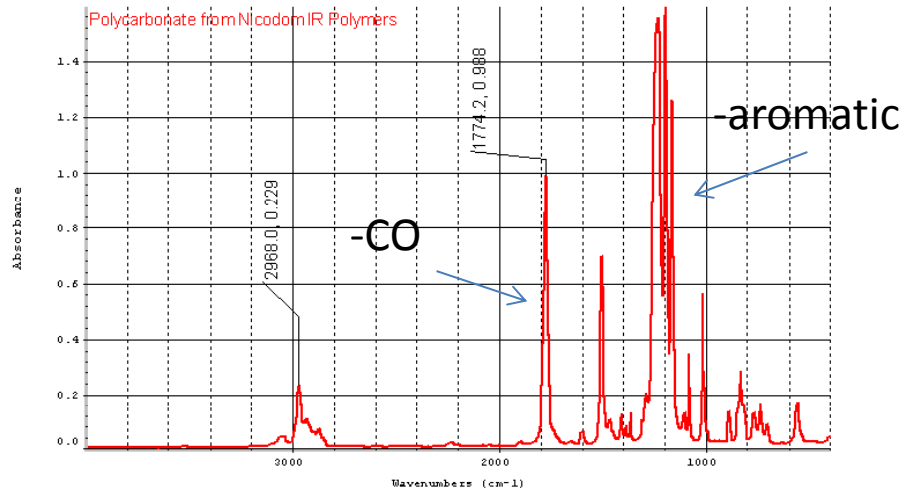

cm⁻¹
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Alkenes
Alkynes
Aromatics
OH*
C=O
NH2 NH
C≡N
NO2
SH
S=O
O=S=O
m
s
w
m/w
m
s w
w
s
m m
s
m/sh s/br
s
s
m w
m w
s
s/m
w
s
s
s


polietilene
C-H stretching
C-H bending
C-H rocking
Abs
0.8
0.6
0.4
0.2
polipropilene
(additivato)
-CH, -CH2, -CH3
“ombrello”
del metile
no sequenze CH2
polipropilene
0.2
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

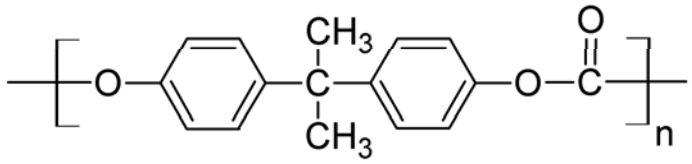

-OH
Absorbance
Wavenumbers (cm-1)

PVA


n
OH


Polycarbonate from Nicodom IR Polymers
1774.2, 0.988
2968.0, 0.229
-aromatic
-CO
Absorbance
Wavenumbers (cm-1)

PC


O
CH3
C
CH3
O
O
C
n