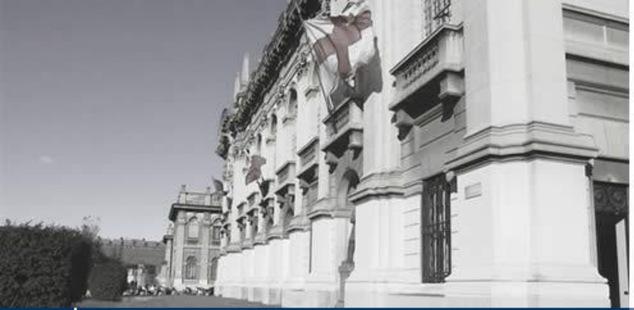


School of Industrial and Information Engineering

Course 096125 (095857)

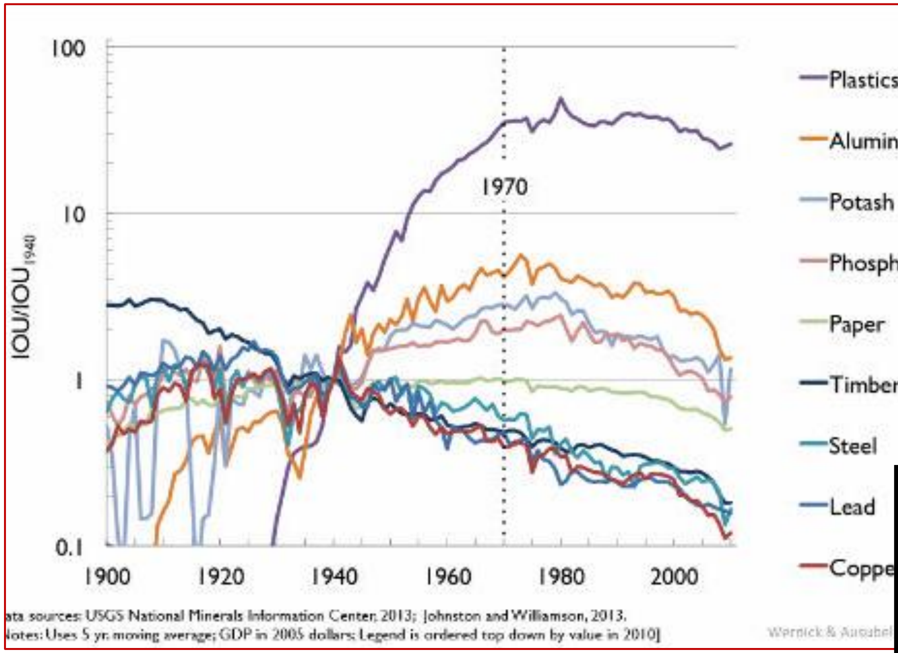
Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Synthetic Polymers – Preparation and Properties.

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
http://iscamapweb.chem.polimi.it/citterio/education/**course-topics/**

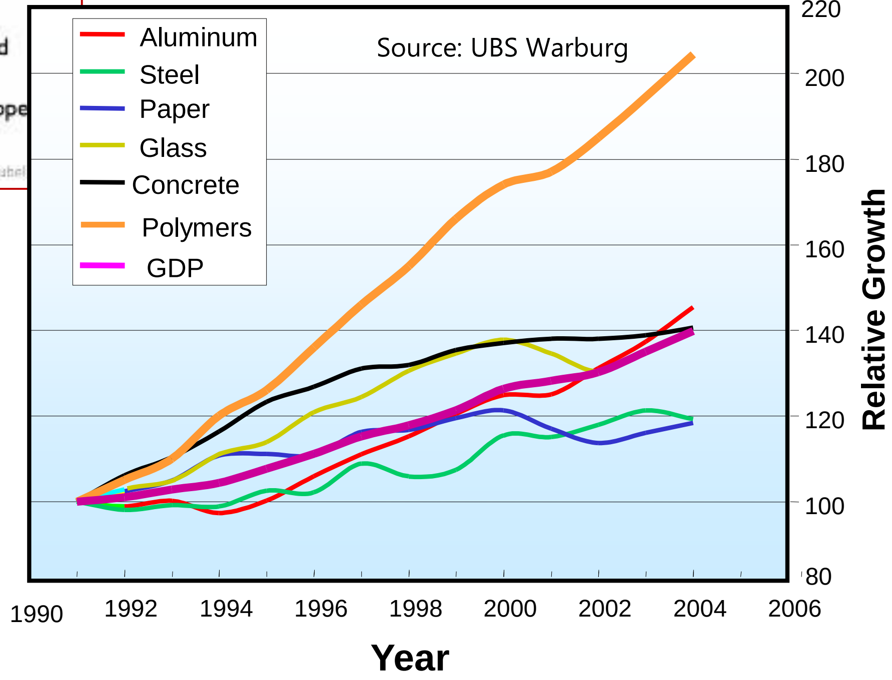
Materials: Intensity of Use.



ata sources: USGS National Minerals Information Center, 2013; Johnston and Williamson, 2013.
Notes: Uses 5 yr. moving average; GDP in 2005 dollars; Legend is ordered top down by value in 2010]

Wernick & Ausubel

Polymers growth is twice the one of other materials.



Plastics

1) Commodity plastics

LDPE, HDPE, PP, PVC, PS

2) Engineering plastics

Acetal, Polyamide, Polyamideimide, Polyacrylate, Polybenzimidazole, etc.

3) Thermosetting plastics

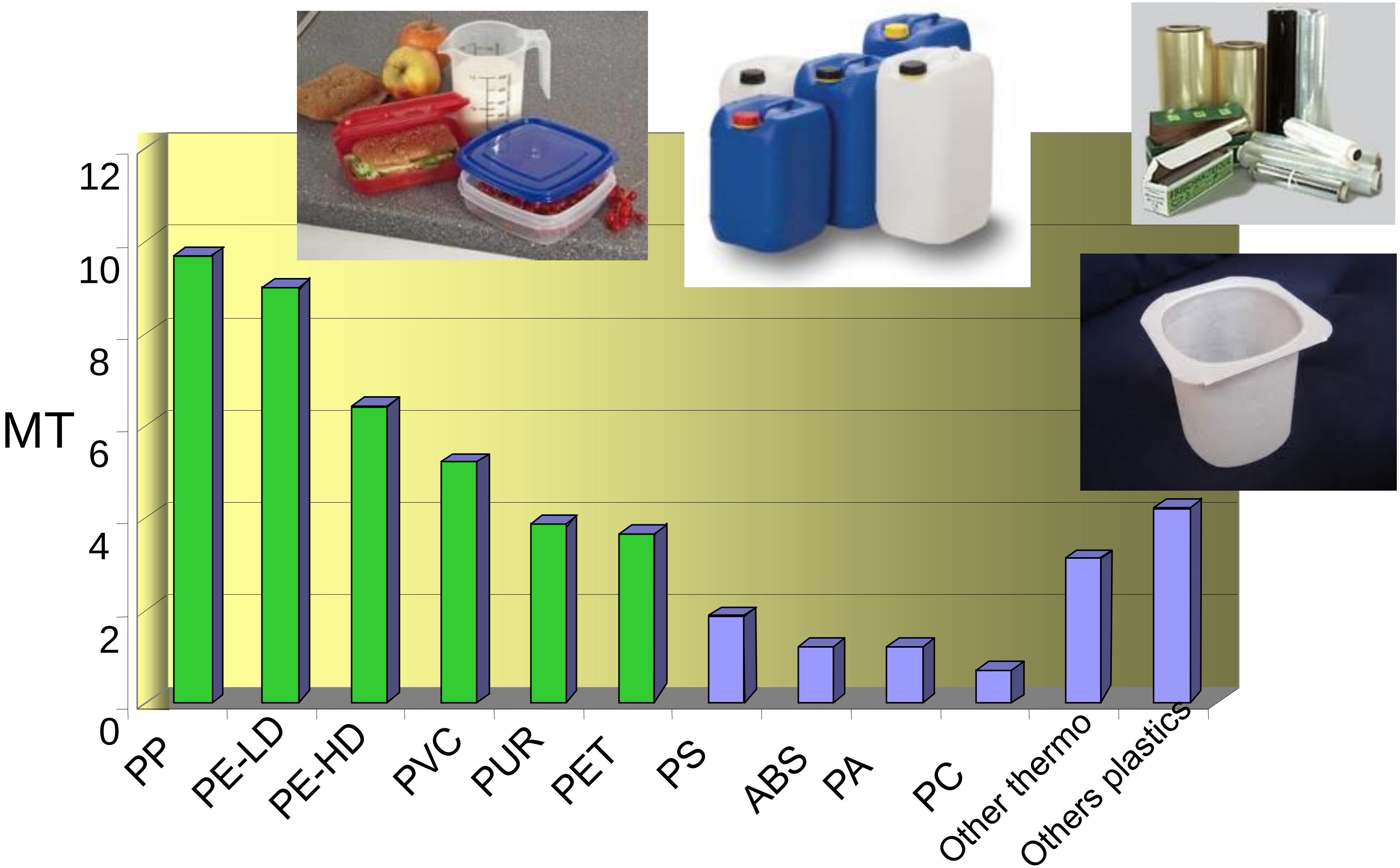
Phenol-formaldehyde, Urea-formaldehyde, Unsaturated polyester, Epoxy, Melamine-formaldehyde

4) Functional plastics

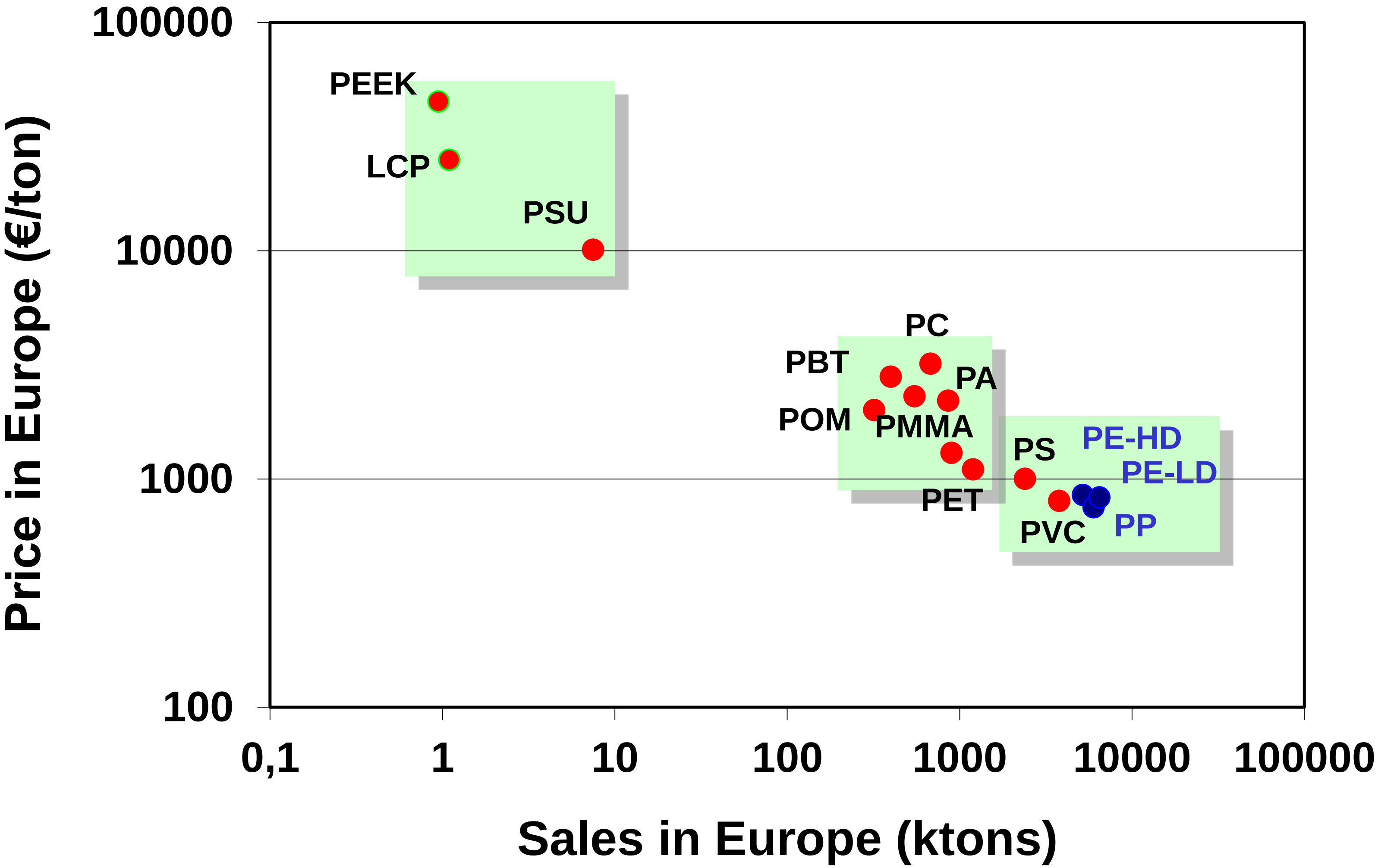
Optics, Biomaterial, etc.

