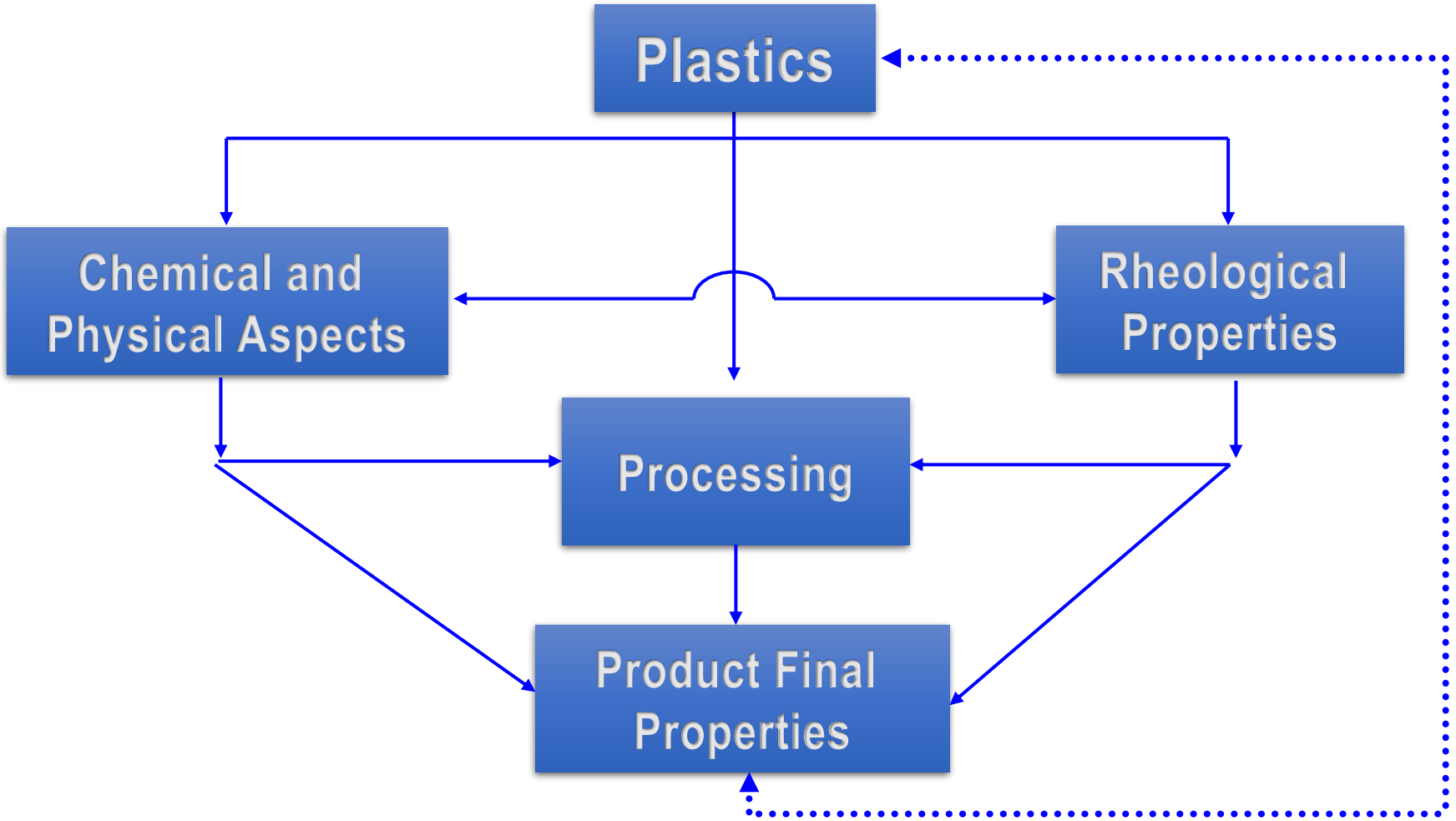
Tecnológico de Monterrey

Chemical and Physical Nature of Polymers

Dr. Jaime Bonilla Ríos

Conceptual map



Activity 1

- Go to the following site:

http://pslc.ws/macrog/level1.htm

and read at least the information in the section called “Pit Lane AutoParts” and the “Helpful Harry´s Hardware Heaven”.

Physical and Chemical Aspects

- Definitions
- Classification
- Effect of chemical bonds and their reactions on:
  - Spatial orientation
  - Glass transition temperature
  - Molecular weight distribution (MWD)
  - Effect of MWD on some rheological properties

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Chemical and Physical Nature of Polymers

Definitions and Classification

Dr. Jaime Bonilla Ríos

Definitions

Polymers are "giant" molecules of molecular weight which range varies from 10,000 to 10,000,000 gr/mol *[~0.11mm]*

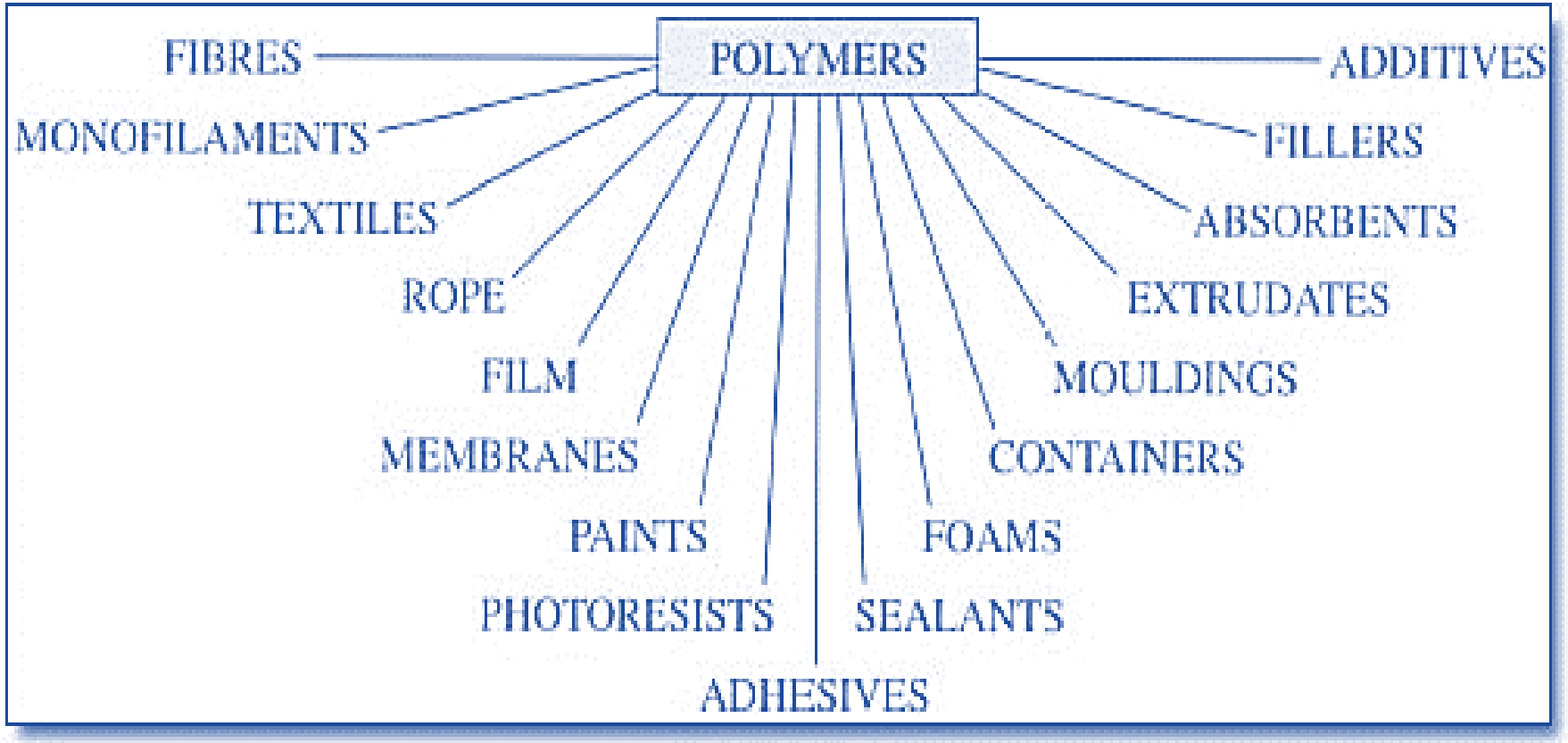
Some of them have an origin in nature (cellulose, silk, rubber, DNA, etc.) while others are produced by people (polyester, nylon, polystyrene, polypropylene polycarbonate, etc.)

Activity 2

Given that the length of the carbon to carbon bond is 1.54 Angstroms…

- Calculate the length of “giant” polyethylene molecules whose molecular weight is 10,000 and 10,000,000.
- Compare those sizes with that of the water.

Words related…



Polymer classification

- Based on their use
- Based on their thermal behavior
- Based on their crystallinity
- Based on their chemical origin

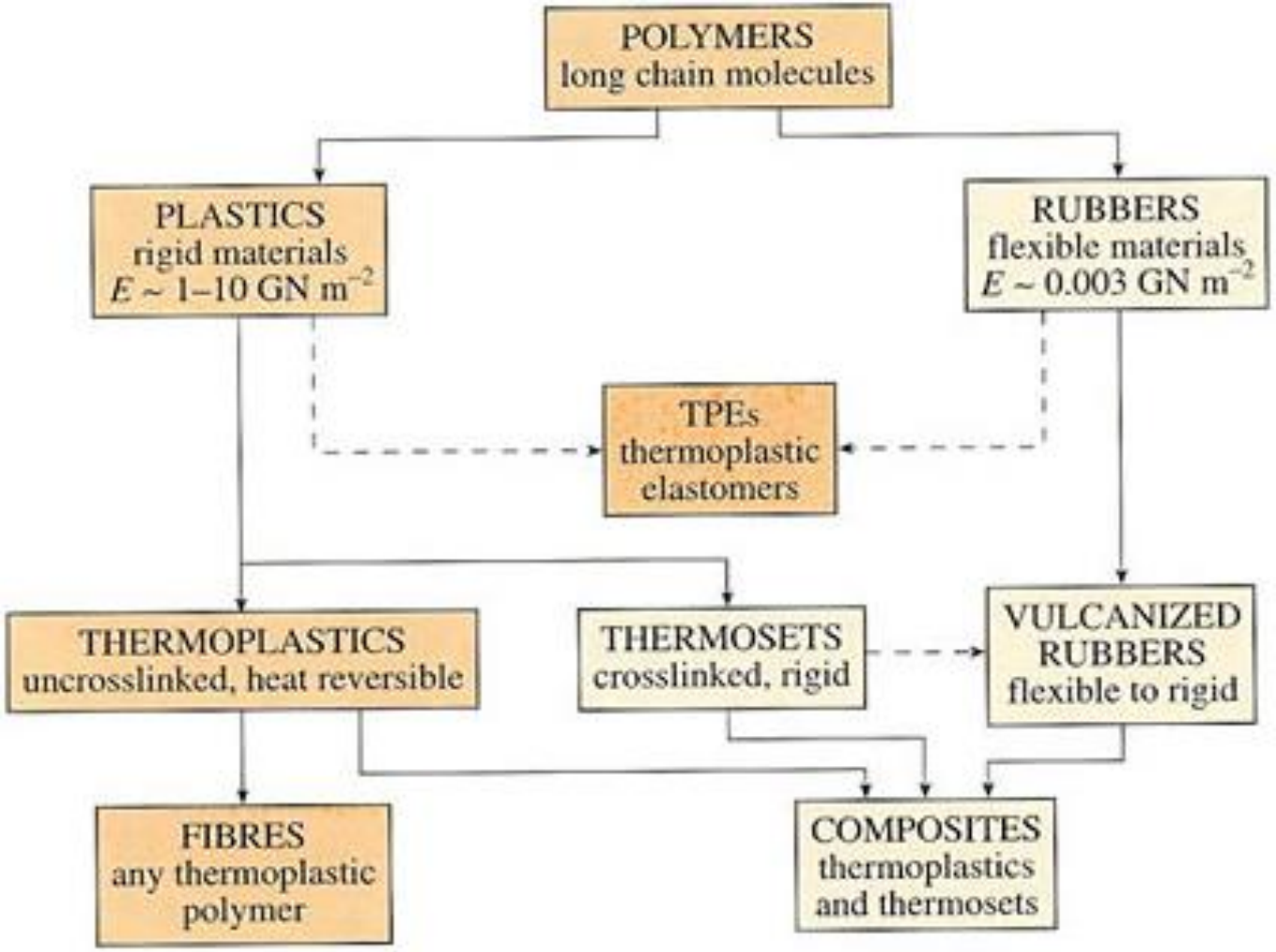
Based on their uses

- **Elastomers**: have the particular elasticity, characteristic of the rubber (polymer must be above Tg, low degree of crystallinity, lightly cross-linked) (vulcanized).
- **Fiber**: long and thin, with a string form very resistant across the fiber, have characteristics of wool, cotton and silk.
- **Plastics**: can be modeled by extrusion to form pipes and sheets, transform in surface painting or modeled in differents objects and forms.

