



# University of Zagreb Faculty of Chemical Engineering and Technology

# Structure and properties of polymer materials

seminars

Zagreb, October 2021

Fundamental properties of particles:

- mass (interaction with gravitational field)
- charge (interaction with electric field)
- spin (interaction with magnetic field)

electrons, protons, neutrons  $\rightarrow$  spin = +1/2 or -1/2



Particle with a net spin can absorb a photon:

$$v = \gamma B$$

v- frequency  $\gamma-$  gyromagnetic ratio (42.58 MHz / T for hydrogen) B- magnetic field

spin pairing for nucleons (just as for electrons):





Nuclei	Unpaired Protons	Unpaired Neutrons	Net Spin	γ (MHz/T)
<sup>1</sup> Н	1	0	1/2	42.58
<sup>2</sup> H	1	1	1	6.54
<sup>31</sup> P	1	0	1/2	17.25
<sup>23</sup> Na	1	2	3/2	11.27
<sup>14</sup> N	1	1	1	3.08
<sup>13</sup> C	0	1	1/2	10.71
<sup>19</sup> F	1	0	1/2	40.08

nuclei have to be naturally abundant to make the signal stronger!

spin of a proton – imagined as a magnetic moment vector:

aligning of spins with the external magnetic field:



aligning is possible only if the movement of the particles is allowed NMR is used primarily in solutions – deuterated solvents are used solid state NMR is possible – *complicated physics* 

Continuous wave NMR – the simplest technique

Constant energy Constant magnetic field energy energy energy hν, hν ð Ð absorbance magnetic field magnetic field absorbance magnetic field

Chemical shift – variation in local magnetic fields

Shielding – electrons circulating around the nucleus will generally produce magnetic field that will oppose the applied external one – the nucleus will feel a slightly lower field

$$B=B_0\left(1-\sigma\right)$$

**Deshielding** – circulation of  $\pi$ -electrons will generally produce magnetic field aligned with the applied external one – the nucleus will feel a slightly higher field

Almost every nucleus feels a different magnetic field Almost every nucleus absorbs at a slightly different resonance frequency vThe nuclei are easily distinguished?

The absorbance (signal) is proportional to the number of absorbing nuclei

Chemical shift:  $\delta = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6 \text{ [ppm]}$ 

Spin-spin coupling

Same chemical shift – equivalent nuclei

Different chemical shift – nonequivalent nuclei

Physically close nuclei (up to 3 bond lengths) affect each other by spin-spin coupling

The effect is visible on nonequivalent nuclei





 $\delta_{\scriptscriptstyle \mathsf{B}}$ 

 $\delta_{\text{A}}$ 

Hardware – very very simplified



https://www.cis.rit.edu/htbooks/nmr/inside.htm

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https://commons.wikimedia.org/wiki/File:NMR\_Bruker\_Avance\_II\_700.jpg

#### Nuclear magnetic resonance – Polymer characterization – Copolymer composition



F. Bovey, High Resolution NMR of Macromolecules, Academic Press, London, 1972.

## Nuclear magnetic resonance – Polymer characterization – Copolymer composition



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#### Nuclear magnetic resonance – Polymer characterization – Copolymer composition

%(St) = A(St) / [A(St) + A(H-Butad)]



**Figure 1.** <sup>1</sup>H NMR spectrum of styrene hydrogenated-butadiene copolymer.

# Nuclear magnetic resonance – Polymer characterization – Copolymer Composition



A characteristic <sup>1</sup>H NMR spectrum of poly(methylmethacrylate-*co*-dodecyl-methacrylate-*co*-octadecylmethacrylate) terpolymer

A(DDMA + ODMA) = Area(g) / 2

#### Nuclear magnetic resonance – Polymer characterization – Tacticity



Nuclear magnetic resonance – Polymer characterization – Tacticity

# Stereoisomerism and probability

2 adjacent monomers :