Six Polymers Have Around ~75% Share

Distribution of European (EU28+NO/CH) plastics converter demand by resin type in 2016.



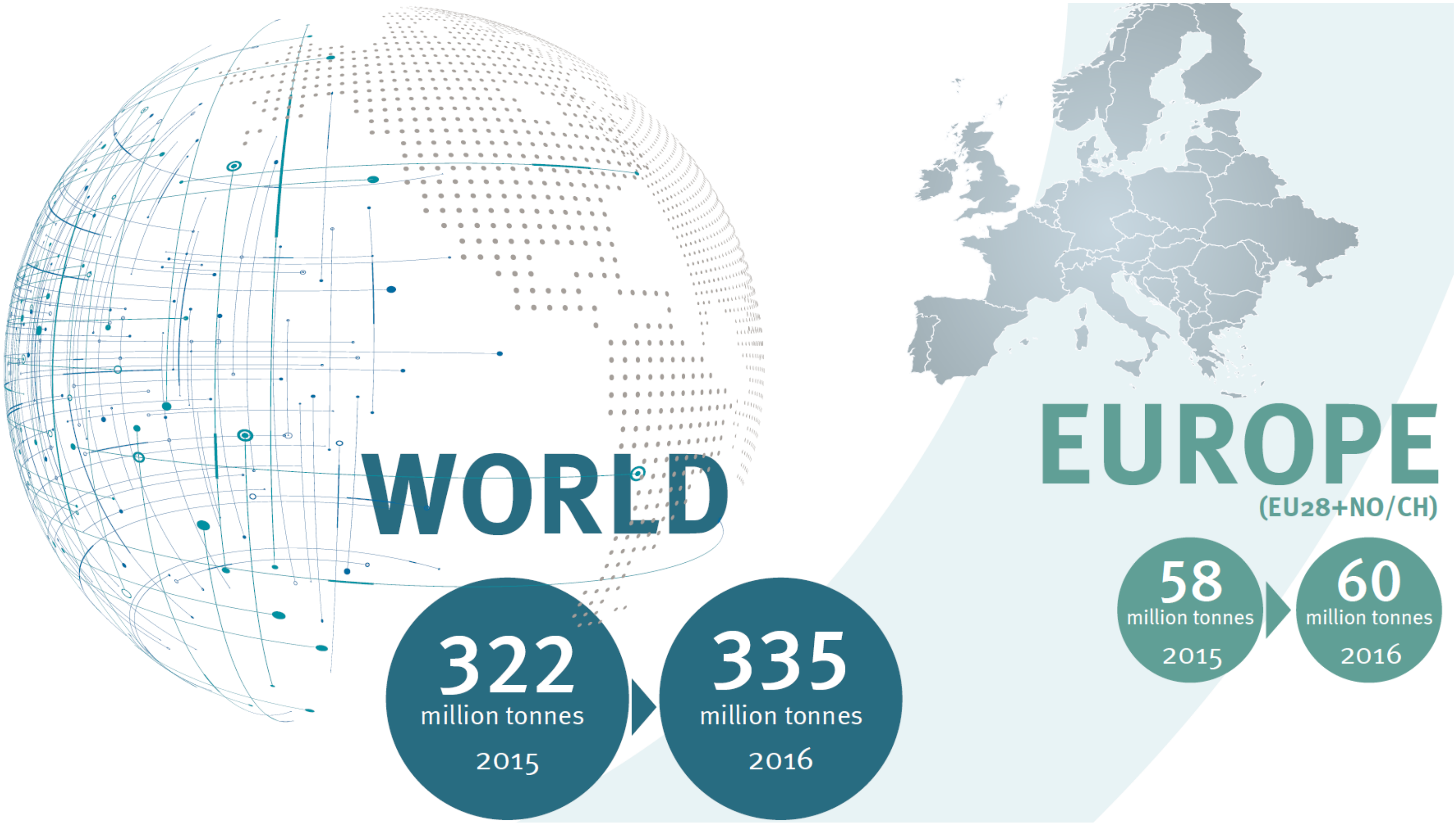
Polymers Price as Function of Sale Volume.



Source Biomer-UrsJ. Haenggi

World and EU plastics production data (2017).

Includes plastic materials (thermoplastics and polyurethanes) and other plastics (thermosets, adhesives, coatings and sealants). Does not include: PET fibers, PA fibers, PP fibers and polyacryls-fibers.



Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH

World Plastics Production (2011).

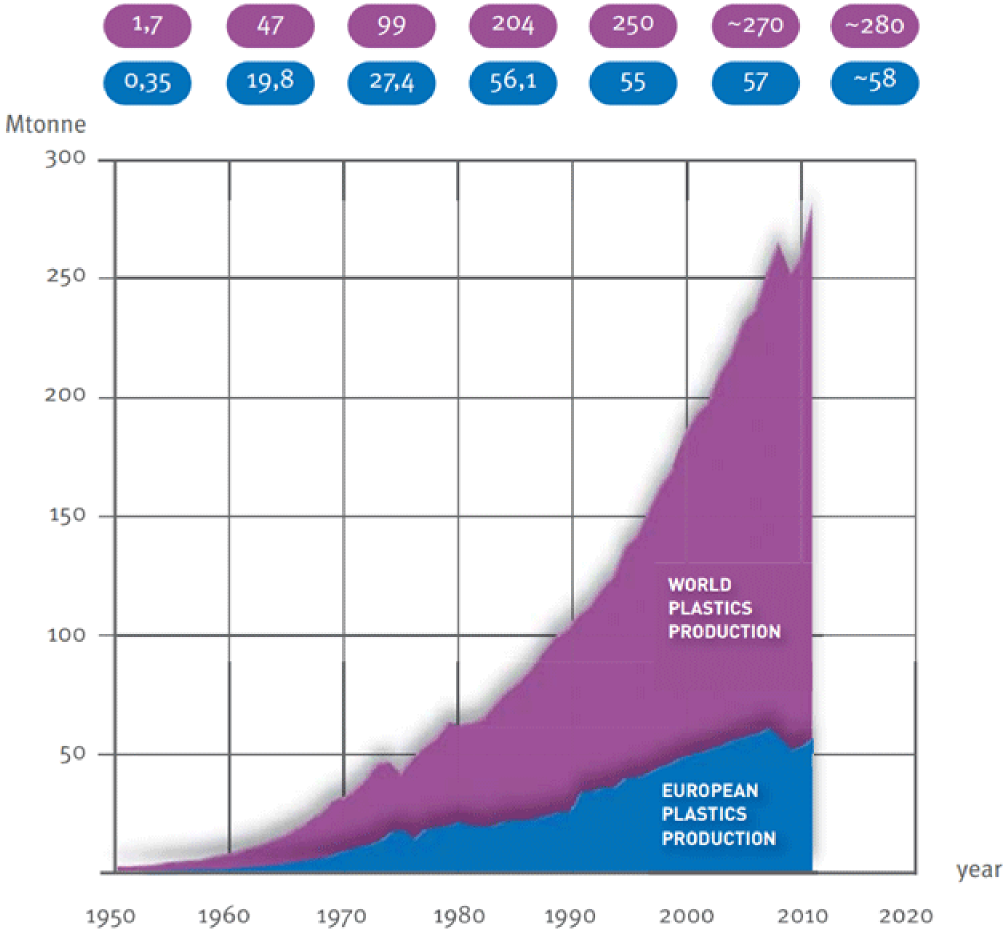


Fig. 2 - World Plastic Material Production 1950-2011
Includes Thermoplastics, Polyurethanes, Thermosets, Elastomers, Adhesives, Coatings and Sealants and PP-Fibers. Not included PET, PA and Polyacrylic Fibers

Source: Plastic Europe Market Research Group (PEMRG)

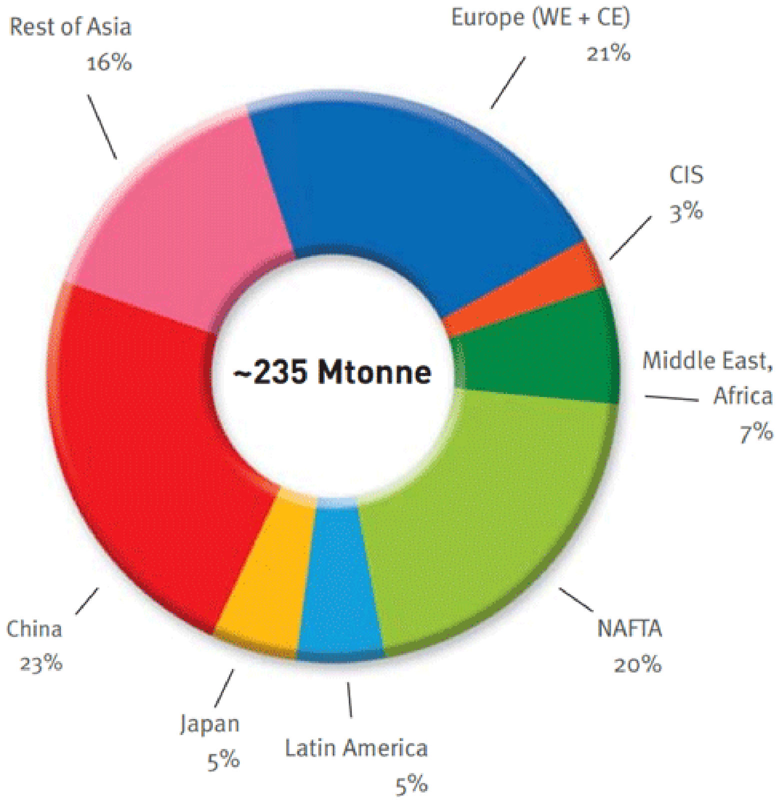


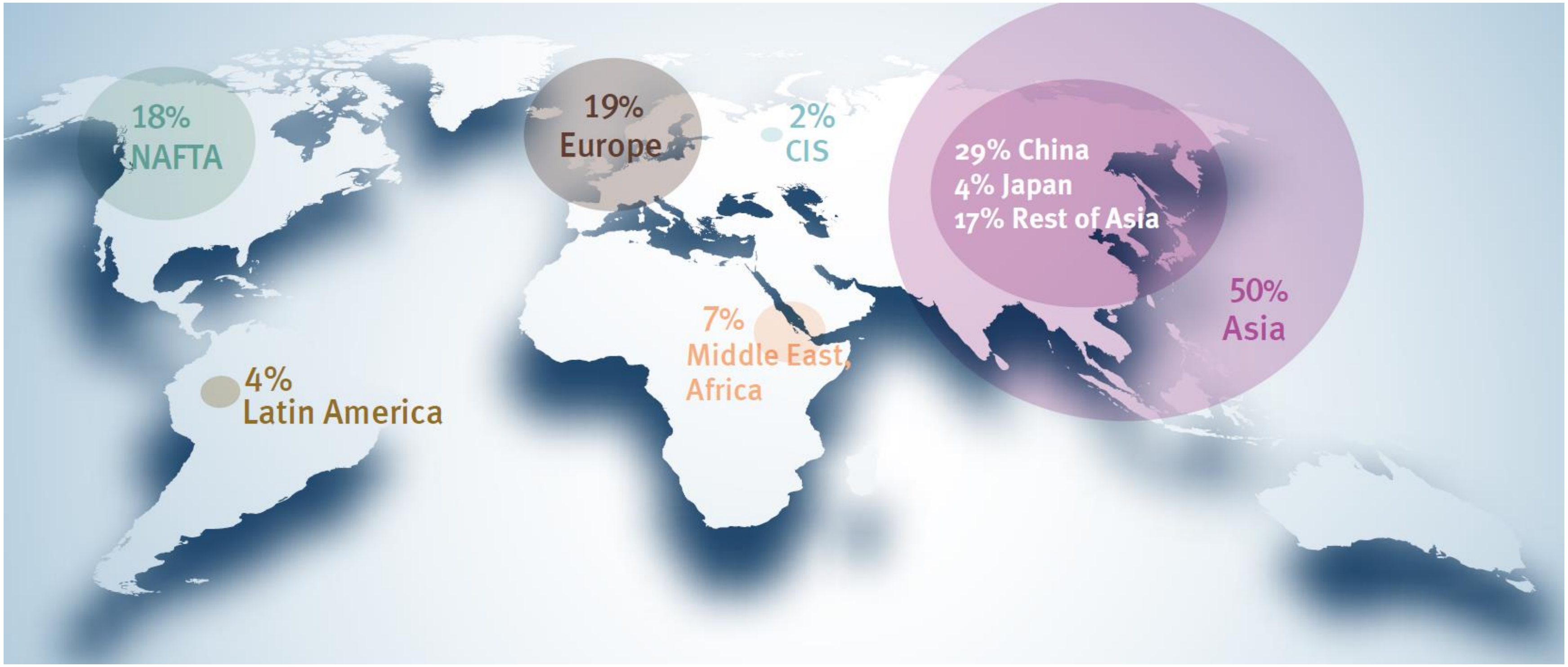
Fig. 3 - World Plastic Material Production 2011
w/ o Other Plastics (-45 Mtonne)

Source: Plastic Europe Market Research Group (PEMRG)

Distribution of Global Plastic Materials Production.