Based on their thermal behavior…

- **Thermoplastic:** materials that soft and flow when heat and pressure is applied. Can me re-modulate several times, but…
- **Thermoset:** are materials that react irreversibly, it means that when heat and pressure are applied they cant be modulate again.

Classification



Based on their crystallinity

- **Semi-crystalline**: characterized for having a big percentage of polymer forming crystals. The rest of the polymer is amorphous. The material looks opaque or translucent, due to the crystals that disperse the light.
- **Amorphous**: are formed for randomly packed chains. These materials do not have melting point, instead they have a "soften temperature". This temperature is called glass transition temperature (Tg). Examples: polystyrene y polycarbonate.

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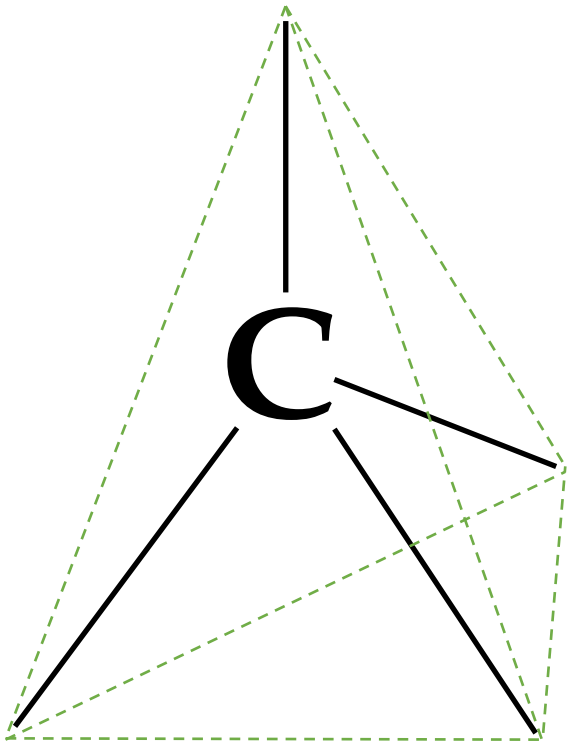
Chemical and Physical Nature of Polymers

Space and orientation

Dr. Jaime Bonilla Ríos

The carbon atom:

The great protagonist in polymer nature.

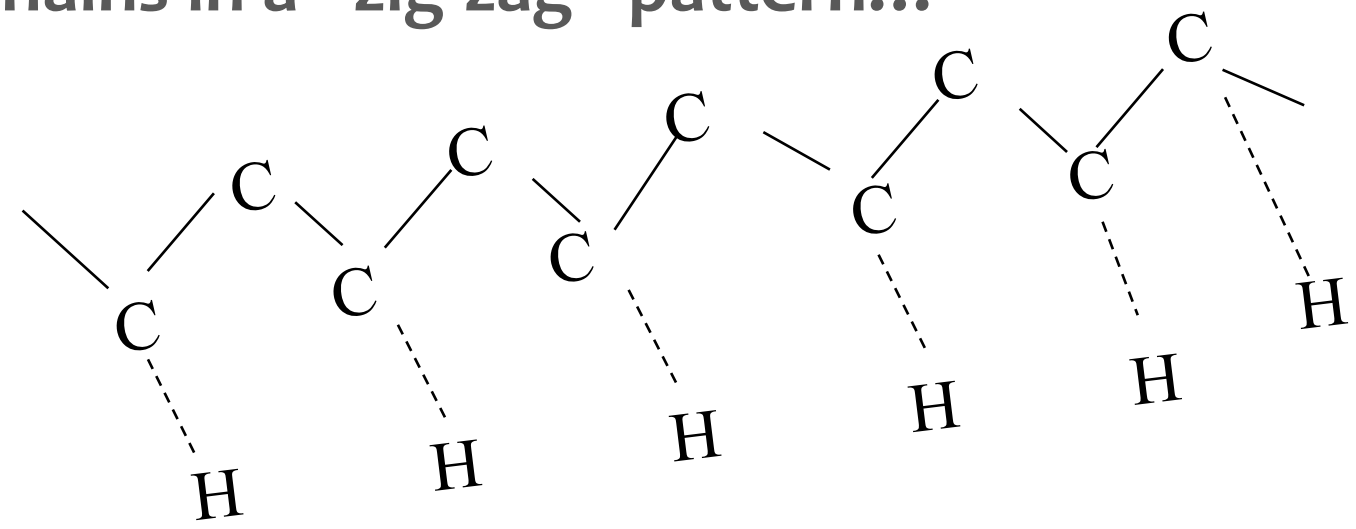


1. It has the ability t combine covalently with up to four atoms simultaneously (single bond; hybridization sp^3)
2. Their bonds are spatially distributed in such way that the angles among them are:_____ degrees
3. When they combine with other Carbon and Hydrogen atoms, they form hydrocarbons which in turn can combine and form polymers