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

	Table 6.3 Configurational Sequences.					
Туре	Designation	Projection	Bernoullian Probability			
Diad	meso, m	-1+1-	Pm			
	racemic, r	<del>_</del> ++ <u>+</u>	(1 - P <sub>m</sub> )			
	isotactic, mm	<del>-1+1+1</del>	Pm <sup>2</sup>			
Triad	heterotactic, mr	<u>++++</u>	2 P <sub>m</sub> (1 - P <sub>m</sub> )			
	syndiotactic, rr	<u></u>	(1 - P <sub>m</sub> ) <sup>2</sup>			
	mmm	$\frac{1}{1}$	Pm <sup>3</sup>			
	mmr	╂┅┠┅┠	2 Pm <sup>2</sup> (1 - Pm)			
Tetrad	mr	$\frac{1}{1}$	P <sub>m</sub> (1 - P <sub>m</sub> ) <sup>2</sup>			
	mrm	<u>_</u> ++++++++	P <sub>m</sub> <sup>2</sup> (1 - P <sub>m</sub> )			
	m	╶ <u>╁╷╀╷┧╷╁</u>	$2 P_m (1 - P_m)^2$			
	m	<del>_<u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u></del>	(1 - P <sub>m</sub> ) <sup>3</sup>			

#### Nuclear magnetic resonance – Polymer characterization – Tacticity



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# Nuclear magnetic resonance – Polymer characterization – HEAD-to-TAIL isomerism

Polyvinylidine fluoride (PVDF) in <sup>19</sup>F NMR

There is no tacticity (no chiral C-atoms)

There are sequence isomers only (head-to-tail isomerism)

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** 



# Nuclear magnetic resonance – Polymer characterization – *cis-trans* isomerism

Polybutadiene (PBd) in <sup>13</sup>C NMR (in <sup>1</sup>H NMR this effect is not visible) Three possible arrangements: 1,4-*cis*; 1,4-*trans*; 1,2



<sup>13</sup>C nmr spectrum of polybutadiene containing 34% trans-1,4-; 24% cis-1,4- and 42% 1,2- placements.

(Vinilydene chloride)-co-isobutylene (VDC-co-IB) in <sup>1</sup>H NMR



Styrene-*co*-(methyl methacrylate) (ST-co-MMA) in <sup>1</sup>H NMR <sup>1</sup>H NMR data for the calculation of copolymerization reactivity ratios

Terminal model (Mayo & Lewis)

$$-\frac{dM_1}{dt} = k_{11}M_1R_{(1)} + k_{21}M_1R_{(2)}$$

$$-\frac{dM_2}{dt} = k_{12}M_2R_{(1)} + k_{22}M_2R_{(2)}$$

Monomer disappearance

$$\frac{dM_1}{dM_2} = \frac{k_{11}M_1R_{(1)} + k_{21}M_1R_{(2)}}{k_{12}M_2R_{(1)} + k_{22}M_2R_{(2)}}$$

Instantaneous copolymer composition

 $k_{21}M_1R_{(2)} = k_{12}M_2R_{(1)}$ 

Steady state assumption Rates of conversion of one radical type into another are equal

 $\frac{dM_1}{dM_2} = \frac{(r_1M_1 + M_2)M_1}{(M_1 + r_2M_2)M_2}$ 

After replacement:  $r_1 = \frac{k_1}{k}$ 

$$r_{11} = r_2 = \frac{k_{22}}{k_{21}}$$

COPOLYMERIZATION REACTIVITY RATIOS

Styrene-*co*-(methyl methacrylate) (ST-co-MMA) in <sup>1</sup>H NMR <sup>1</sup>H NMR data for the calculation of copolymerization reactivity ratios



Styrene-*co*-(methyl methacrylate) (ST-co-MMA) in <sup>1</sup>H NMR <sup>1</sup>H NMR data for the calculation of copolymerization reactivity ratios



Nuclear magnetic resonance – Polymer characterization – Branching in PE

Two forms of branching in polyethylene:

1) Short chain branching

a) copolymerization with another olefin (*i.e.* butene or octene)

b) backbiting in LDPE

low degree of solid state crystallinity

2) Long chain branching

c) chain transfer to polymer in LDPE decreasing solid state crystallinity (if significant) affecting melt properties as well

Detected by <sup>13</sup>C-NMR:

The chemical shift:

a) depends on the branch length for branches up to six carbons long

b) does not depend on length for longer branches.

# Nuclear magnetic resonance – Polymer characterization – Branching in PE

Classification of carbon atoms:

- a) methylene carbon bonded to two other C atoms
- b) methine carbon bonded to three other C atoms
- c)  $\alpha$ -carbon next to a methine carbon
- d)  $\beta$ -carbon next to an  $\alpha$ -carbon
- e)  $\gamma$ -carbon next to a  $\beta$ -carbon
- f) 2C second carbon atom from an end of a short branch



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