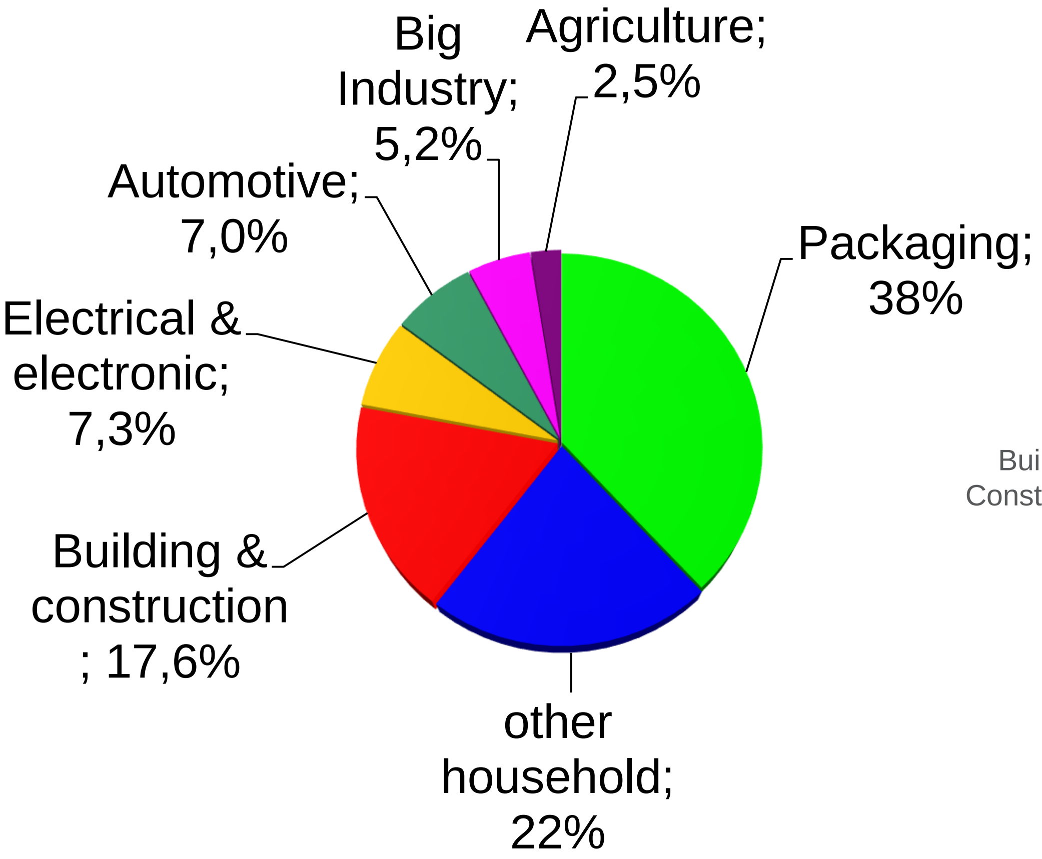
China is the largest producer of plastic materials*, followed by Europe and NAFTA.

World production of plastic materials in **2016**: 280 million tonnes. (*Plastic materials: only thermoplastics and polyurethanes)

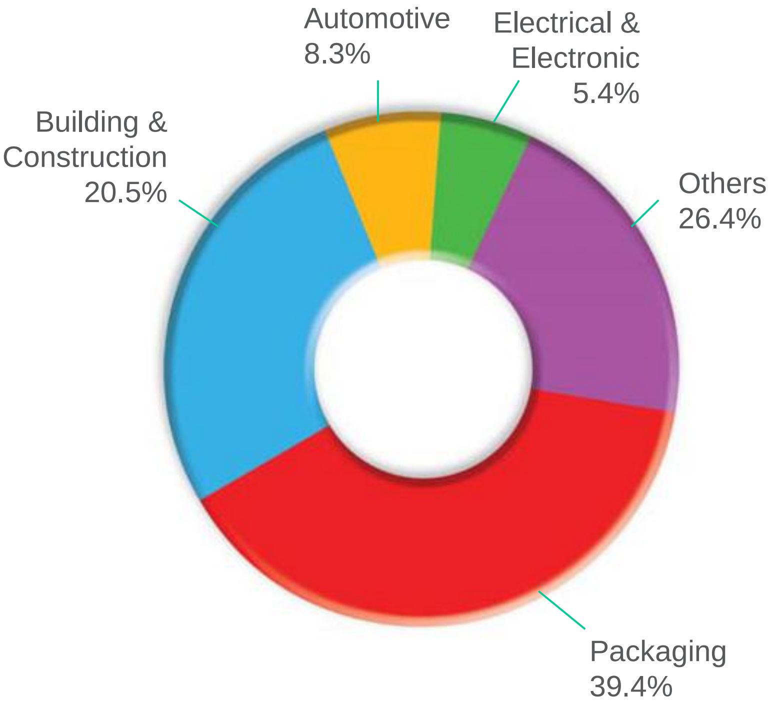


Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH

European Plastics Demand by Segment (weight %).



Total: 38.123.000 ton. (**2002**)

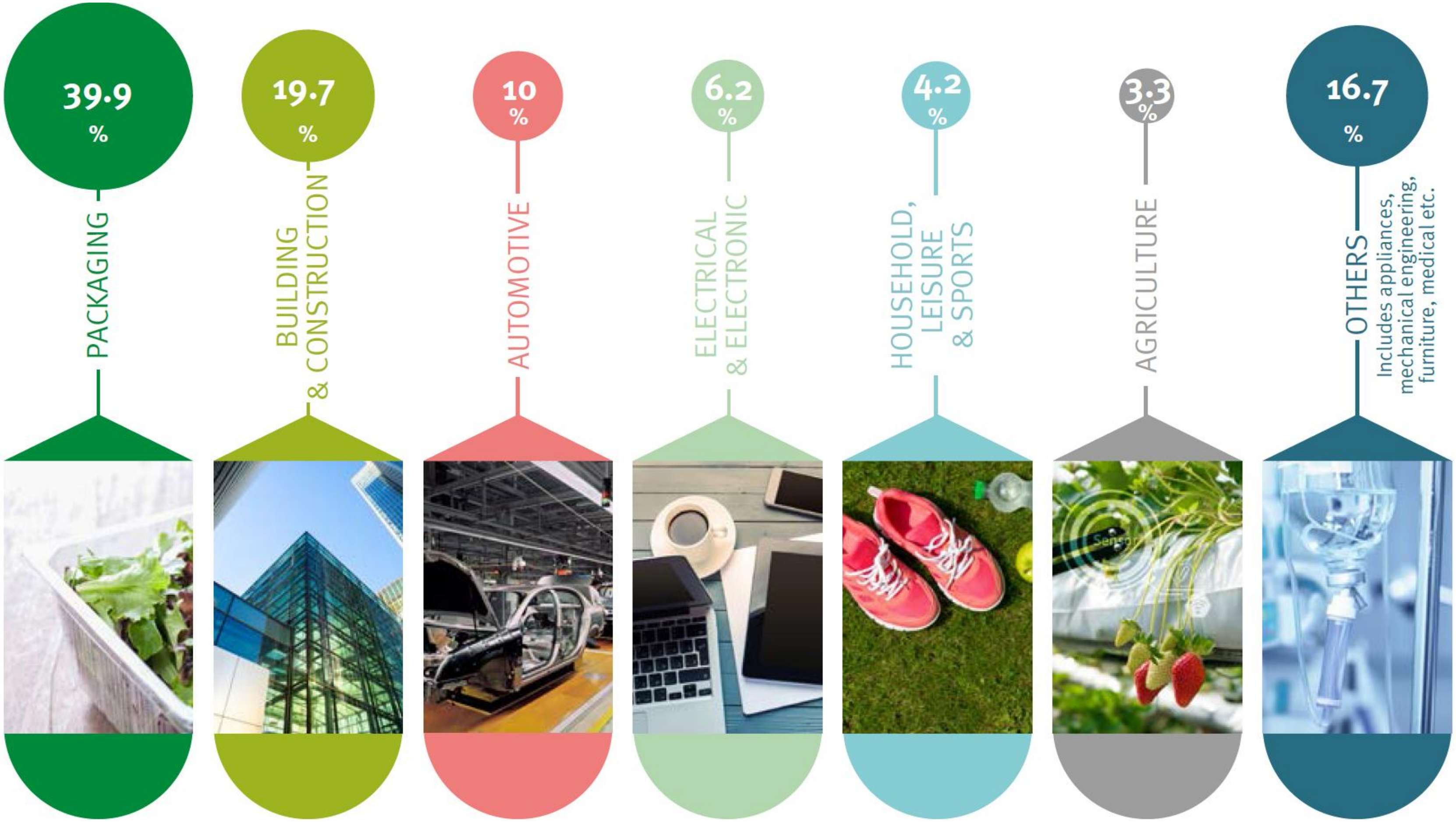


Total: 58.000.000 ton. (**2011**)

Plastics Converter Demand Main Market Sectors.