http://es.slideshare.net/nbeatriz/hibridaciones-del-carbono

Effect of the single bond angle on the spatial structure of a polymer

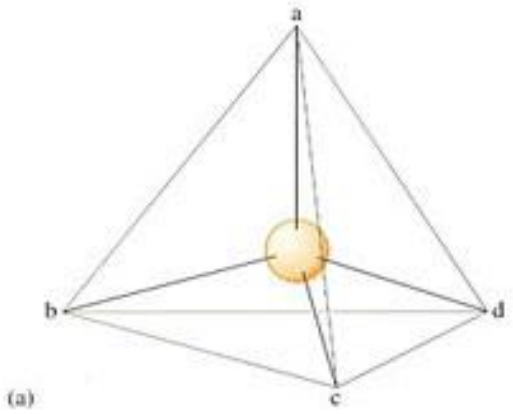
Polymer chains in a "zig-zag" pattern…

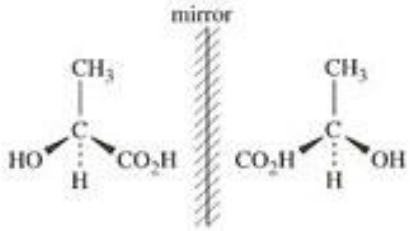


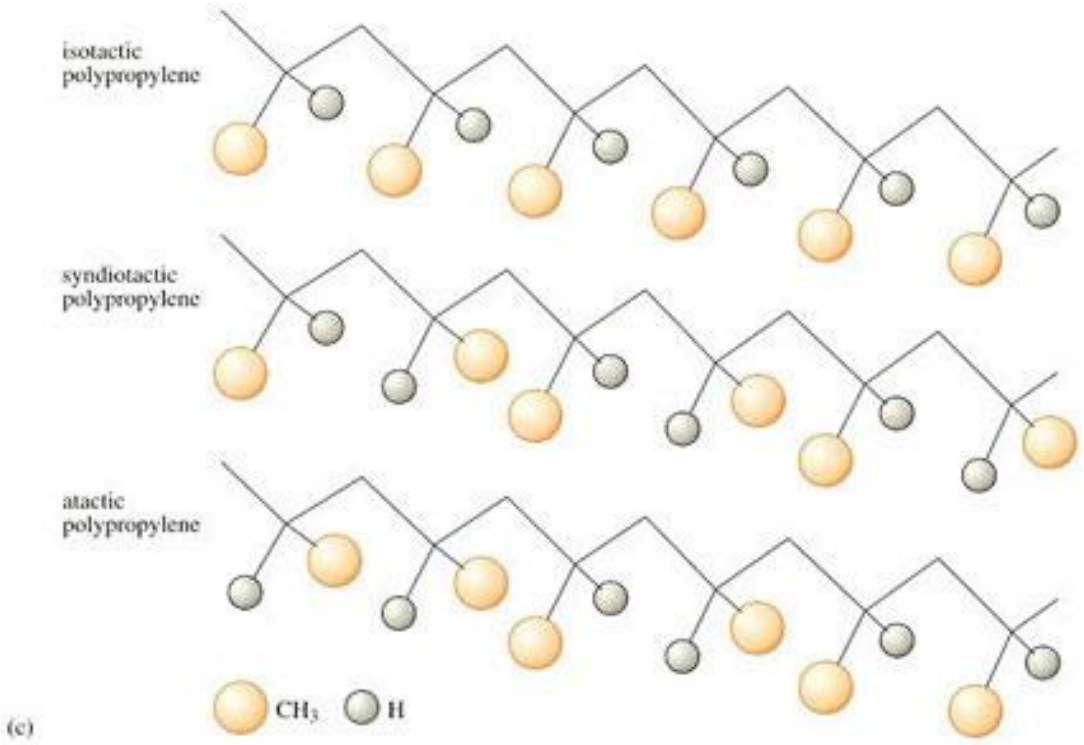
… forming <u>stereo-isomers</u>

Isotactic; Syndiotactic; Atactic

Stereoisomers

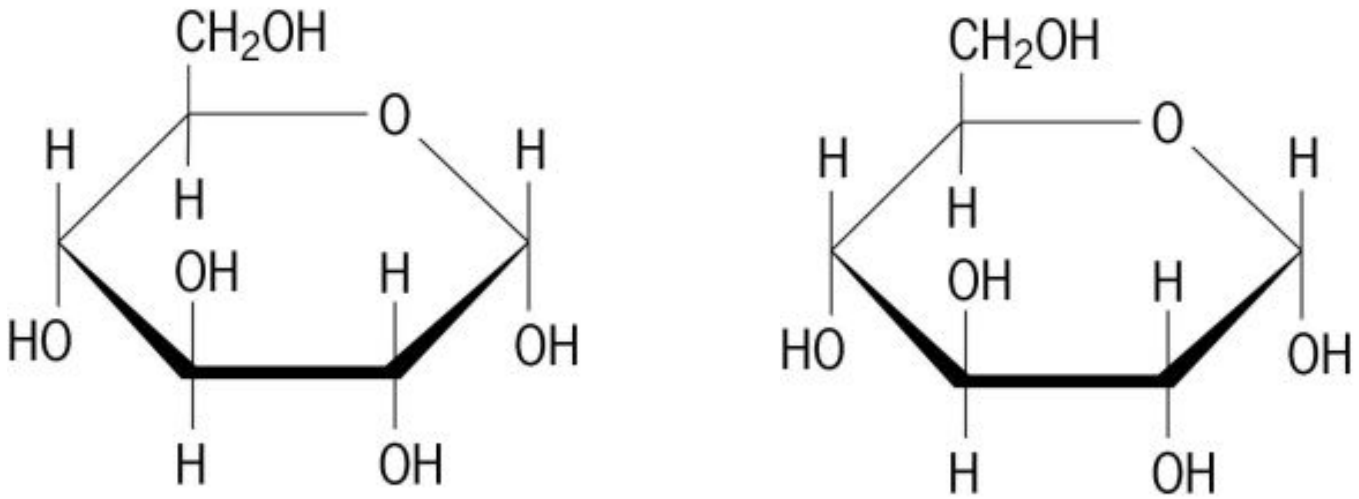






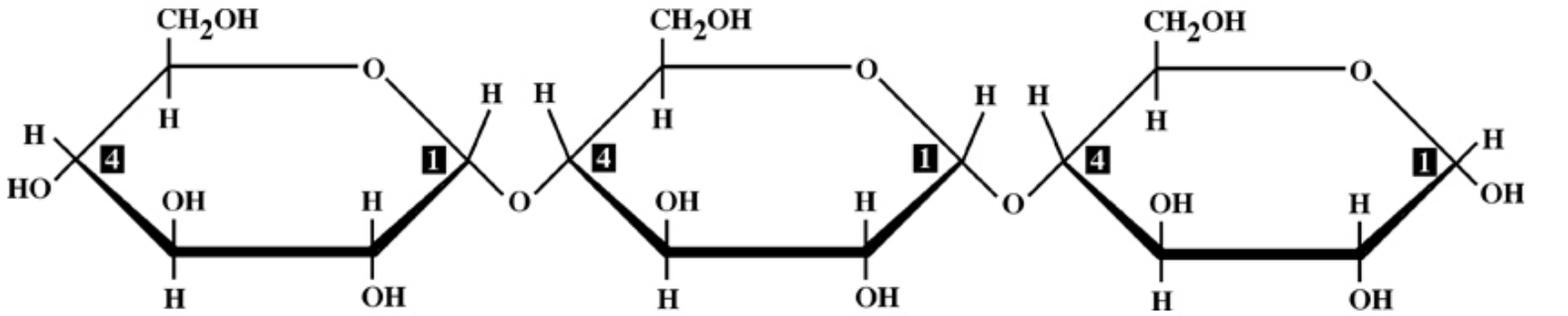
Polysaccharides

Glucose



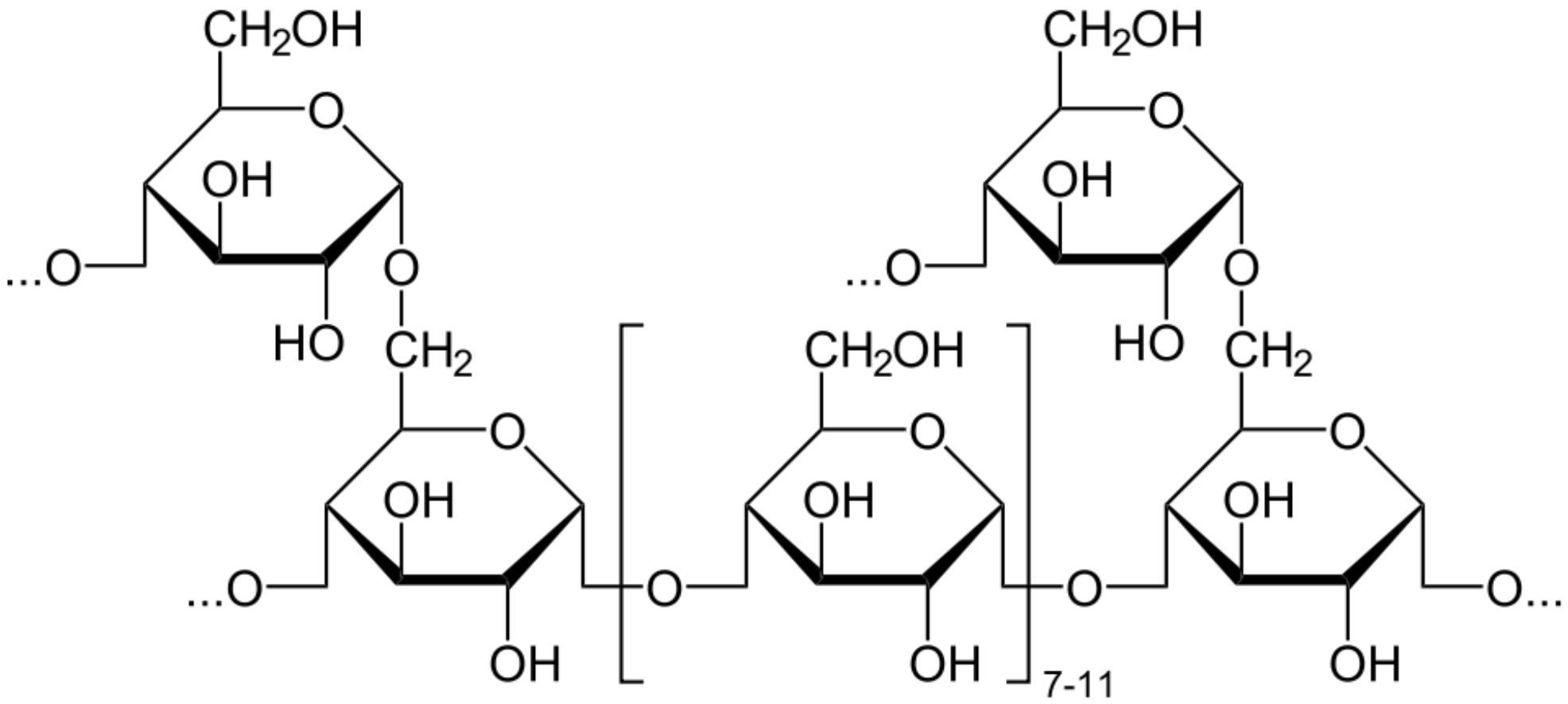
α 1-4 Bonds Between 3 Molecules of Glucose

Starch



© U of M 2005 (J. France)

Glycogen


CH2OH
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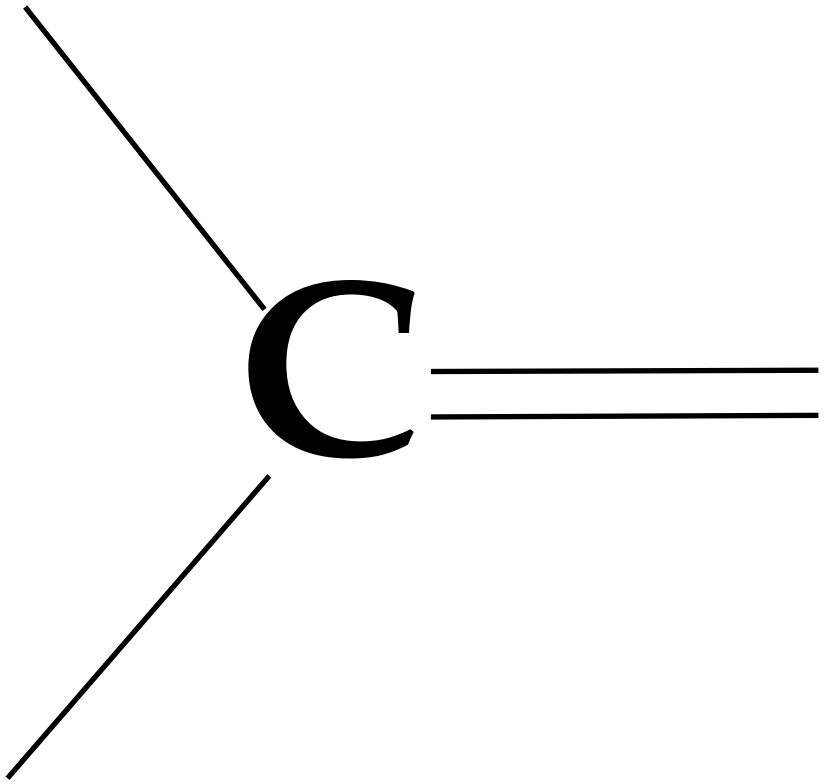
OH

The carbon atom

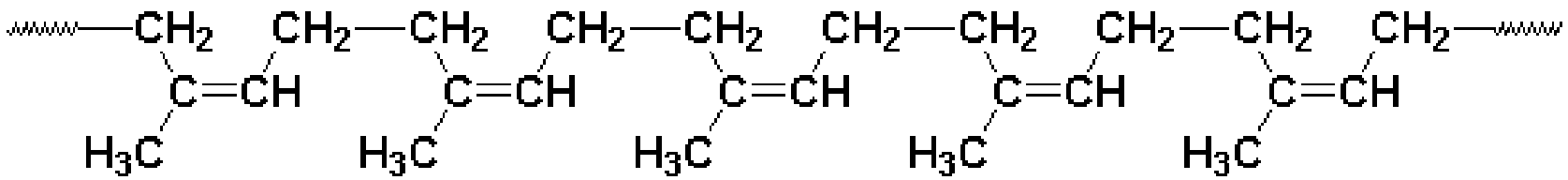
The great protagonist in polymer nature

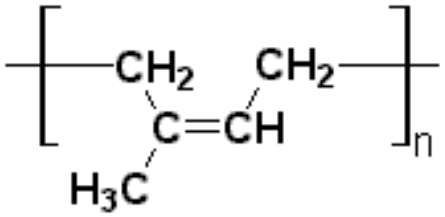


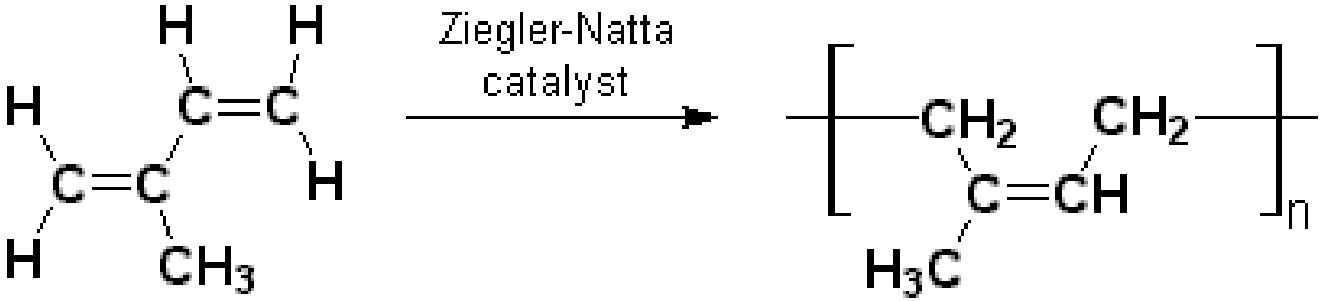
1. It also has the ability combine covalently with thre atoms simultaneously (double bond; hybridization sp^2)
2. Their bonds are spatially distributed in such way that the angles among them are: _____ degrees
3. When they combine with other Carbon and Hydrogen atoms, they form hydrocarbons called alkenes which in turn can combine and form polymers

JBR-20

Poly-isoprene







isoprene

polyisoprene

Activity 3

- Look for the structure of the rubber called polybutadiene and identify if the double bond has any effect on the spatial structure of the polymer…

Activity 4

- Go to the following site

http://pslc.ws/macrog/level2.htm

and read, at least, the information in the section called "Polyispoprene" and the "Nylon"

Quiz

Go to the Blackboard platform/Exams and do the following :

QUIZ 2: CPNP-CQ1

Recommendation:

Read the PDF manuscript: **1-3, butadiene.** You will find it in the Blackboard platform/Course Resources.

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Chemical and Physical Nature of Polymers

Methods of synthesis

Dr. Jaime Bonilla Ríos

Based on their chemical origin…

- Free radical polymerization
- Condensation polymerization
- Polymerization by catalysts (Ziegler-Natta, Metallocenes, etc.)
- Ionic polymerization

Polymerization

- These macromolecules are formed, basically, by the union of the monomers (for example: styrene, propylene). This union is through covalent bonds.
- This chemical process is called “polymerization”:

n Styrene	Polystyrene
(monomer)	(polymer)
E	EEEEEEEEEEEE

Free radical polymerization (1)*

- Characterized by using petrochemical monomers named alkenes (double bonds).
  - One way is to add initiators (peroxides) to produce free radicals to attack the double bond and start de polymerization process.
  - Other way is to increase their temperature until a partial decomposition form free radicals.
  - The polymerization occurs randomly.
- The process produce a lot of chains.
- One of the materials produced in this form is polystyrene.

Free radical polymerization (2)

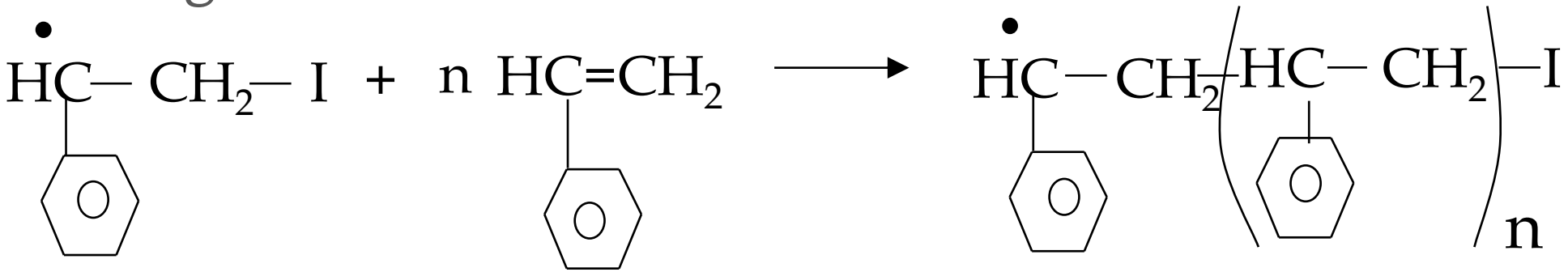
Free radical activation

$$I_2 \longrightarrow 2I\bullet$$

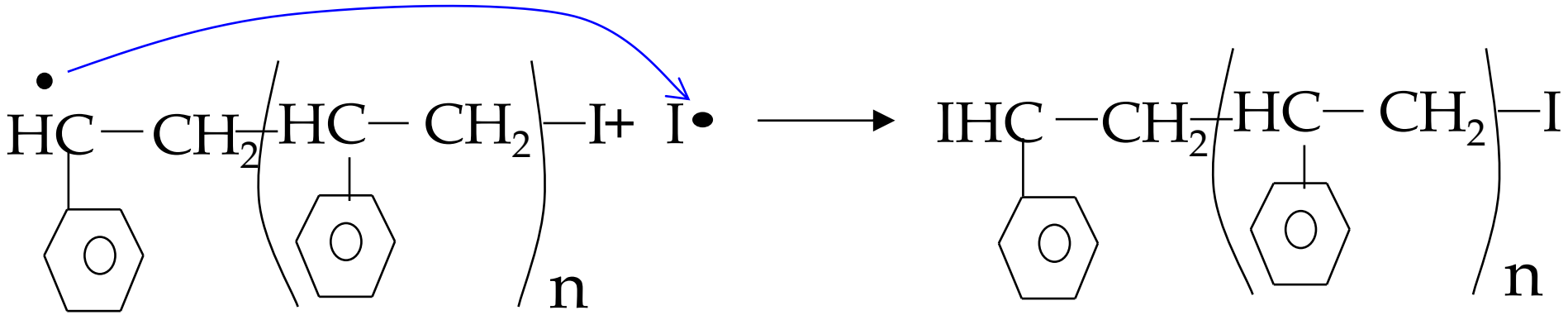
Initiation: the free radical attacks the monomer.