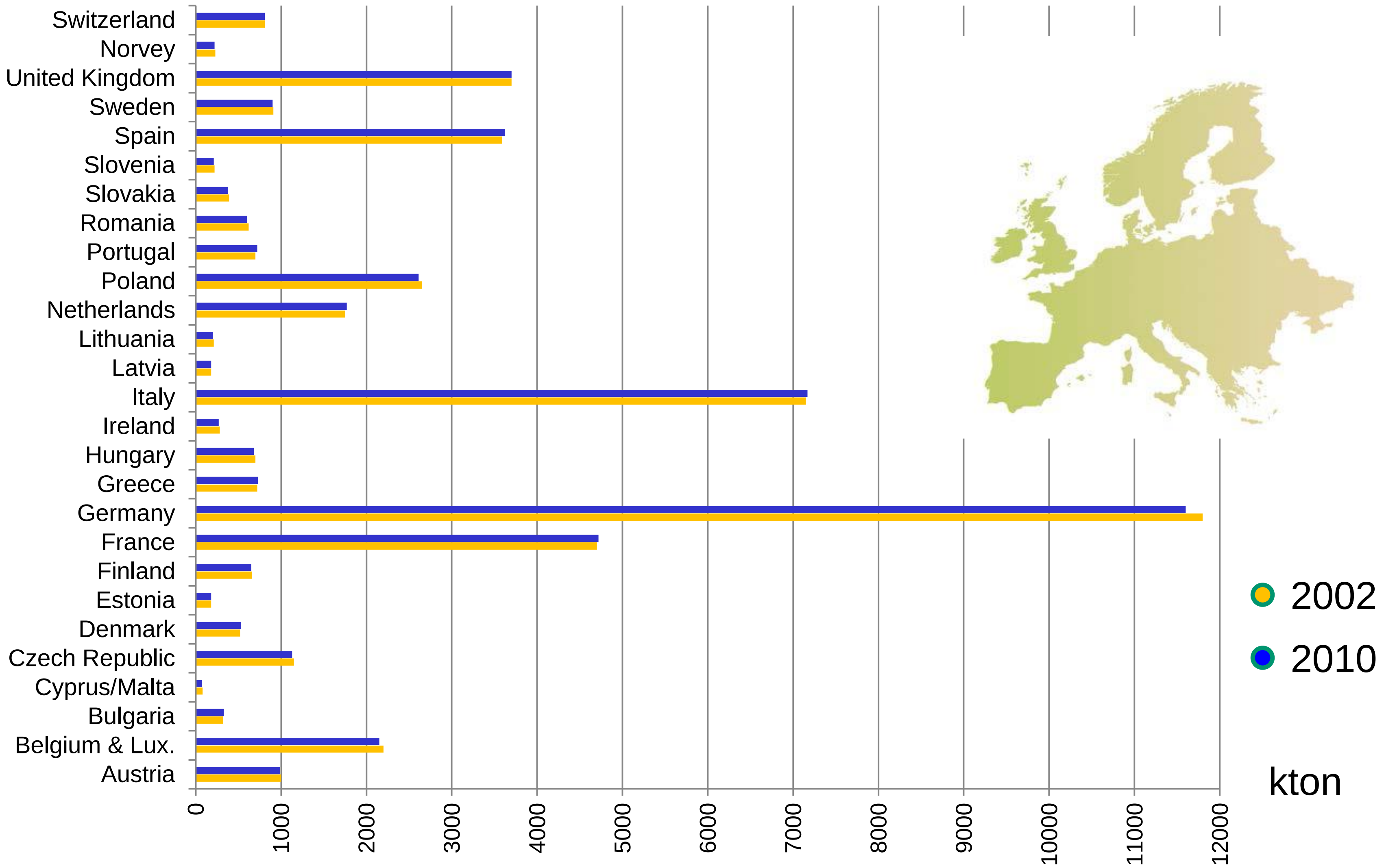
2016

Total converter demand: 49.9 MT



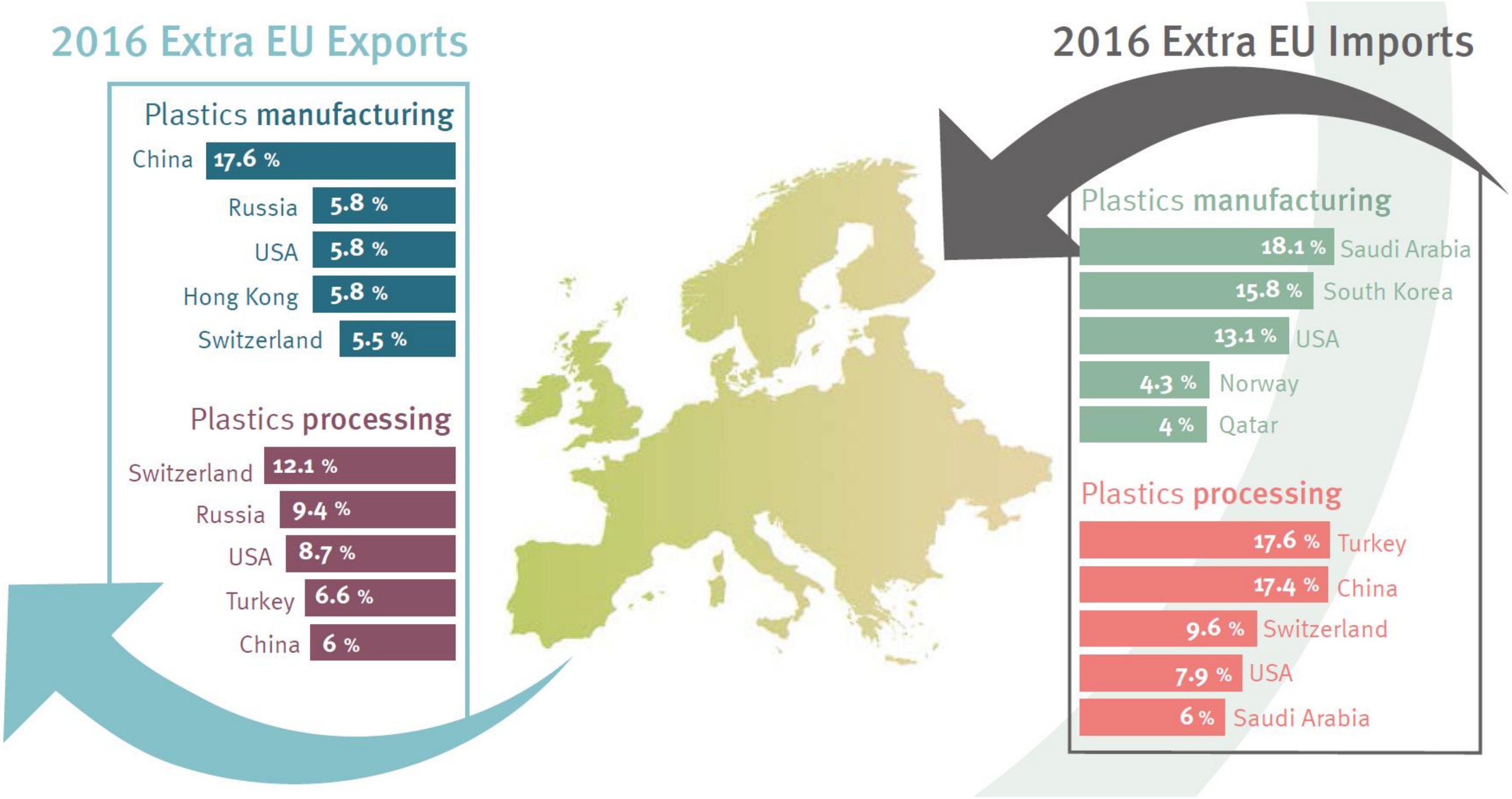
Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH

European Plastics Demand by Country (kton/year).



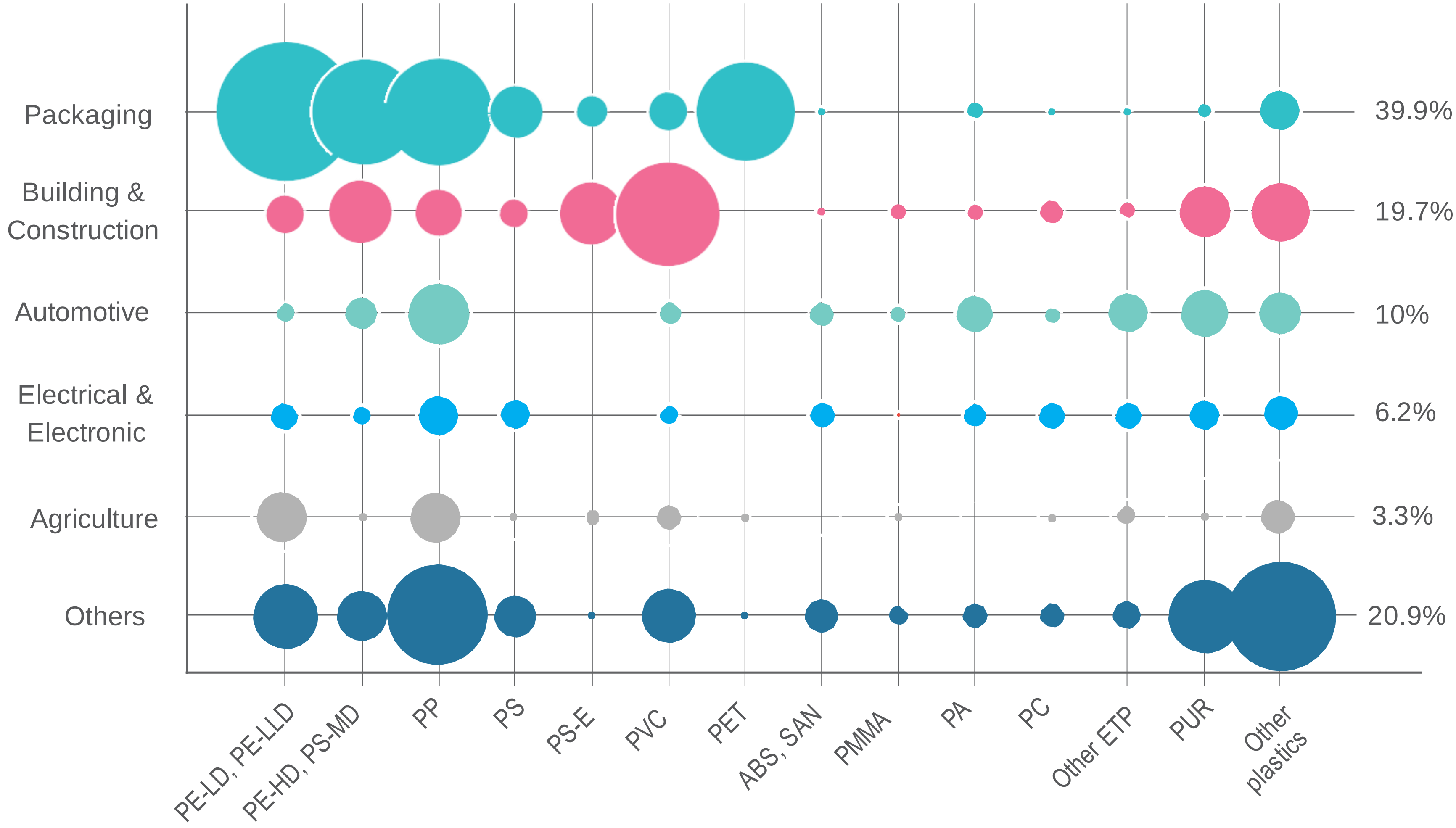
Source: PlasticsEurope Market Research Group (PEMRG)

Top Extra EU Trade Partners of Plastics in Value.



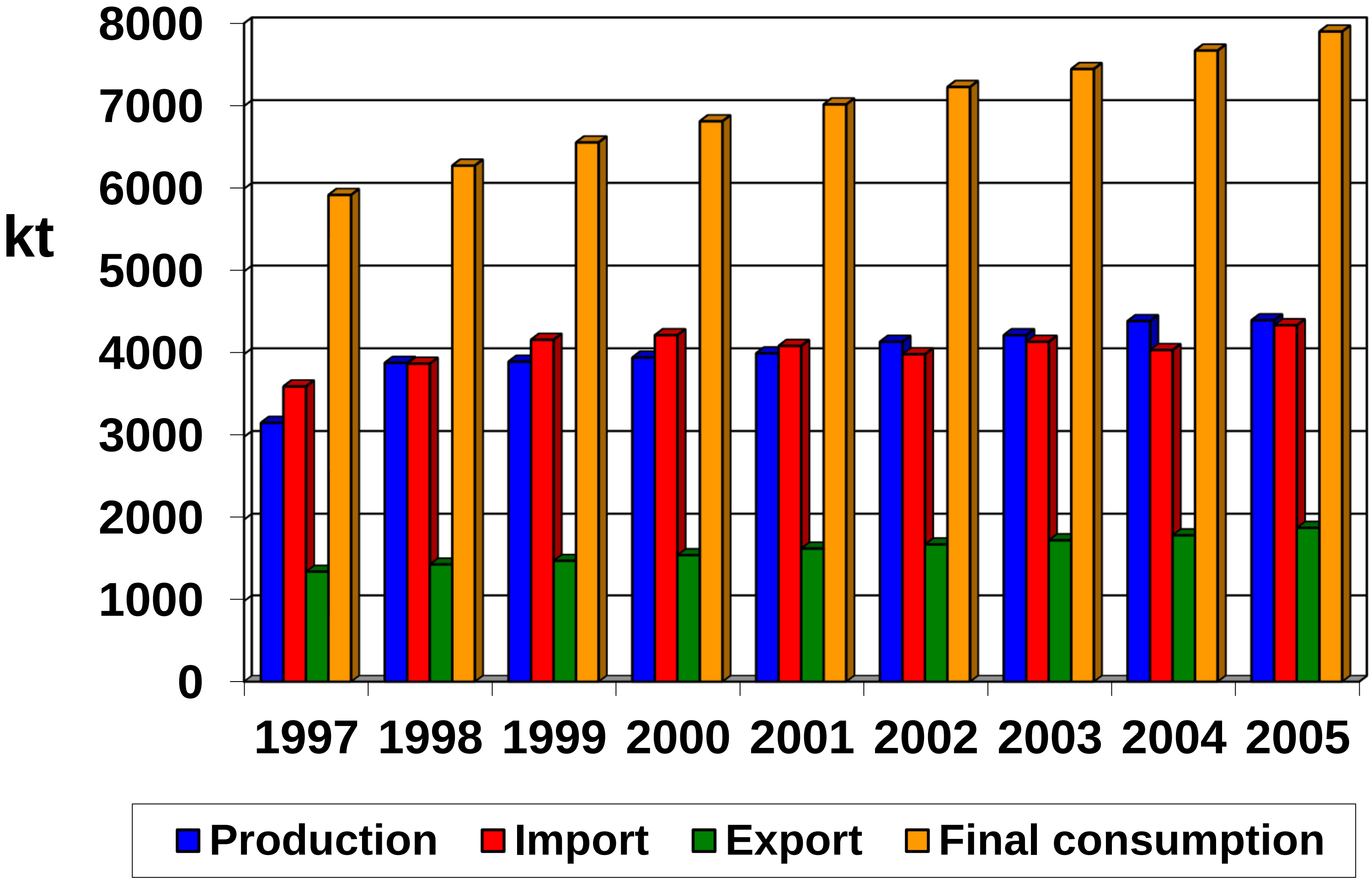
Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH

European plastics converter demand by segments and polymer types in 2016.