Free radical polymerization (3)

Propagation: the free radical formed on the monomer propagates, attacking more monomers.



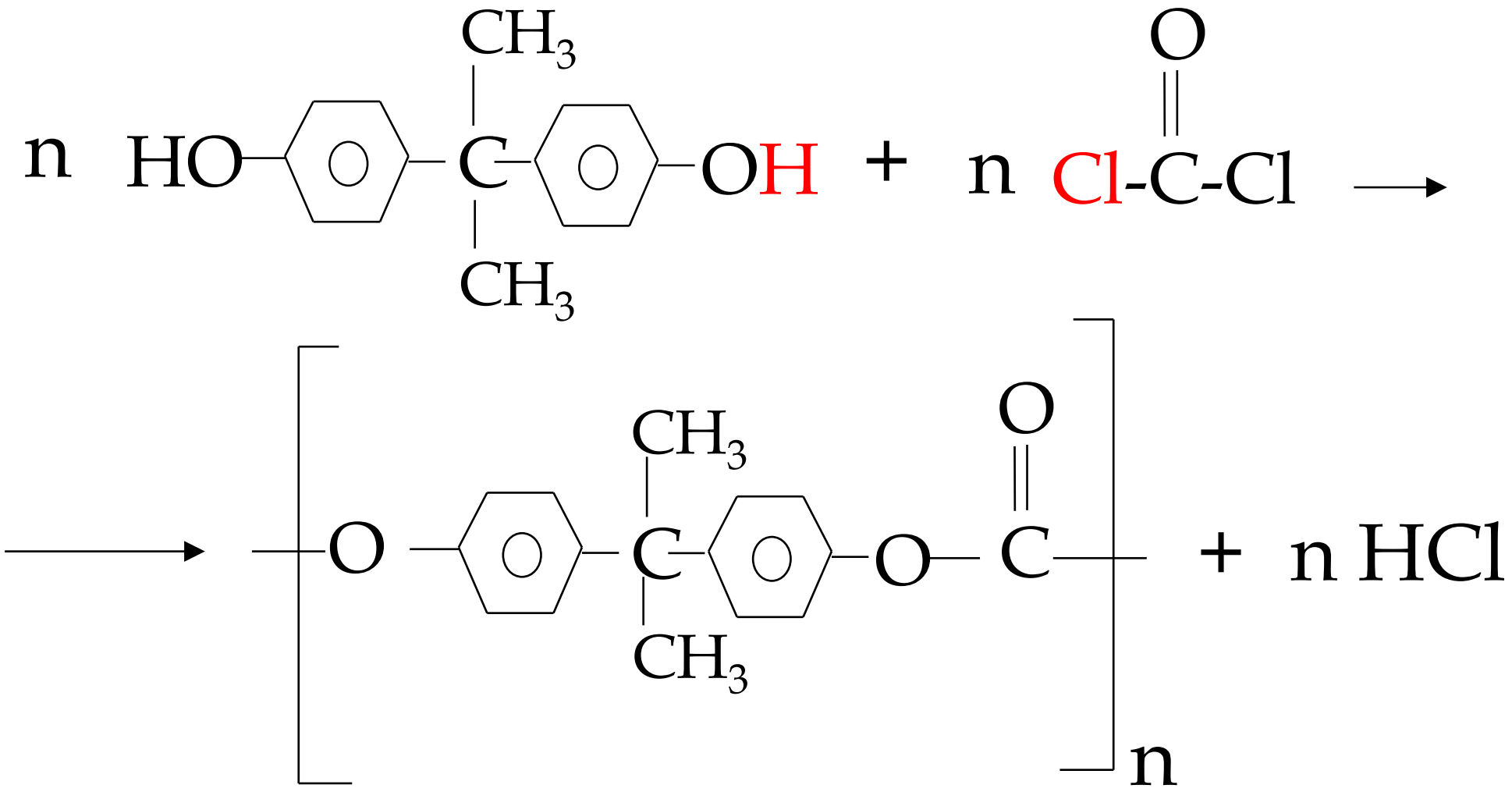
Termination: a polymer with a free radical "kills" itself with another radical.



Condensation polymerization (1)

- The monomers are produced in the polymerization process.
- The monomer production requires two petrochemical products:
  - for example: a di-alcohol and a di-acid
- The di-alcohol and the di-acid react producing the polymer and a volatile sub product is eliminated from the reactor.
- The process is random and produces chains with different sizes.
- One of the polymers produced in this way is polyester (sub-product: water) and the polycarbonate (known as Lexan) (sub-product: hydrochloric acid).

Condensation polymerization (2)



Polymerization by catalyst (1)

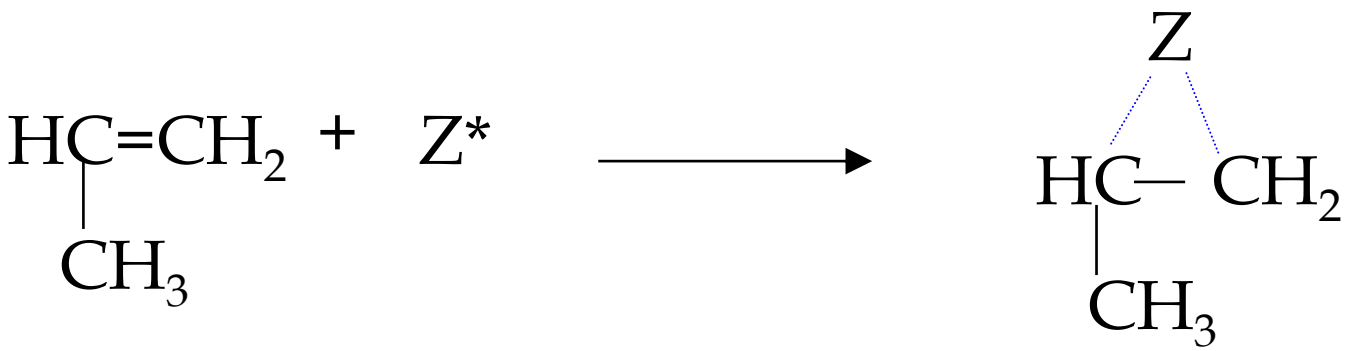
- In general, the main characteristic is that the polymerization requires a substance called catalyst (impregnated on alumina or silica).
- The monomer is added to the catalyst.
- The monomer addition occurs following a spatial arrangement, but sometimes mistakes happen forming another *isomer* with different properties.
- The process is random and produces chains of different sizes
- The process ends when hydrogen is added.
- Polyethylene and polypropylene are produced with this process.

Condensation polymerization (2)

Activation: catalyst

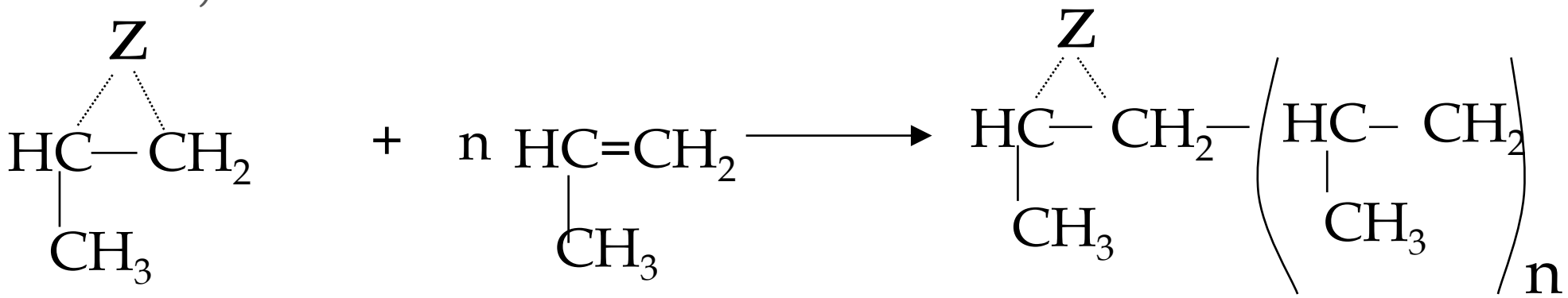
$$\text{Catalyst} \longrightarrow Z^*$$

Initiation: the monomer adds to the catalyst.

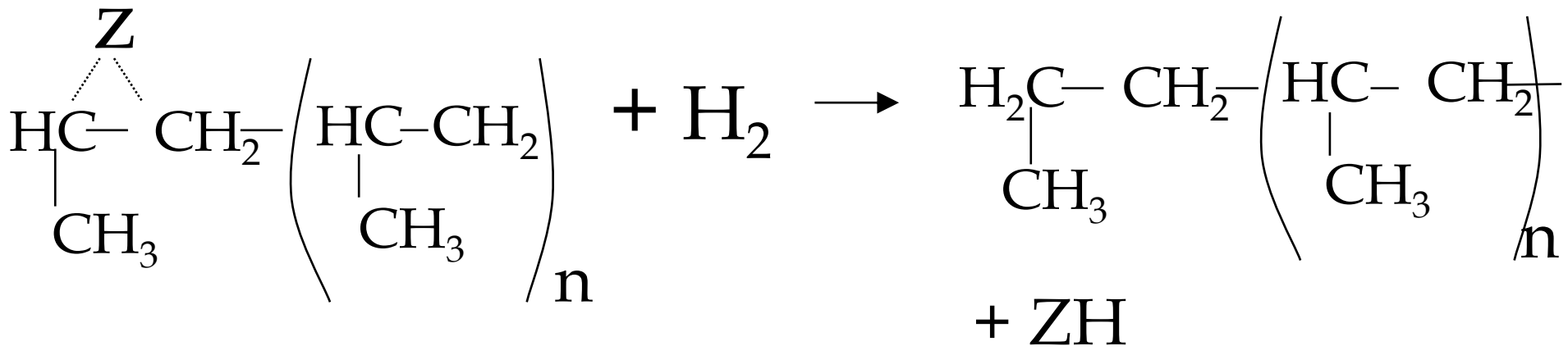


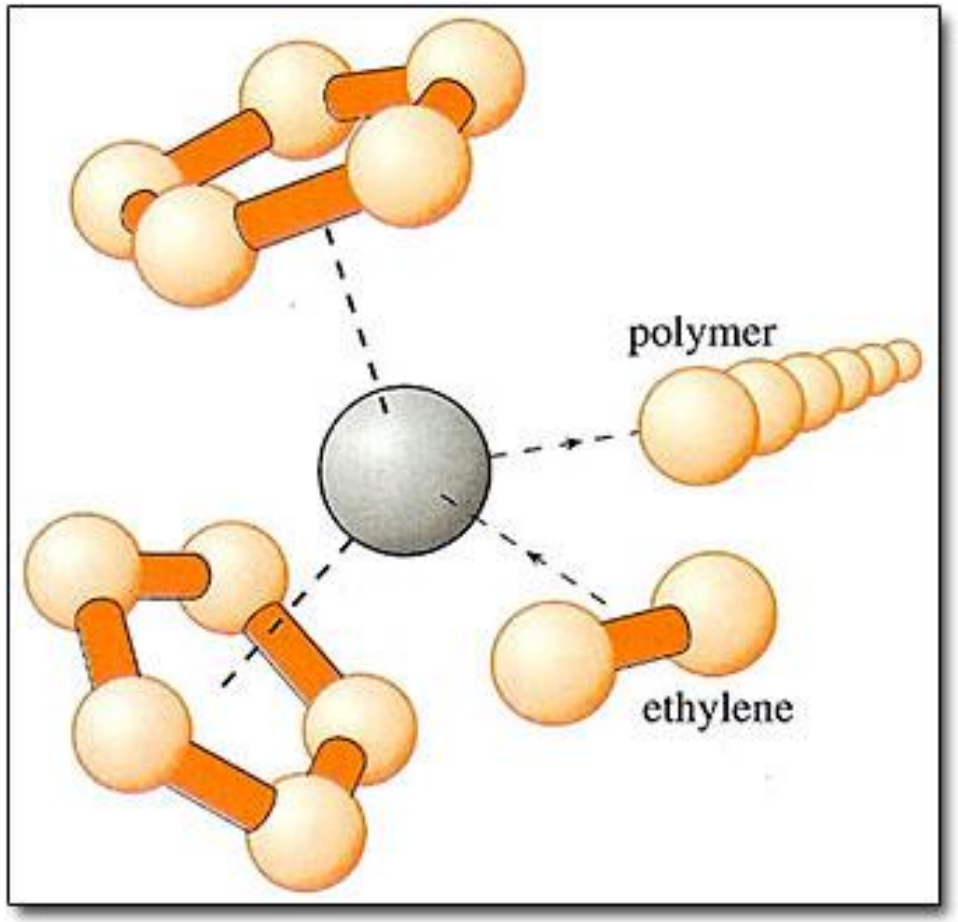
polymerization by catalyst (3)

Propagation: the monomer keeps adding to the Z complex *(mistakes can occur in the addition).*



Termination: the process is finished by adding hydrogen.




polymer
ethylene

- Go to the Blackboard Platform/Course Resources.
- Read the **TJC** presentation.