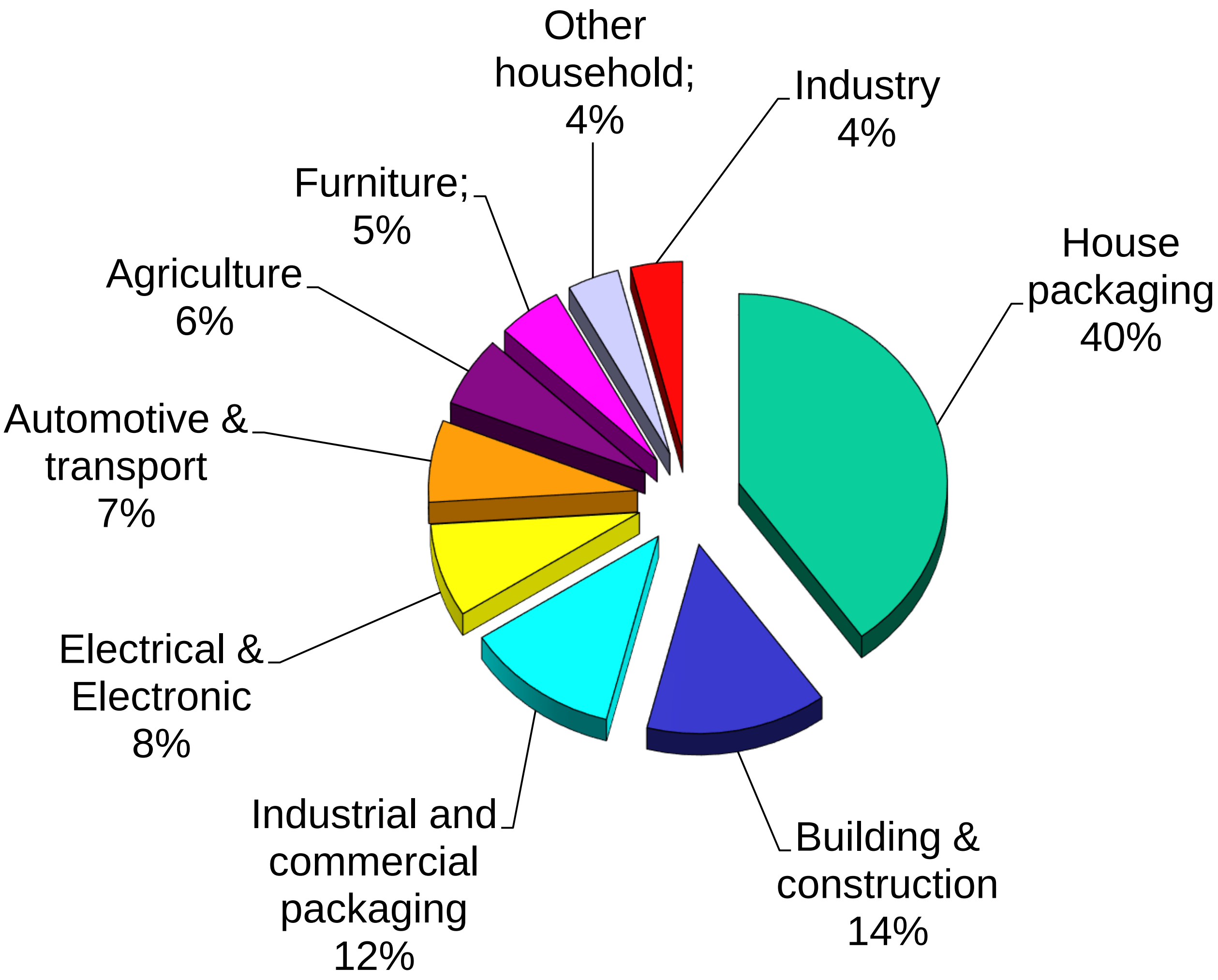


Source: PlasticsEurope (PEMRG) / Conversio Market & Strategy GmbH

Production and Consumption of Plastics in Italy.



Plastics Uses in Italy by Segments (2010).



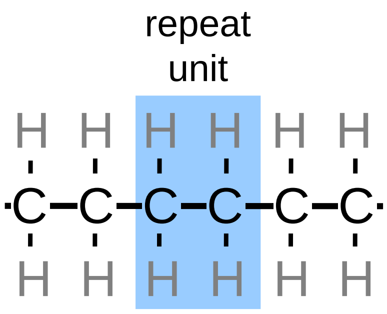
POLITECNICO DI MILANO

Polymers: Synthetic Methods and Manufacturing.

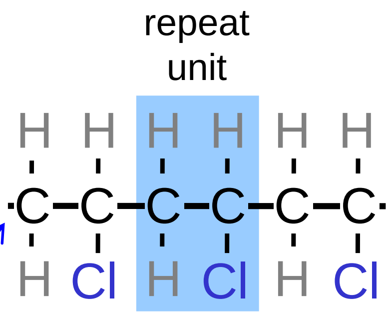
What is a Polymer?

Poly mer

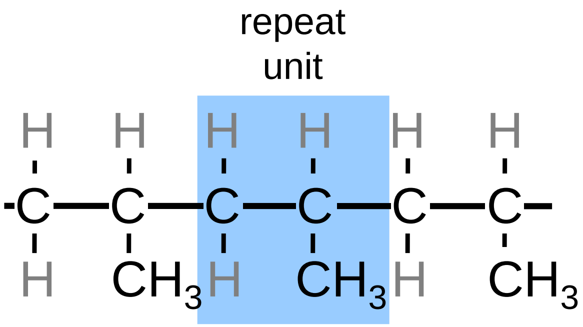
many repeat unit (building blocks)



Polyethylene (PE)



Poly(vinyl chloride) (PVC)

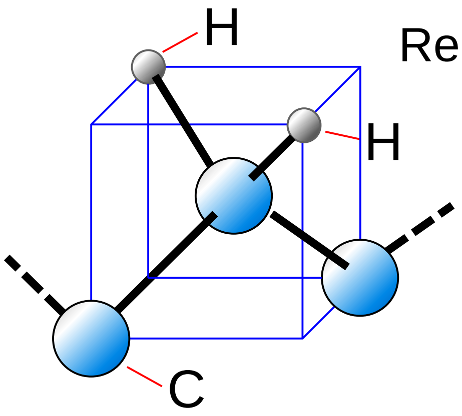


Polypropylene (PP)

Only carbon chain backbone

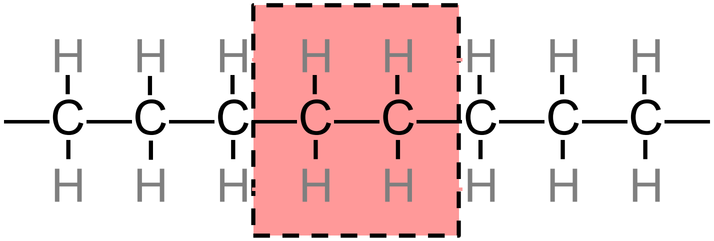
Polymer (from Greek terms = “poly” + “mer”) means several units and emphasizes what the polymer is: a long chain (macromolecule) of one, two or occasionally more units of small identical molecules bonded together. The term “Polymer” firstly used by Berzelius in 1833.

Structure of Polyethylene.

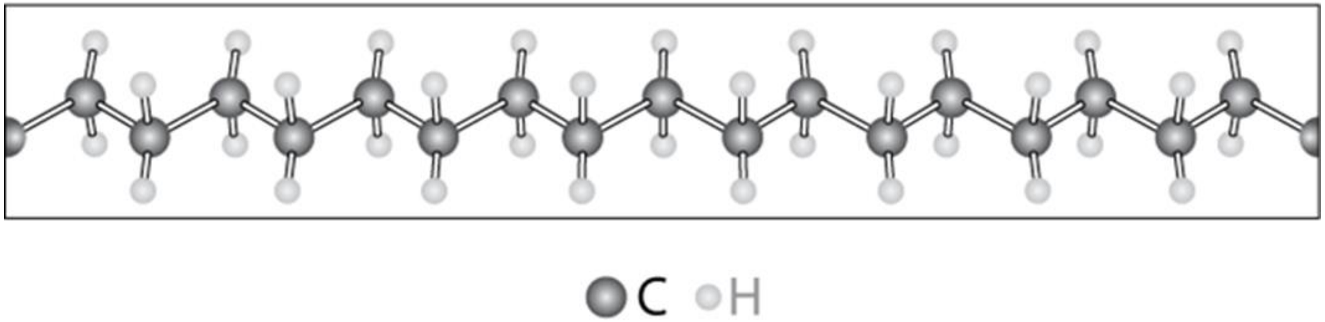


Tetrahedral arrangement of -CH_2- unit

Repetitive Unit



Repetitive Unit



- Polyethylene is a long-chain hydrocarbon.
- Top figure shows repeat unit and chain structures.
- Other figure shows zigzag backbone 3D structure.

Polymer Classification.

Polymers consist of high molecular weight molecules, generally organic, known as macromolecules.

Macromolecules originate by bonding a large number of small units, called monomers, to form very long chains.

- Main synthetic polymers are old of ~100 years, some were discovered more recently (<50 years).

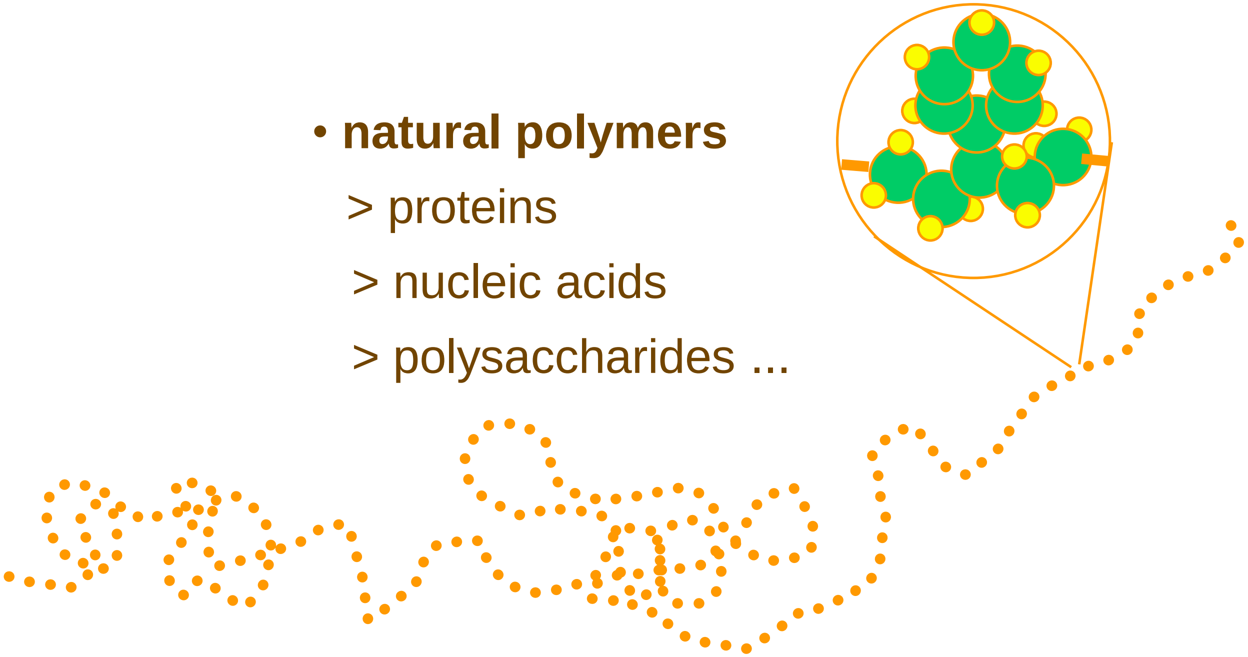
- Major classes:
  - plastics
  - rubber
  - coatings
  - adhesives
  - fibers

• natural polymers

> proteins

> nucleic acids

> polysaccharides ...



Definitions.

A. According to the amount of repeating units

- **monomer** : one unit
- **oligomer** : few units
- **polymer** : many units (poly – several, mer – part)
- **telechelic polymer** : polymer containing reactive end group

  (tele = far, chele = claw)
- **telechelic oligomer** : oligomer containing reactive end group
- **macromer (= macro monomer)** : monomer containing long chain

Definitions (2).