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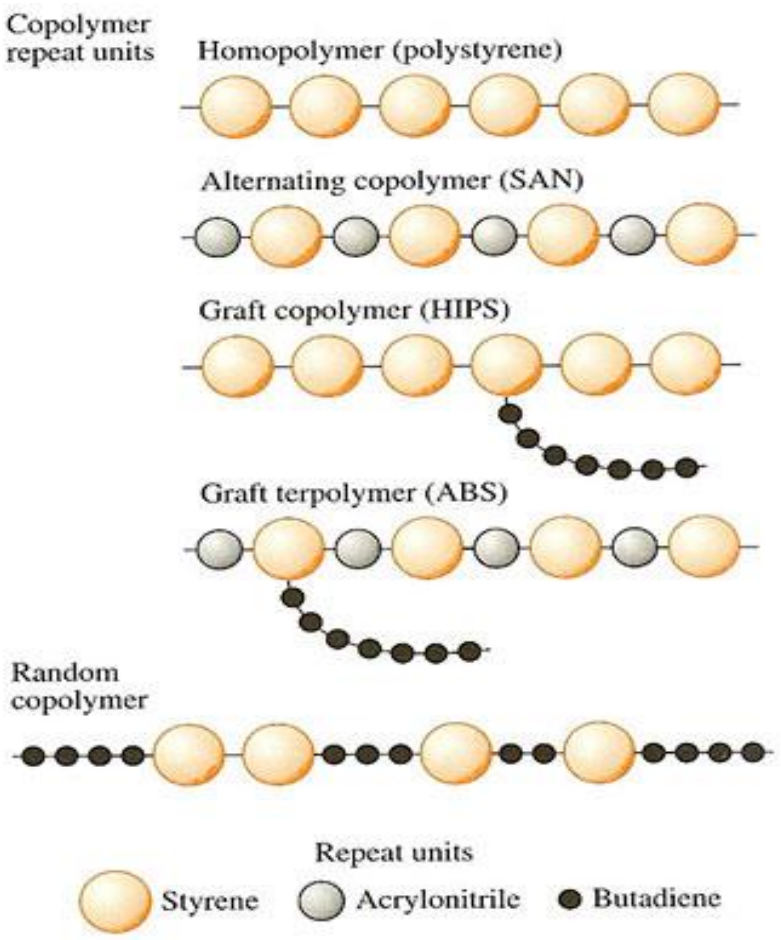
Chemical and Physical Nature of Polymers

Copolymers

Dr. Jaime Bonilla Ríos

Copolymers

- Materials formed by a combination of different monomers (A, B and even C).
- The resultant molecule has desirable properties of each homopolymer.
- Types:



openlearn.open.ac.uk/.../formats/T838_1_rss.xml

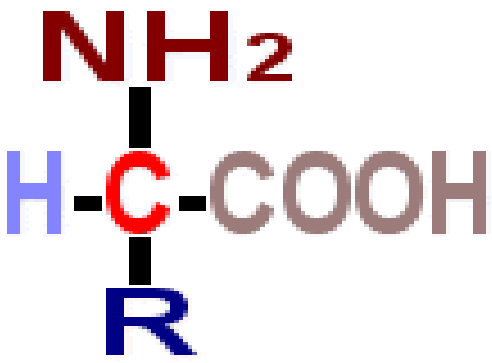
Copolymerization (2)

- High-impact polystyrenes (HIPS) are produced by copolymerization (by grafting) or by mixing polystyrene (PS) with rubber.
- By grafting: the synthetic rubber is added to the reactor where the PS is forming. The rubber concentration is very low and reduces the glass transition temperature of the PS.
- When the rubber is added to the reactor, is necessary to obtain a good dispersion and to add an antioxidant. The main reason is that the rubber has a double bond which make it susceptible to the oxygen.

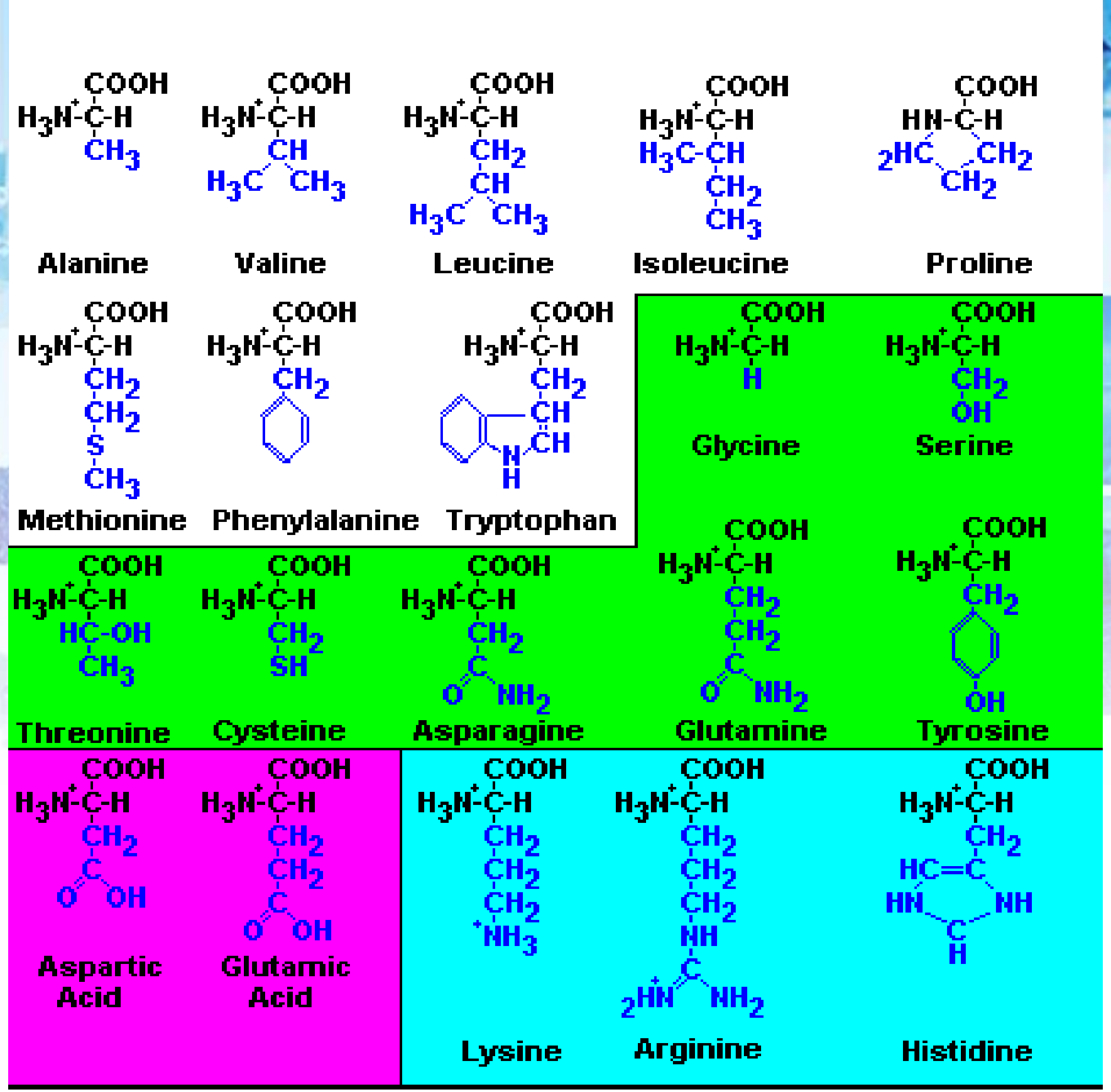
PROTEINS

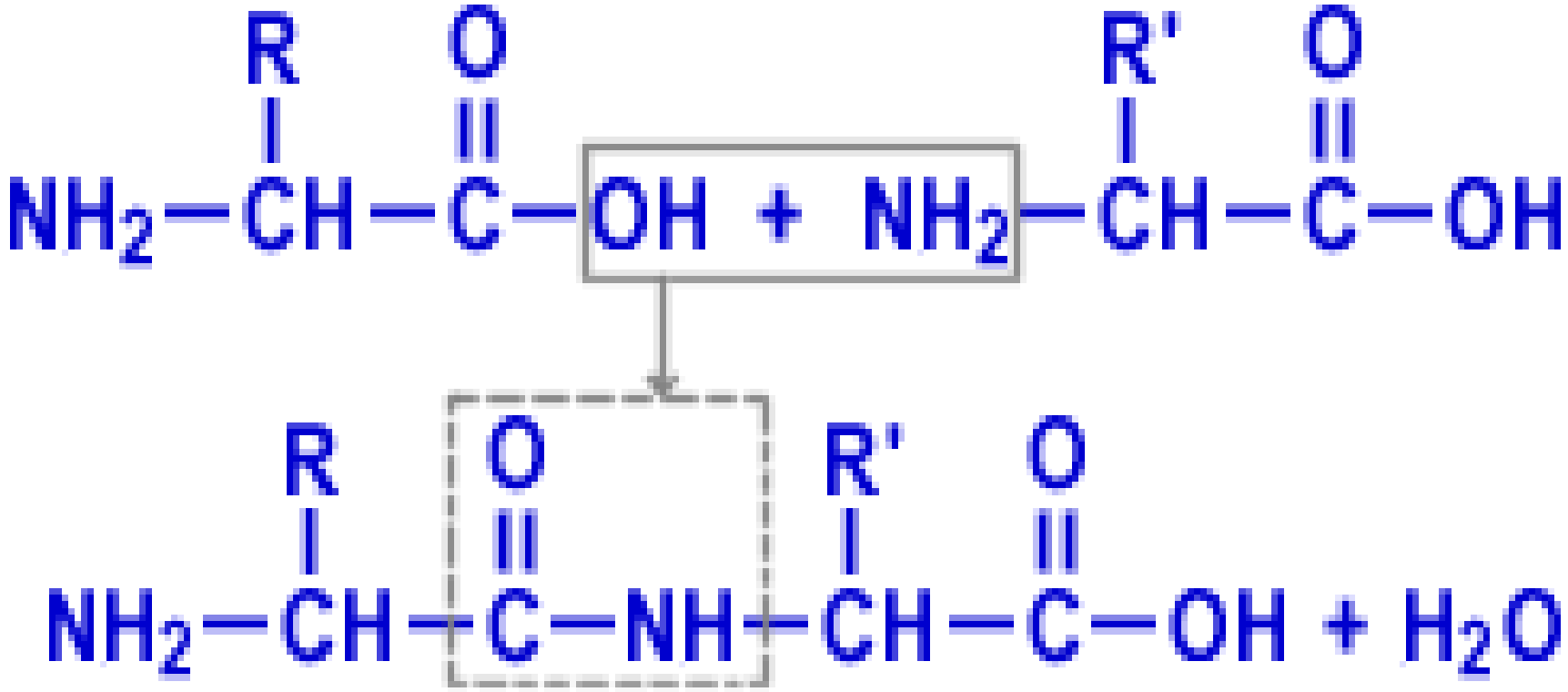
Made by aminoacids

Amino group

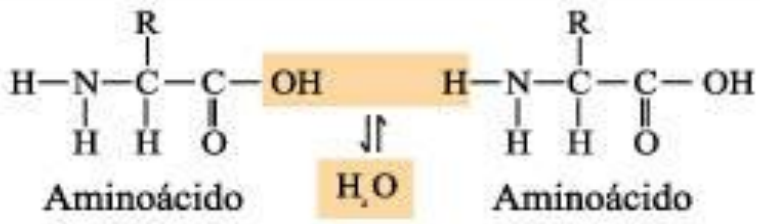


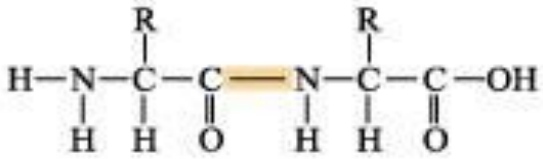
Acid group


Alanine
Valine
Leucine
Isoleucine
Proline
Methionine
Phenylalanine
Tryptophan
Glycine
Serine
Threonine
Cysteine
Asparagine
Glutamine
Tyrosine
Aspartic Acid
Glutamic Acid
Lysine
Arginine
Histidine