B. DP : Degree of polymerization

The total number of repeating units in the polymer chain including terminal group

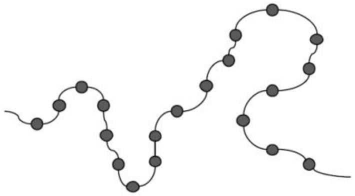
C. The kinds of applied monomers

- One kind : Homopolymer
- Two kinds : Copolymer
- Three kinds : Terpolymer

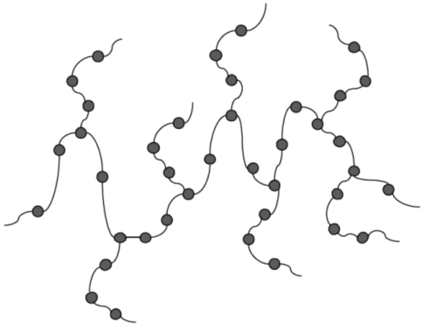
D. The space arrangement of chains

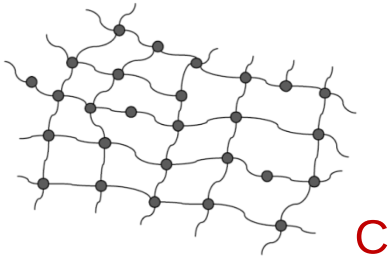
- Linear
- Branched
- Crosslinked

Linear polymer



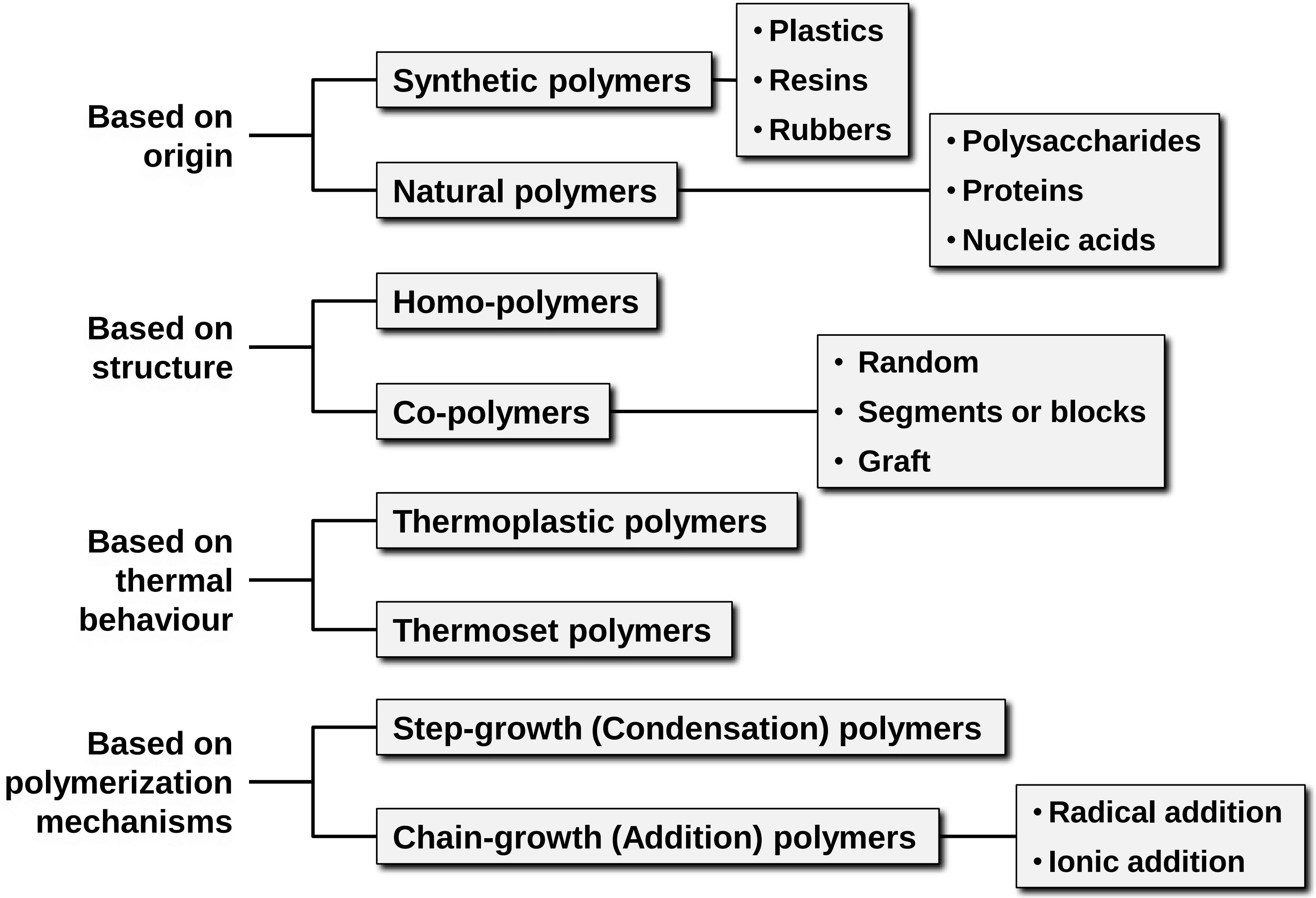
Branched polymer





Crosslinked polymer

Polymer Classification.



Based on origin

- Synthetic polymers
  - Plastics
  - Resins
  - Rubbers
- Natural polymers
  - Polysaccharides
  - Proteins
  - Nucleic acids

Based on structure

- Homo-polymers
- Co-polymers
  - Random
  - Segments or blocks
  - Graft

Based on thermal behaviour

- Thermoplastic polymers
- Thermoset polymers

Based on polymerization mechanisms

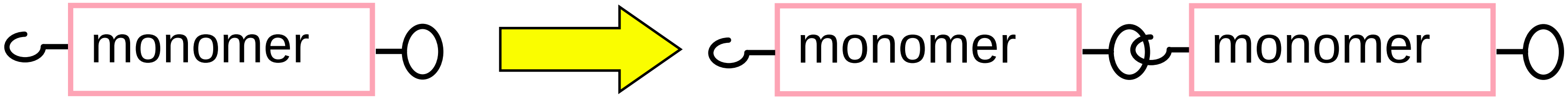
- Step-growth (Condensation) polymers
- Chain-growth (Addition) polymers
  - Radical addition
  - Ionic addition

Homopolymers and Copolymers.

Monomeric units (or Base Units) are repeating units in the polymer:

- Polymers are made by one or more monomeric unit.
- These are bonded together to form a chain.
- The monomeric units must be bifunctional – they must have two functional groups or a double bond to form long chains.

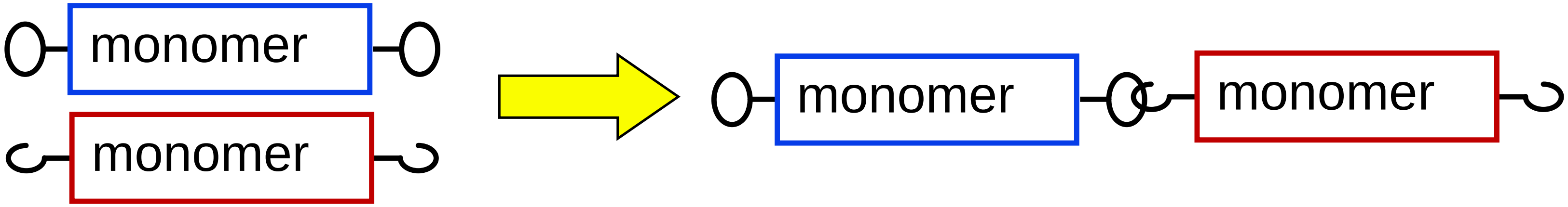
Homopolymer:



monomer

monomer monomer

Copolymer:



monomer

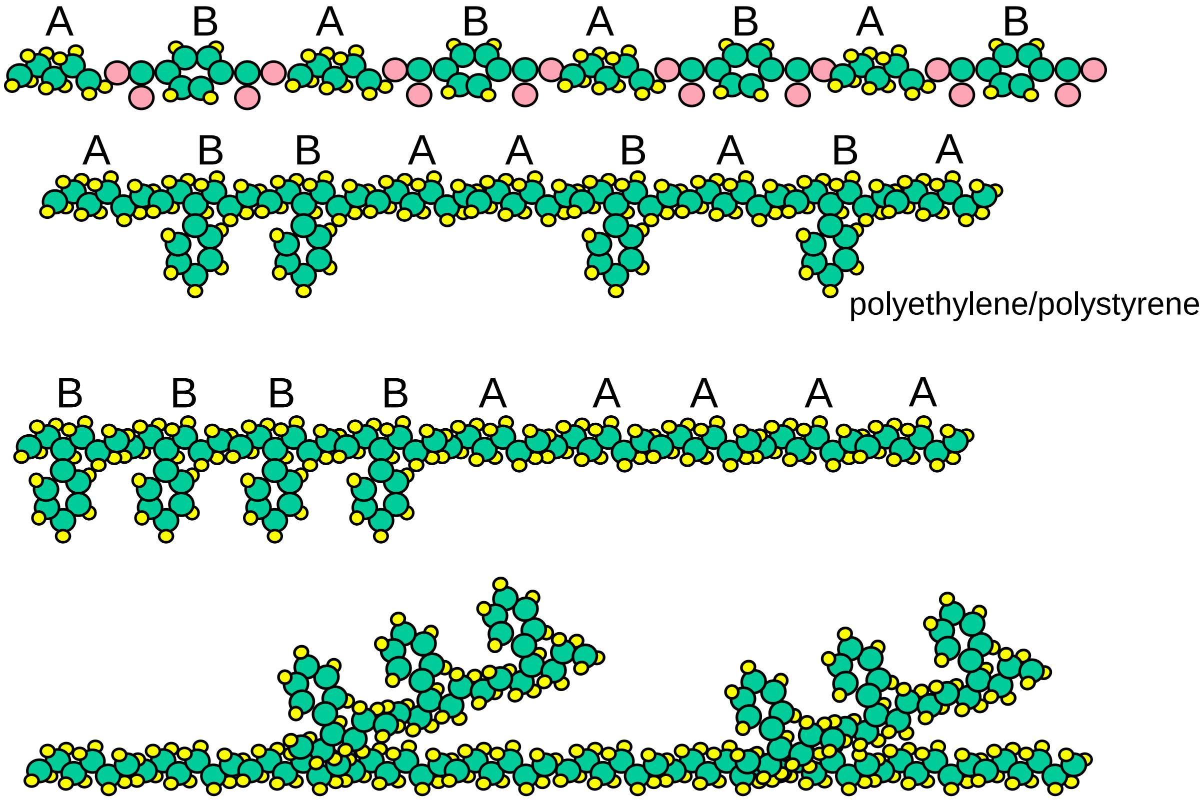
monomer

monomer monomer

Copolymers.

When multiple subunit are used to assemble a polymer, the result is called a copolymer.

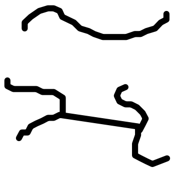
- Types of copolymer:
  - Alternating
  - Random
  - Block
  - Graft



Structures and Chemistry of Polymers.

E. Representation of polymer types and architectures:

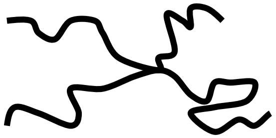
- Linear
- Branch
- Network ,...



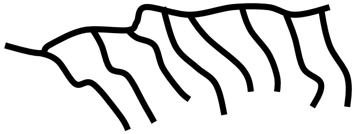
- Amorphous
- Partially crystalline

- Rigid
- Flexible

(a) star polymer

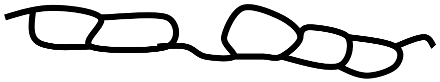


(b) comb polymer

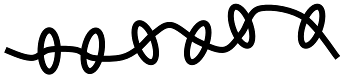


(c) ladder polymer

(d) semi- ladder polymer

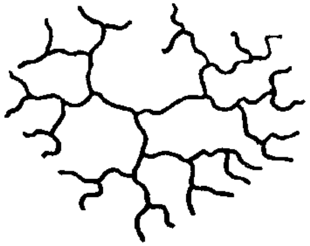


(e) polyrotaxane



(f) polycatenane

(g) dendrimer



Types of Nomenclature.

a. **Source name: to be based on names of corresponding monomer**

Polyethylene, Poly(vinyl chloride), Poly(ethylene oxide)

b. **IUPAC name: to be based on CRU, systematic name**

Poly(methylene), Poly(1-chloroethylene), Poly(oxyethylene)

c. **Functional group name: According to name of functional group in the polymer backbone**

Polyamide, Polyester

d. **Trade name: the commercial names by manufacturer, i.e. Teflon, Nylon**

e. **Abbreviation name: PVC, PET**

f. **Complex and Network polymer: Phenol-formaldehyde polymer**

g. **Vinyl polymer: Polyolefin**

Chemistry of Polymers.

- Polar
- Unpolar
- Reactivity

- Stability
  - Reorganization
  - Hydrolysis
  - Photolysis,
  - ...

- Single monomer
- Copolymer
- Intercolled (Additives)
  - plasticizers
  - antioxidant
  - …….

Classification of polymers:

- **Addition polymers: repeating units and monomers are the same.**
- **Condensation polymers: repeating units and monomers are different, by splitting out small molecule.**

Polymerization Processes.

Modern classification of polymerization processes is according to polymerization mechanism:

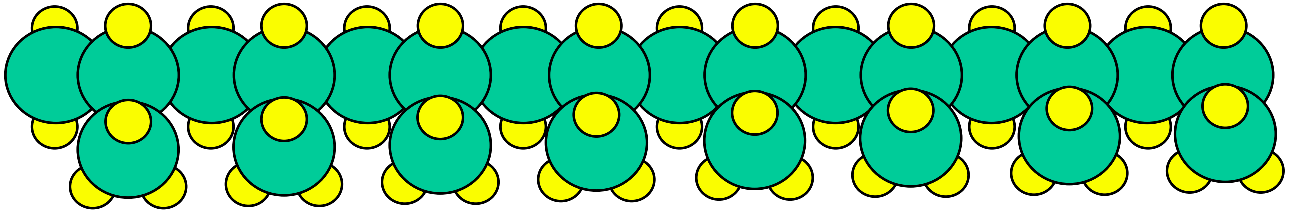
- Step growth polymerization : Polymers build up stepwise.
- Chain growth polymerization : In addition polymerization molecular weights increase successively, one by one monomer.
- Ring-opening polymerization : may be either step or chain reaction.

Stereochemistry of Polymers.

Tacticity:

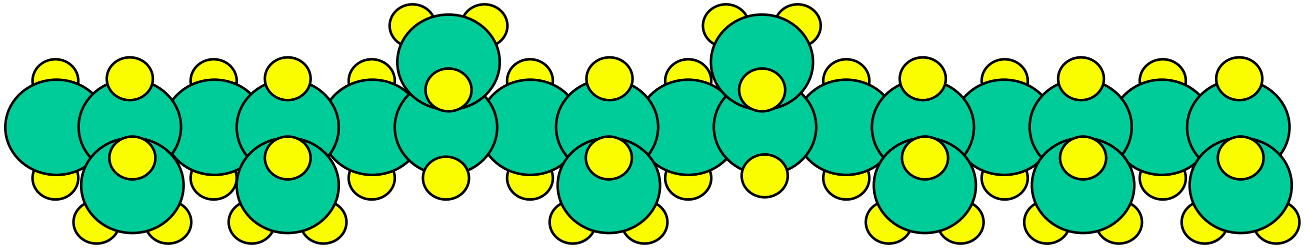
- Polymers with functional groups bonded have different properties depending on the structure of the insertion of functional group:

Isotactic:



Polypropylene (PP)

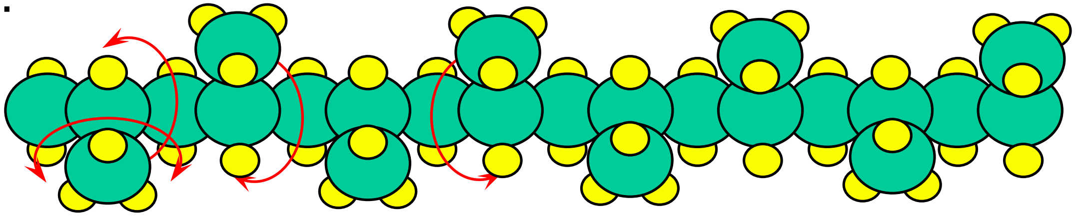
Atactic:



Polymers – Flexibility.

Some polymers are very flexible, others are rigid:

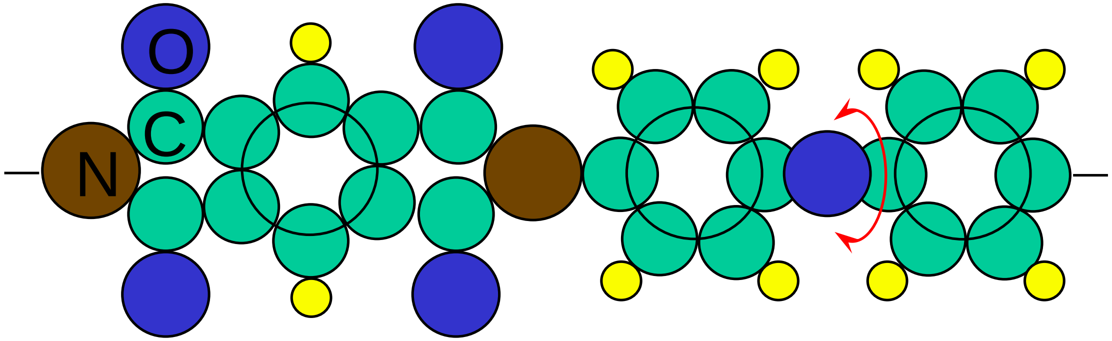
Flexible:



polypropylene

“Rigid”:

(only rotations around oxygen atom induce flexibility)



polyimide

Physical Properties of Polymers.

The physical properties of polymers depend on many factors, among which:

- the polymerization degree;
- the molecular weight and associated distribution;
- the temperature;
- the chain arrangement;
- the chemical composition.

Polymerization Degree (DP).

DP is one of the most important parameters to determine the physical properties of a polymer.

It is defined as the number of monomer units (Mer) for the linear chain of the polymer.

The relationship between molecular weight of the chain (M_P) and the degree of polymerisation is:

$$M_p = DP \times M_{Mer}$$

where M_{Mer} is the molecular weight of monomer.

Average Molecular Weight (M_n).

Each chain can have a more or less large number of monomeric units depending on the polymerization conditions.

Thus, for polymers two different average molecular weights were defined :

a) number average molecular weight M_n

$$M_n = \frac{\sum_{i=1}^{n} X_i \cdot M_i}{\sum_{i=1}^{n} X_i}$$

where X_i is the number of molecules with molecular weight M_i

(colligative property and end group analysis)

Weight Average Molecular Weight (M_w).

b) weight average molecular weight is defined as:

$$M_w = \frac{\sum_{i=1}^{n} W_i M_i}{\sum_{i=1}^{n} W_i} = \frac{\sum_{i=1}^{n} X_i M_i^2}{\sum_{i=1}^{n} X_i M_i}$$

(light scattering)

where W_i is the weight of molecules of molecular weight M_i .

Therefore, is $M_W > M_n$.

Definition of Average Molecular Weight.

c. z average molecular weight (M_z)

$$\overline{M}_z = \frac{\sum_{i=1}^{n} X_i M_i^3}{\sum_{i=1}^{n} X_i M_i^2}$$

(ultracentrifugation)

d. general equation of average molecular weight:

$$\overline{M} = \frac{\sum_{i=1}^{n} X_i M_i^{\alpha+1}}{\sum_{i=1}^{n} X_i M_i^{\alpha}}$$

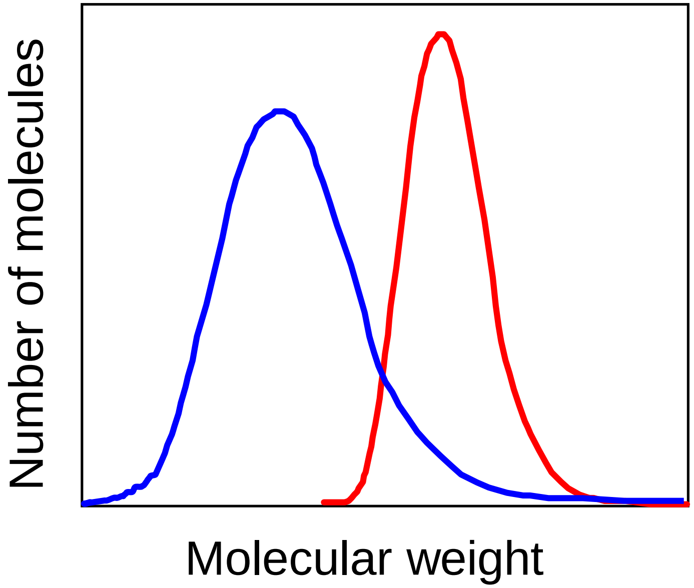
a=0 , M_n
a=1 , M_w
a=2 , M_z

e. $M_z > M_w > M_n$

Polymers – Molecular Weight.

Synthetic polymers cover a wide range of molecular weights. The MW distribution (length) influences the properties.

Several natural polymers have fixed length making them quite uniform in behaviour.

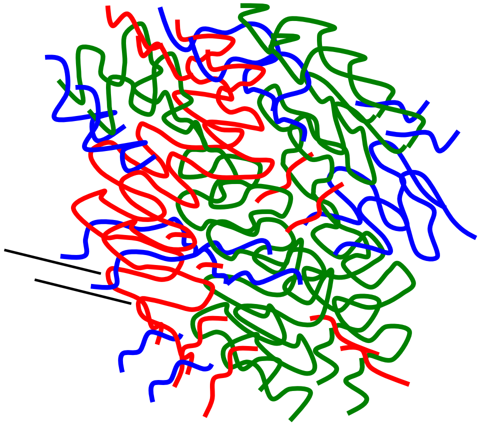


Different synthetic processes produce different distributions of molecular weight.

The heavier molecules are prone to be less soluble and to have higher melting points.

Mean number M_n = mass/mol
Mean mass $M_w = \Sigma n_i M_i^2 / \Sigma n_i M_i$

Molecular Weight and Dispersion - an Example:



Here are:
10 chains of 100 molecular weight
20 chains of 500 molecular weight
40 chains of 1000 molecular weight
5 chains of 10000 molecular weight

$$\overline{M}_n = \frac{(10\cdot100)+(20\cdot500)+(40\cdot1000)+(5\cdot10000)}{10+20+40+5} = 1347$$

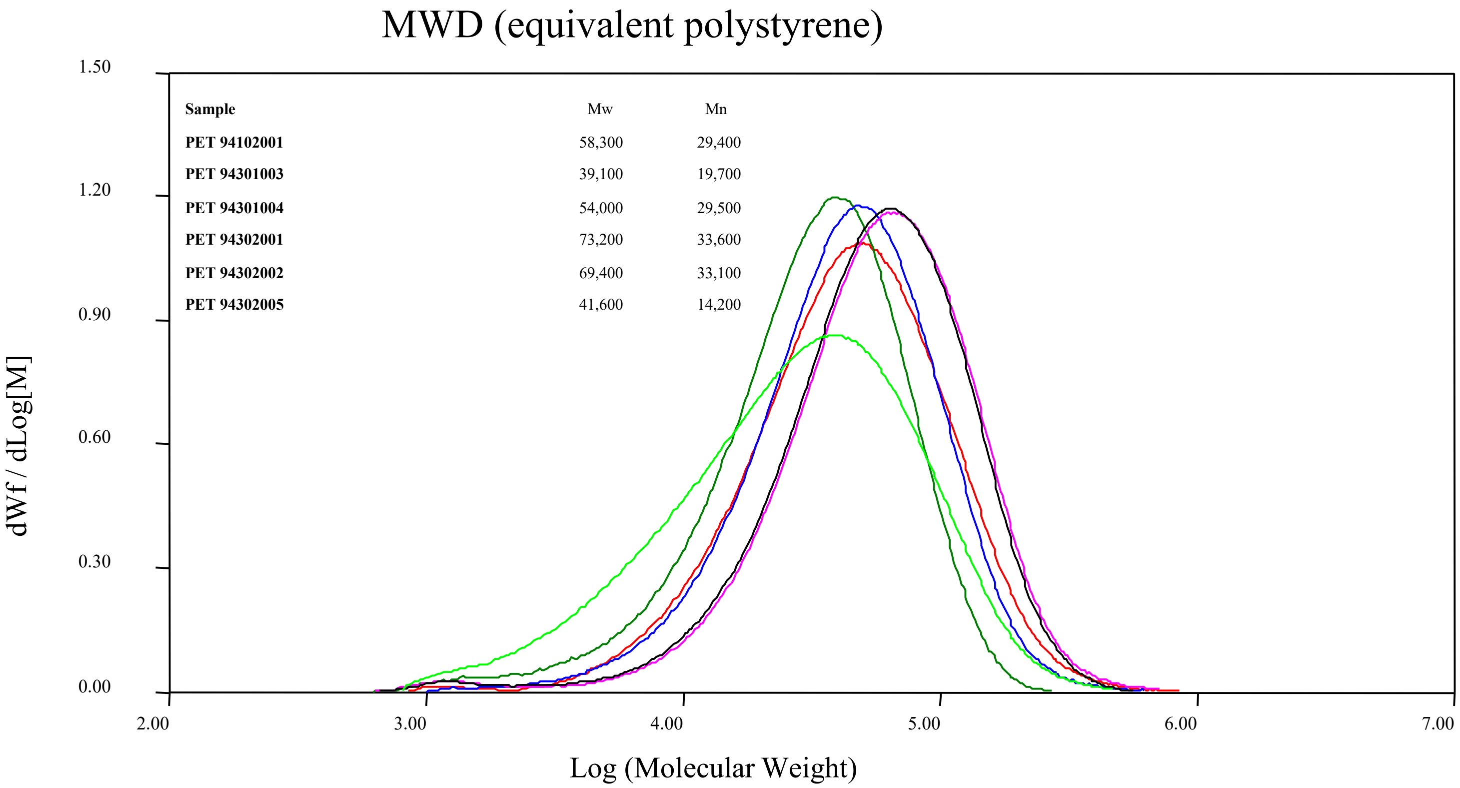
$$\overline{M}_w = \frac{(10\cdot100^2)+(20\cdot500^2)+(40\cdot1000^2)+(5\cdot10000^2)}{(10\cdot100)+(20\cdot500)+(40\cdot1000)+(5\cdot10000)} = 5390$$

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n} \approx 4$$

Determination of Molecular Weight.