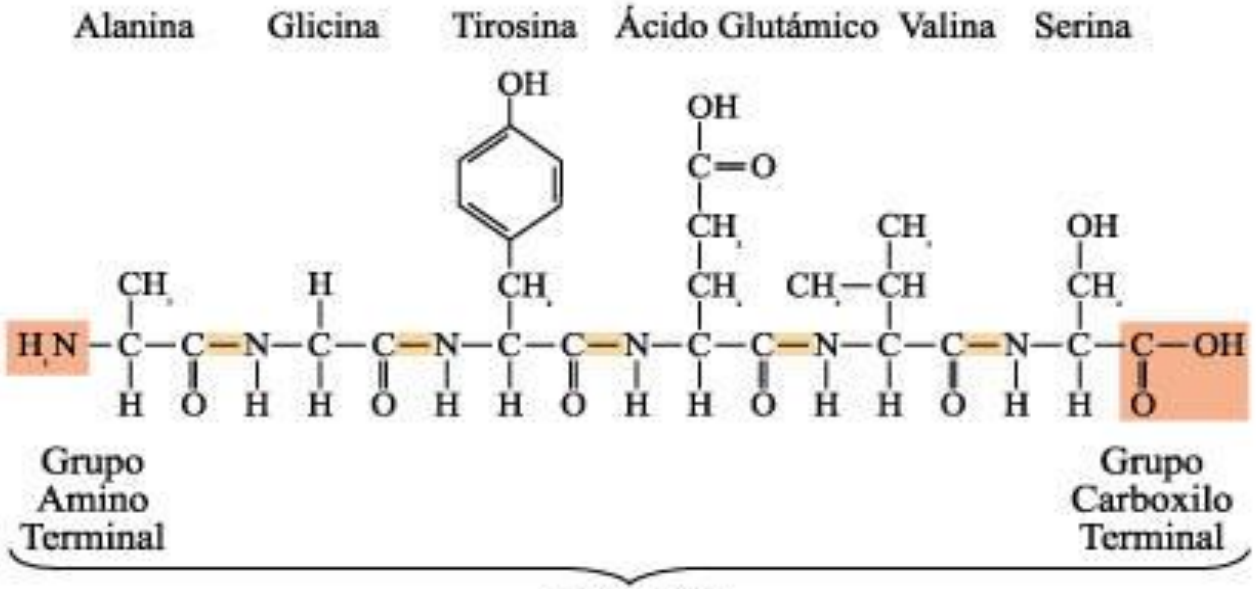


Peptic Acid





Dipéptido
(a)



Polipéptido
(b)

Summary

1. Stereoisomers
2. Polymerization reactions
3. Copolymers
4. Articles review
5. Homework
6. Next lab session

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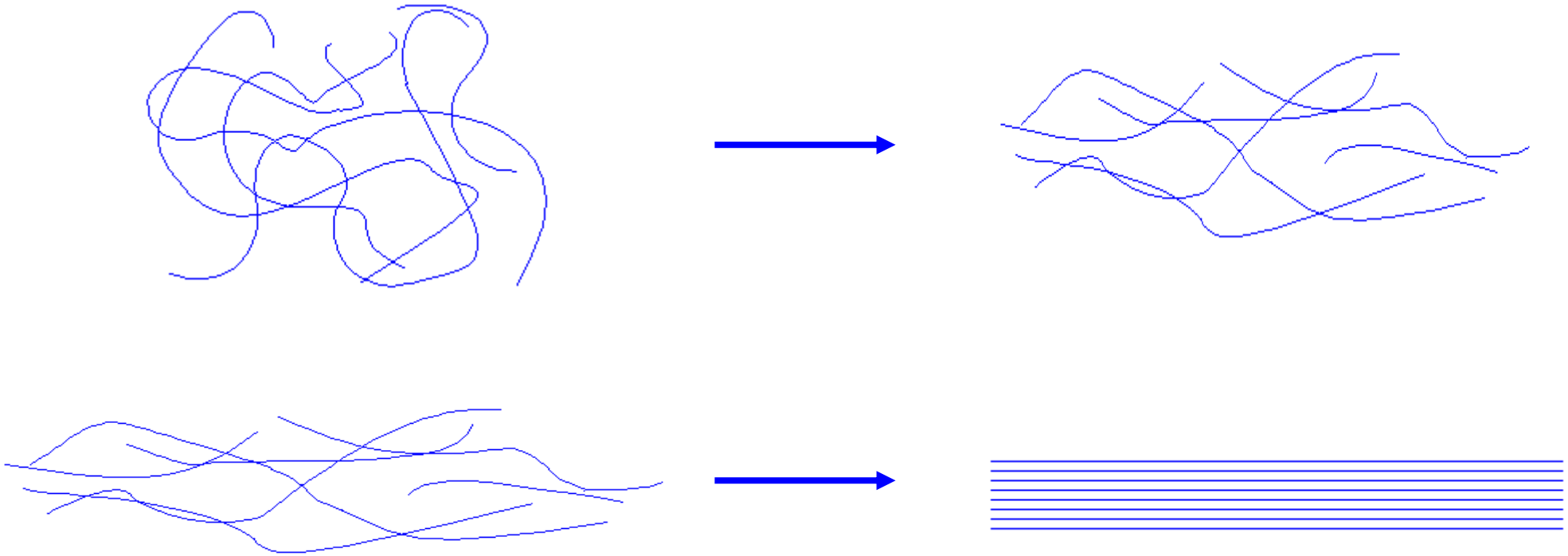
Chemical and Physical Nature of Polymers

Interesting Information on Polymer Behavior

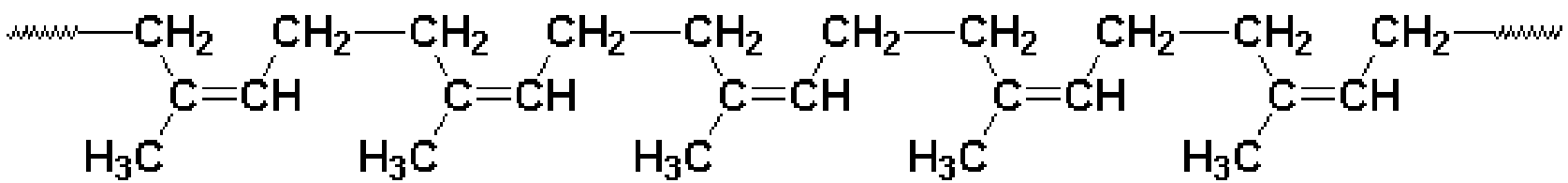
Dr. Jaime Bonilla Ríos

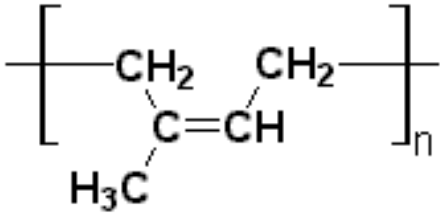
Strain effect inthe chains

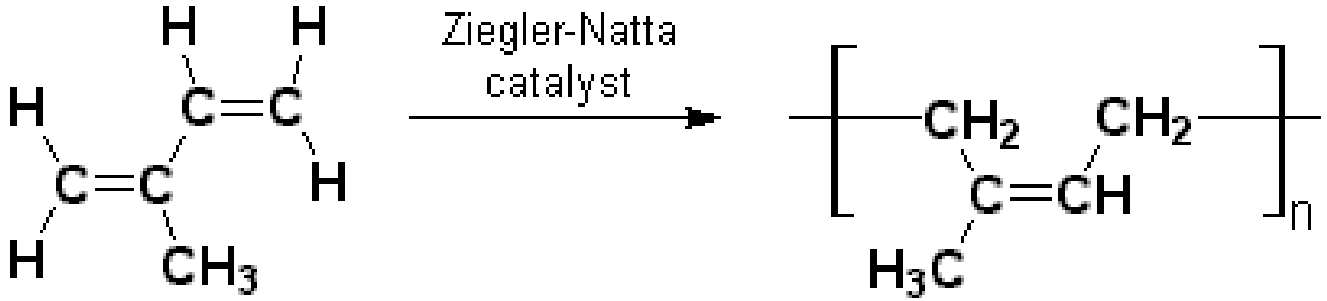


Source: http://pslc.ws/macrog/index.htm

Poly-isoprene



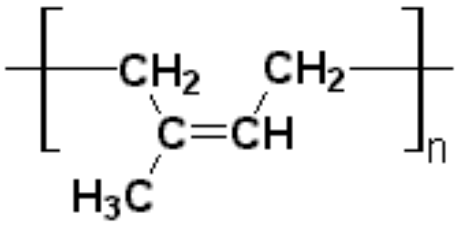




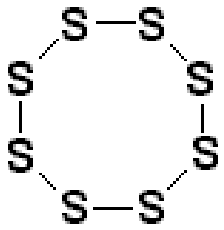
isoprene polyisoprene

Source: http://pslc.ws/macrog/index.htm

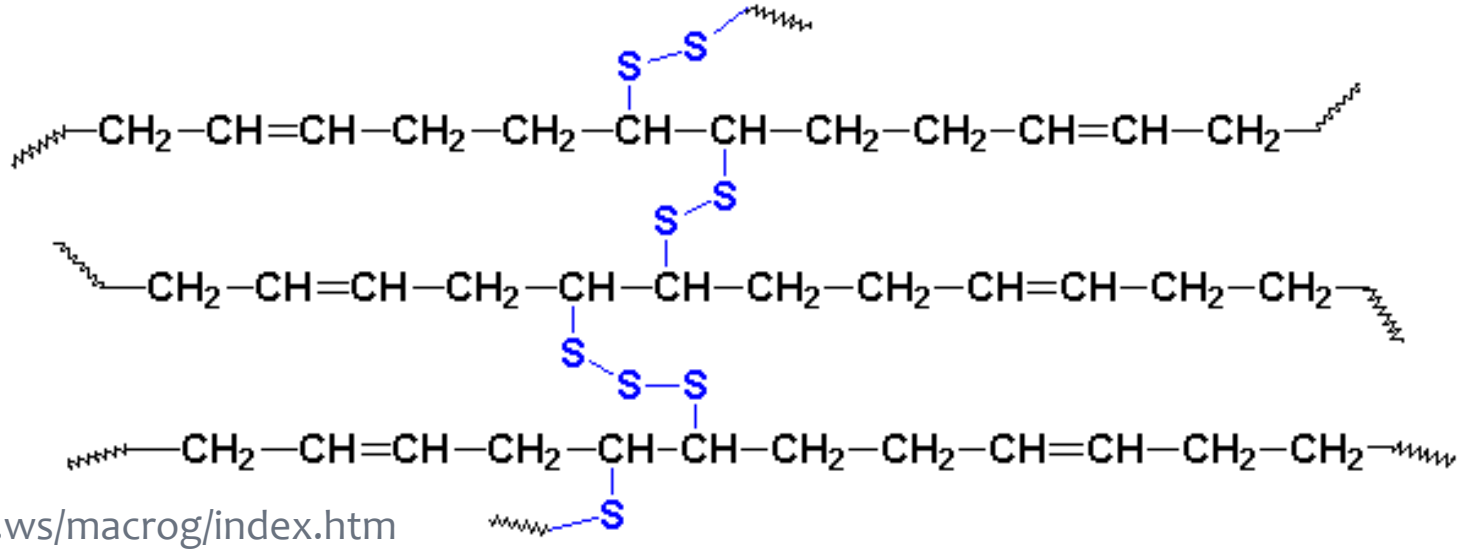
Vulcanization



polyisoprene

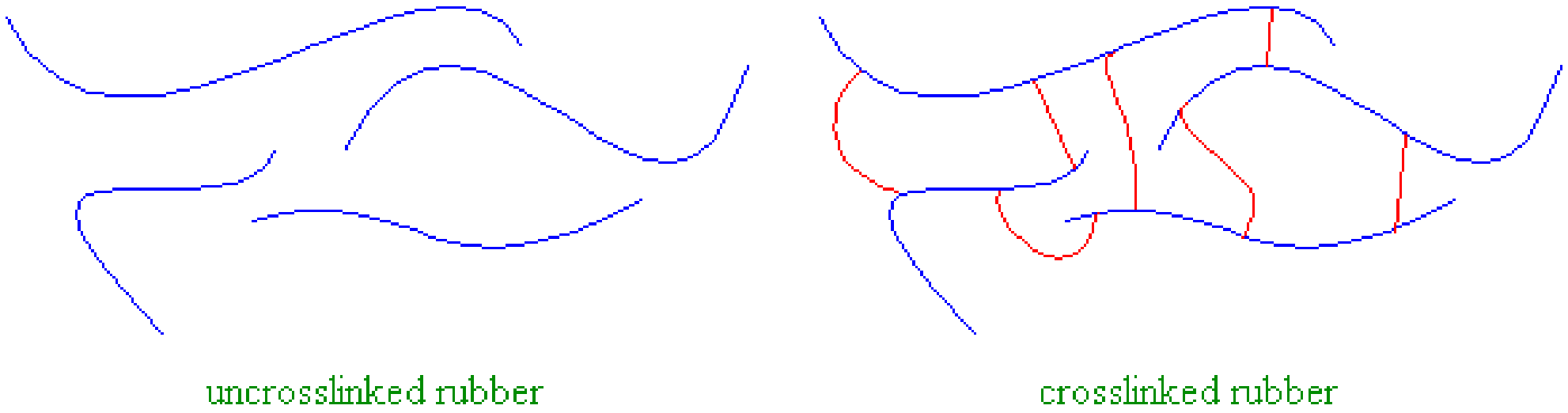


A sulfur (S8) molecule.



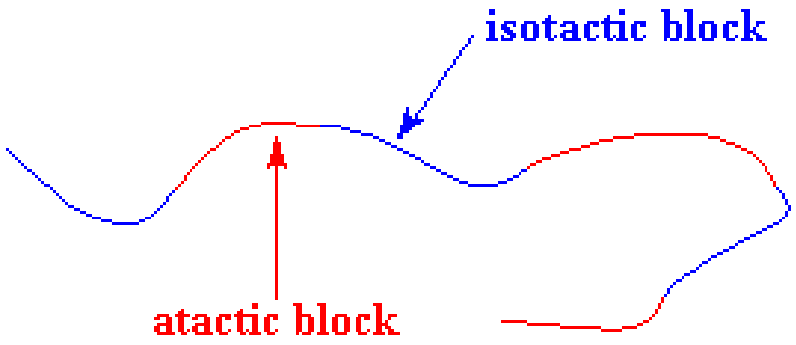
Source: http://pslc.ws/macrog/index.htm

Rubbers

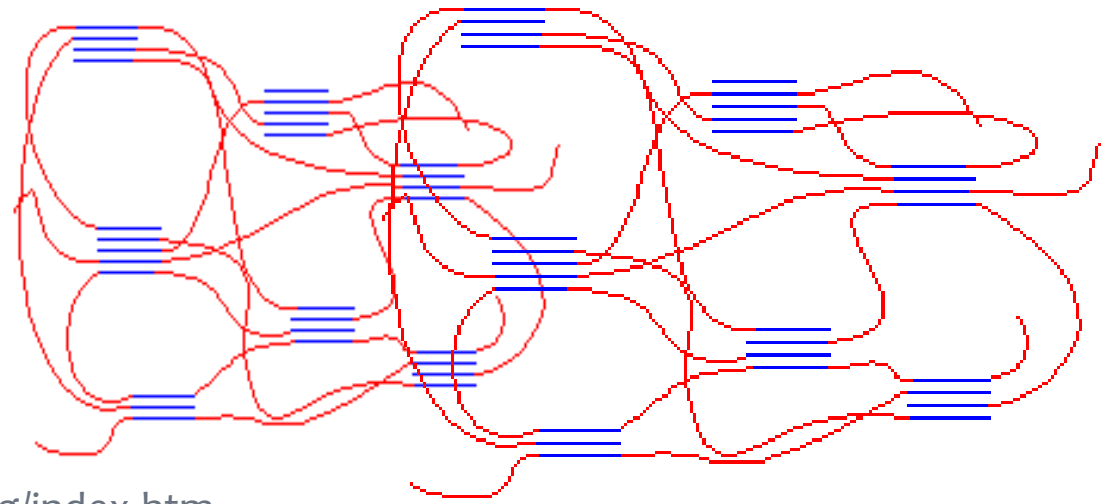


Source: http://pslc.ws/macrog/index.htm

Elastomers

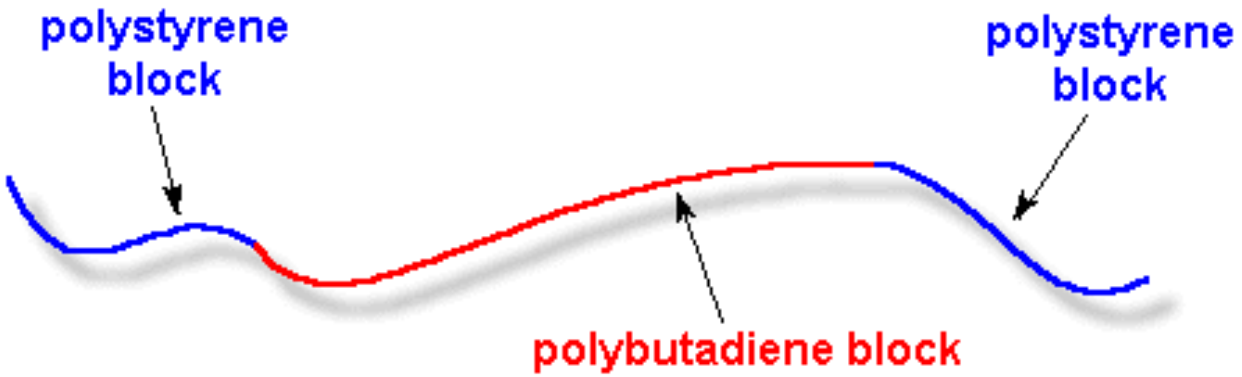


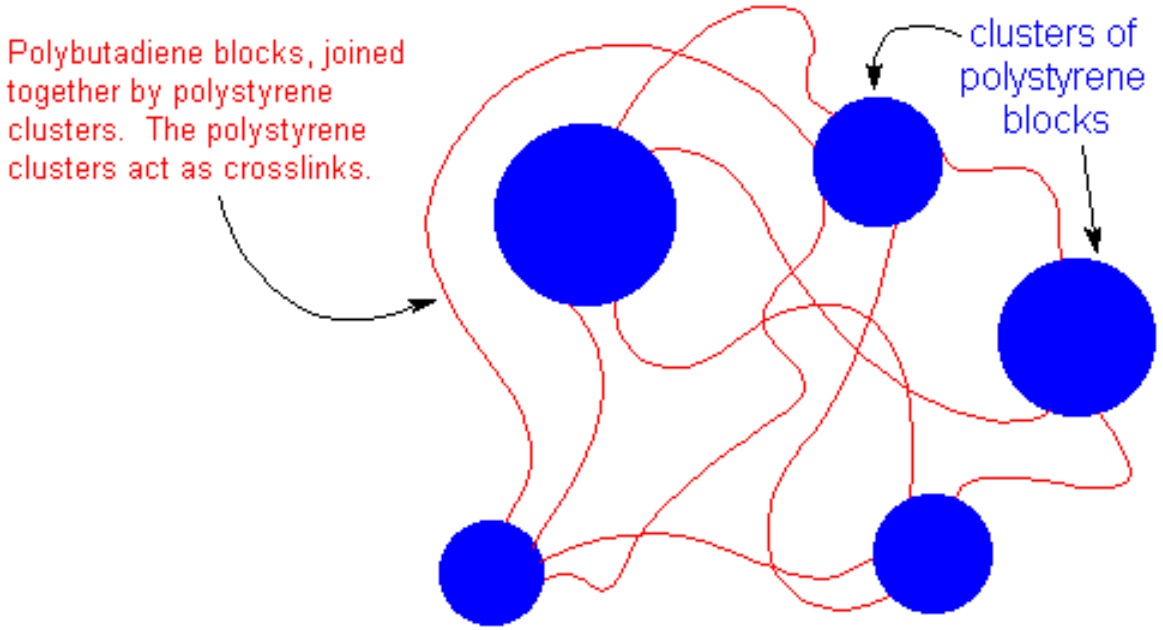
PP by metallocene catalysis polymerization



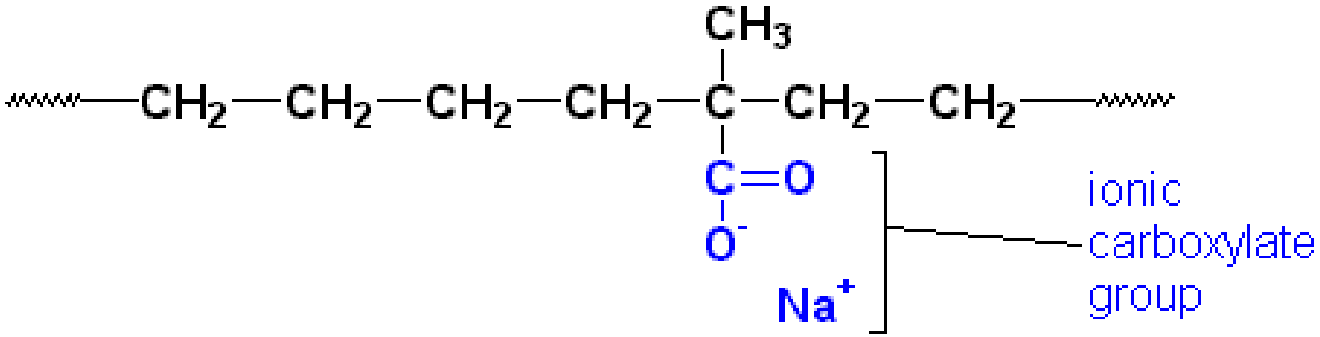
Source: http://pslc.ws/macrog/index.htm

Block copolymers

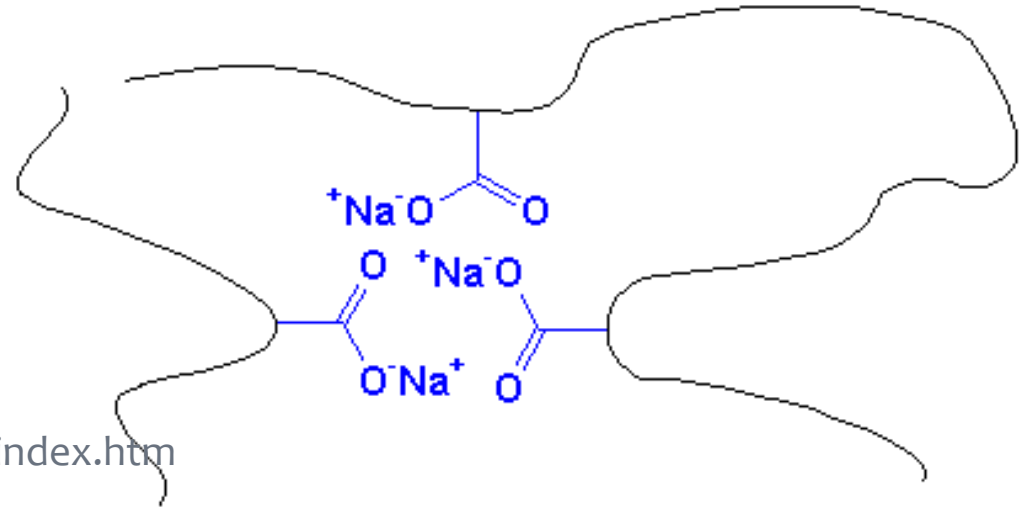




Ionomers

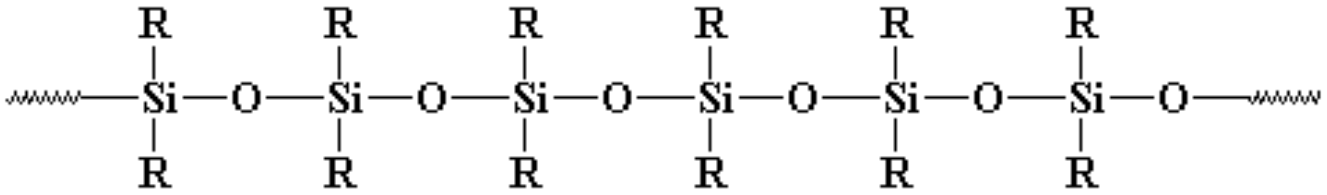


Poly(ethylene-*co*-methacrylic acid), a.k.a. Surlyn®.

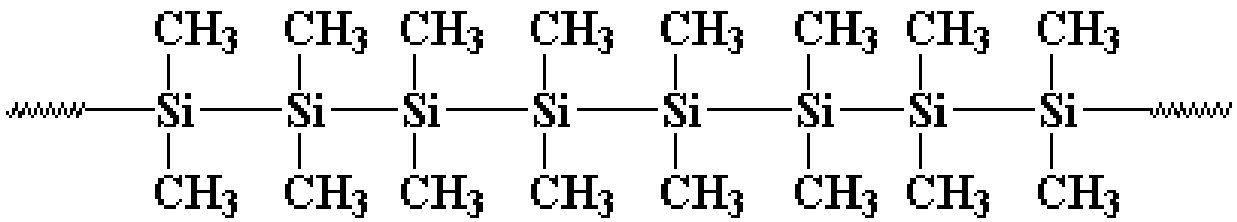


Source: http://pslc.ws/macrog/index.htm

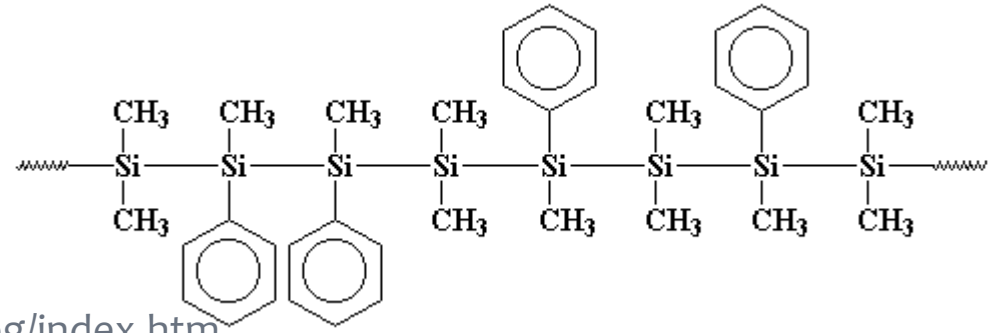
Silicon polymers



polysiloxanes

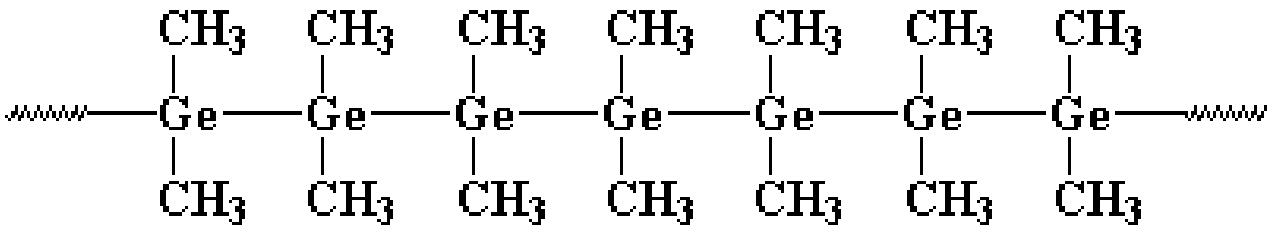


polydimethylsilane

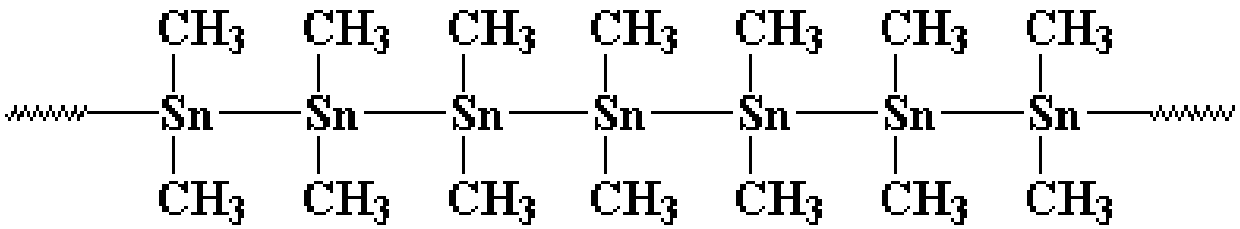


Source: http://pslc.ws/macrog/index.htm

Germanium polymers



polydimethylgermane



polydimethylstannane

Source: http://pslc.ws/macrog/index.htm

Tecnológico de Monterrey

Chemical and Physical Nature of Polymers

Consequences of the random polymerization process

Dr. Jaime Bonilla Ríos

Inherent results of the polymerization process

Polymerization

- Production of a countless number of molecules, with different molecular weight
- Some mistakes in the spatial conformation
- Ultra-high molecular weight material

A set of molecules with different molecular weight???

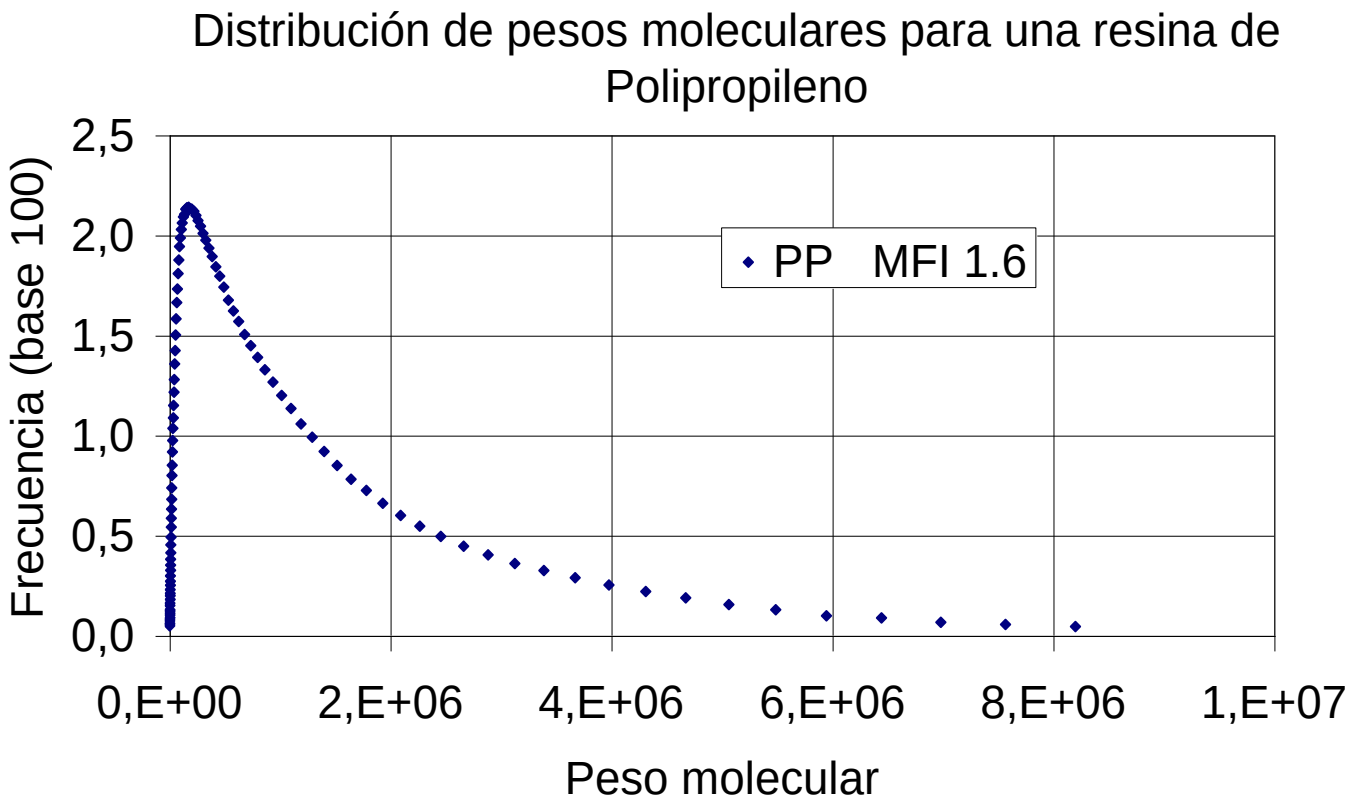
Example: a molecular weight distributon table for a polypropylene resin

Mol Wt.	Grs
3610065	0.056568112
3383827	0.069794147
3171768	0.078820023
2972998	0.098167569
2786685	0.113091541
2612048	0.136952024
2448355	0.147497107
2294920	0.168095764
2151101	0.197452201
2016295	0.215772047
1889936	0.244368881
1771497	0.28127667
1660480	0.309605408
1556420	0.344368434
1458882	0.3826167
1367456	0.42323314
1281760	0.465994343
11377	0.423099092
10664	0.39329583
9995	0.36599479
9369	0.339006528
8782	0.320329221
8231	0.303528581
7716	0.274887065
7232	0.265816507
6779	0.242402849
6354	0.223189351
5956	0.206790854
5583	0.188426325
5233	0.180428148
4905	0.171670368
4597	0.157863459
4309	0.143743772
4039	0.138247818
3786	0.116978923
3549	0.116666145
3326	0.102233681
3118	0.106255111

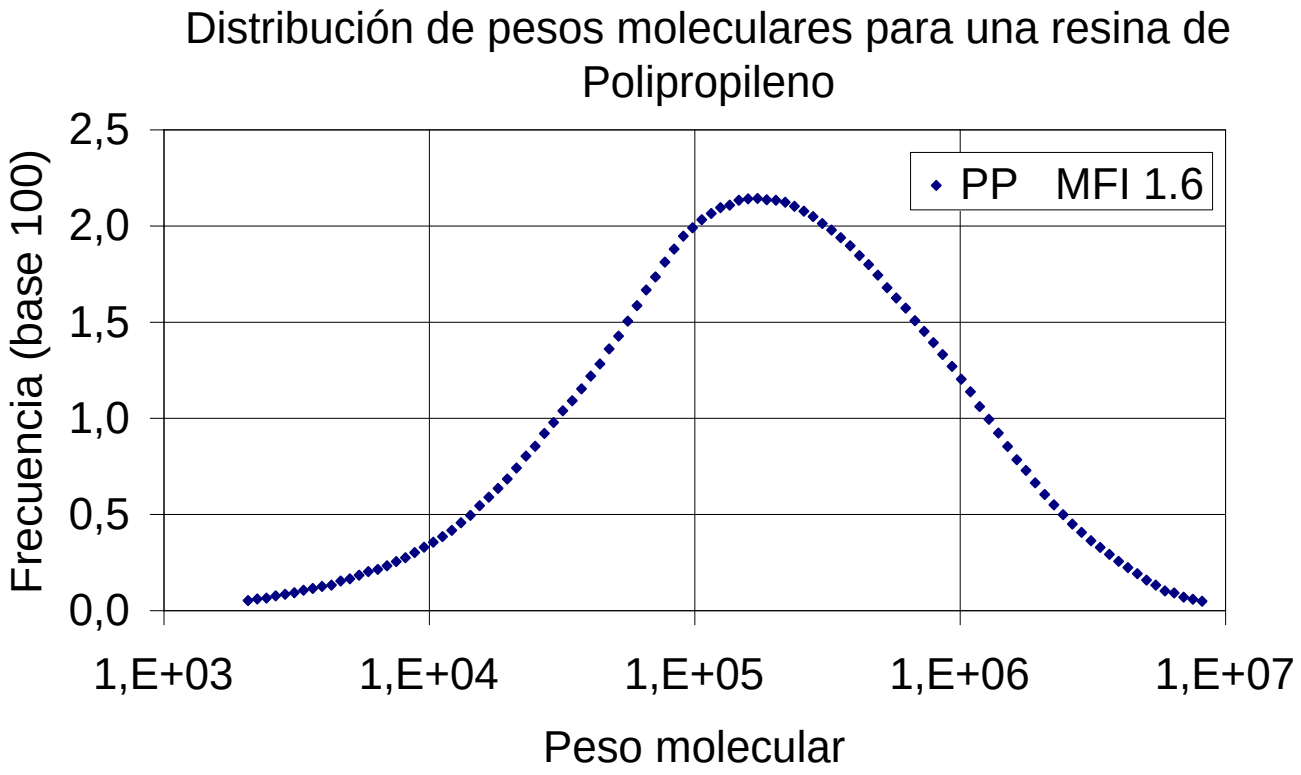
Molecules with different molecular weight ⇒ ***Can be represented by an histogram and looks like a distribution.***

Linear-linear

Molecular weight distribution for a Polypropylene resin



Molecular weight distribution for a Polypropylene resin



Note: this plot is linear-logarithmic

As in every distribution, different represantitive numbers can be obtained (for example mean, variance, etc).

The molecular weight distributions (MWD) are not an exception.

Activity 5

Go to the Blackboard platform/Course Resources/Session 3 and using the information given in the excel file **PB resins.xls**

- Calculate the Mn, Mw, Mz and the polidispersity index of each resim
- Bring the results to class so we can check your answers

Where…

- The number average (Mn) compares the total length of the polymer chain to the number of individual present chains.

- The average weight (Mw) compares the total length of the polymer chain to the mass fraction of the individual chains.

Algebraic expressions of the moleculars weights

Number average molecular weight (Mn)

- Consider an individual chain with length *i*. Its molecular weight is *Mi* and the chains of this size form a fraction *Xi* of the total of the present chains.

$$Mn = \Sigma\, Mi * Xi$$

- But the fraction Xi, is also the number of the i-th chain, related to N, the total number of chains. If Ni chains of the same size are present, then: $Mn = \Sigma\, Mi*Ni/N$

  but as $N = \Sigma\, Ni$, then:

$$Mn = \Sigma\, (Mi*Ni/\Sigma\, Ni)$$

Algebraic expressions ofd the moleculars weights

Weight average molecular weight (Mw)

- Similar to Mn, but now the mass fraction (Wi) is use, instead of individual chains.

$$Mw = \sum Mi * Wi$$

- The reason of Mw/Mn is the polydispersity index (obtained from the molecular weight distribution)
- Polydisperse: different molecular weight mix. Consequence of the random polymerization.

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