- Gel Permeation Chromatography:

  Solution methodology to determine the distribution of molecular weight of a polymer. Use gel of different porosity to differentiate the macromolecules MW by migration.



MWD (equivalent polystyrene)

Sample	Mw	Mn
PET 94102001	58,300	29,400
PET 94301003	39,100	19,700
PET 94301004	54,000	29,500
PET 94302001	73,200	33,600
PET 94302002	69,400	33,100
PET 94302005	41,600	14,200

Polydispersity Index: Width of Distribution.

Polydispersity Index (PI) = $M_w/M_n \geq 1$.

It indicates the uniformity of the molecular weight distribution in a given polymer.

When the chains all have the same length the polydispersion index is equal to 1, and the polymer, which has a molecular weight well defined, is defined monodispersed.

Generally, the commercial polymers have a polydispersity index between 1.5 and 2.5.

Classification of Polymers by DP.

Physical and mechanical properties of a polymer depend both on polymerization degree and on polydispersion index.

Polymers are therefore classified depending on their degree of polymerization DP into:

- oligomers $(2<DP<100)$
- low polymers $(10<DP<100)$
- medium polymers $(100<DP<1000)$
- high polymers $(DP>1000)$.

Properties of Polymer and DP.

Dependence of polyethylene properties on polymerization degree (DP).

DP	M	T_r (°C)	Physical Aspect
70	1000	37.5	oil
280	4000	93.0	waxy
500	7000	98.0	malleable solid
850	12000	104.0	stiff solid
1500	21000	110.0	stiff solid
2700	38000	112.0	stiff solid

M, molecular weigh; T_r, softening temperature.

If polymer is linear, the increase of DP causes the raising of the softening temperature (T_r) resulting in the improvement of the mechanical properties of the material.

The increase in chains length, in fact, increases both the bonds which bind together the chains themselves, and the ones which oppose their sliding when the material is subjected to a force.

Polymer Properties and DP.

The characteristics of a polymer depend strictly on uniformity degree of molecular weight, i.e. from dispersion index.

Therefore a typical target for industry is to found production methods which provide polymers with a minimum degree of dispersion.

The shorter molecules, in fact, work as plasticizers and, consequently, decrease the melting temperature and the glass transition temperature, therefore polymer stiffness.

This effect is due to the relative mobility of small molecules which limit an efficient packaging in the crystal formed by assembling longer chains.

Effect of Temperature.

Polymers undergo substantial changes in their properties on temperature.

Crystalline materials at melt temperature convert from solid state to liquid state.

The transition is more complicated in the case of amorphous or non-crystalline materials owing to the reduced mobility of the constituent molecules.

Effect of Temperature (2).

Amorphous polymeric materials, increasing temperature, show two transitions which occurs around two temperature intervals called, respectively

- Glass transition (T_g);
- Melt transition (T_r).

Glass transition T_g represents the transfer state from a situation in which the polymer is relatively rigid (glassy state) to a situation of extended movement, represented by a rubbery state.

The melting represents on the contrary the transition from the rubbery state to a liquid state.

Effect of Temperature (3).

in the case of a partially crystalline polymer, the glass transition induces minor alteration to the mechanical properties of the material.

The properties, however, become much worse when polymer melt (T_m, melting temperature).

In the case of a three-dimensional crosslinked polymer there are no glass and melting transitions.

For these materials, in fact, no significant changes of properties are observed increasing temperature, obviously above the limit of chemical stability.

For all types of polymeric materials exist a limit temperature of chemical stability (T_L) beyond which the polymer undergoes irreversible transformations and/or degradations.

Effect of Temperature (4).

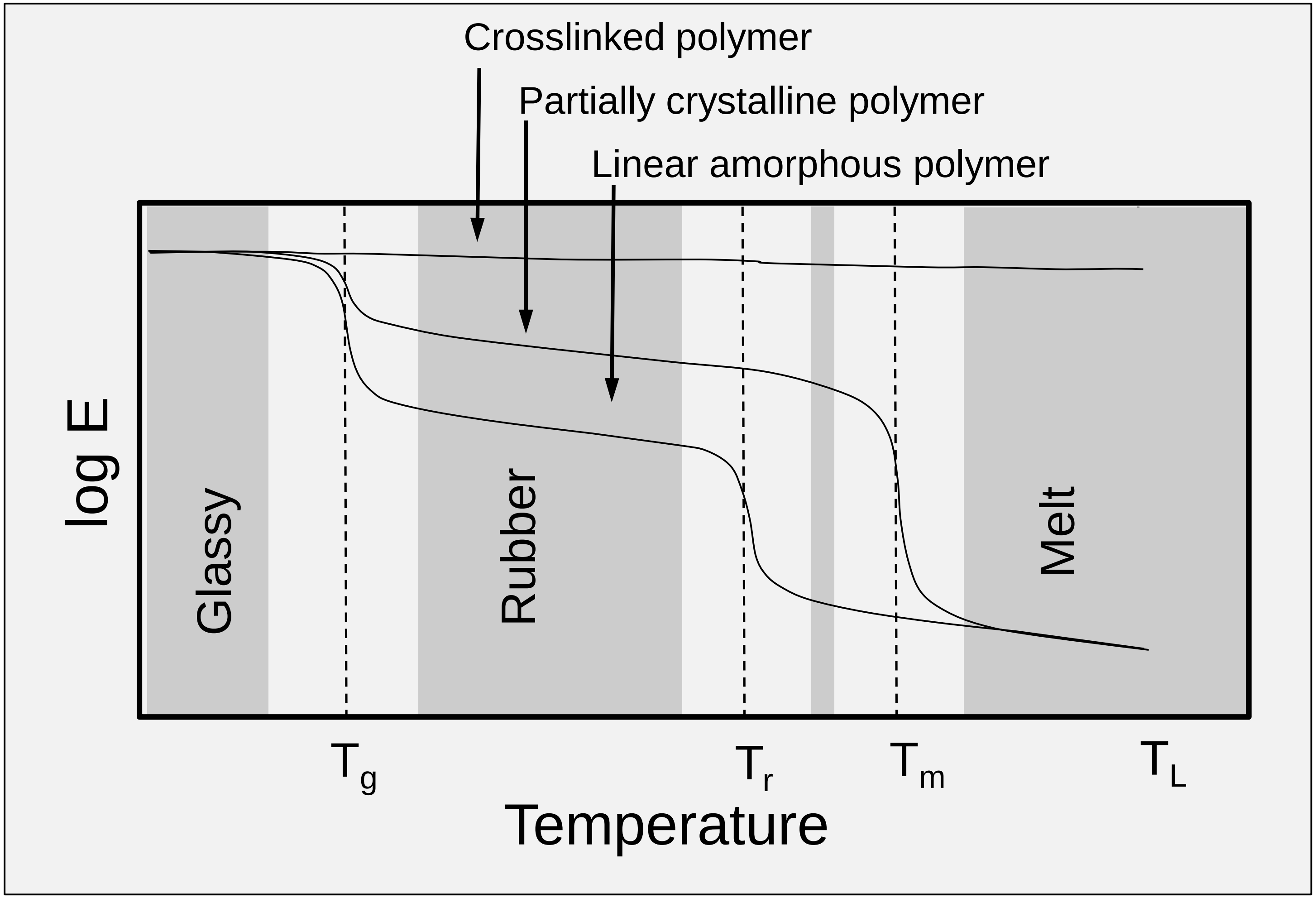
The behavior just described are the basis of the classification of the polymers in thermoplastic and thermosetting.

Thermoplastic, having both linear or branched chains, have a T_g and T_r well defined, and are plastically mouldable in the interval between the two transition temperatures.

Thermosetting, on the contrary, formed by crosslinked chains, after a certain stage of the manufacturing process are not more mouldable.

Moreover, heating these materials causes their further hardening, given that, during the processing and forming of the polymer into the mold, the heat applied causes the cross-linking between the chains.

Effect of Temperature (5).



The Appearance of a Polymer.

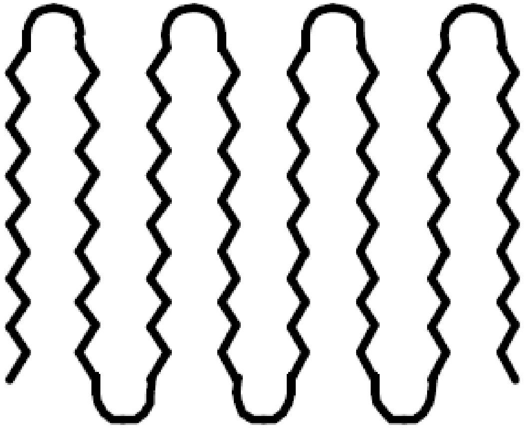
Depends strictly on position and mobility of constituent chains.

Two aspects characterize each filament:

- ✓ the chain structure, if it is linear (extended chain), or folded (folded chain), or random coil;
- ✓ the nature of interactions between the different chains, originated by Van der Waals, dipole-dipole, ionic, hydrogen bonds, etc. forces.

Chain Structure.

Extended Chain
(fibrous polymer)



Folded Chain
(crystalline polymer)

Bonds in Polymers.

Primary bonds in polymers are covalent.

Bonds between chains:

- covalent (crosslink between chains)
- van der Waals (week interactions induce crystallization)
- hydrogen

Typical primary bonds:

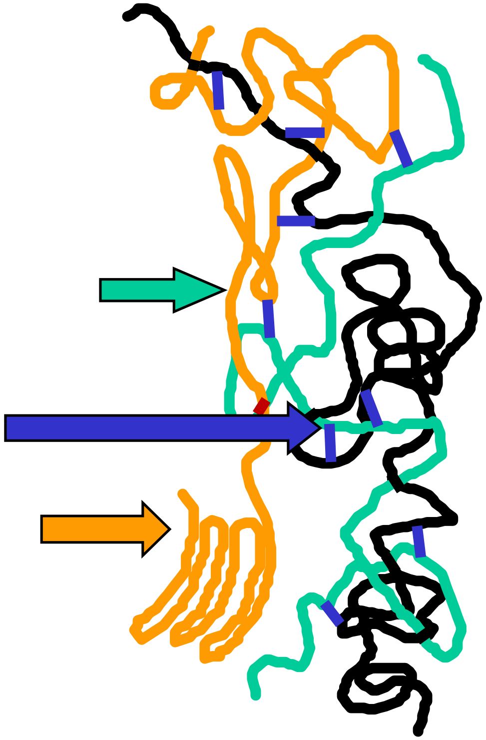
- -C-C- -C-N- -C-O- -C-H -C=O -C=N- ...

Typical crosslinking:

- - S-S- ...

Typical van der Waals bonds:

- >C=O**:**··· H-N< [a dipolar interaction]



Physical State of a Polymer.

In polymers, the characteristic which conditions mostly the properties at the solid state is the size of molecules.

In fact, in the transition from the liquid state to the solid state:

- the viscosity of a polymeric material increases;
- the macromolecules, owing their sizes, show difficulty to move and to settle down with sufficient order to form a crystal.

Therefore:

- ☐ the long chains tangle and polymers cannot reach, unless in rare and specific cases, the limit situations, corresponding to perfect crystalline state and to the fully amorphous state;
- ☐ As the temperature changes, polymers pass from the vitreous to semi-fluid state.

Fibers.

Fibers are long, fine, and threadlike materials.

Typical examples are represented by natural fibers i.e. cotton, wool, silk, etc.

Peculiar characteristic of fibers is the considerable extension resistance to stretching in the direction of the fiber itself.

At molecular level, fibers consist of long linear polymeric chains, which lie lined in the direction of the fiber itself.

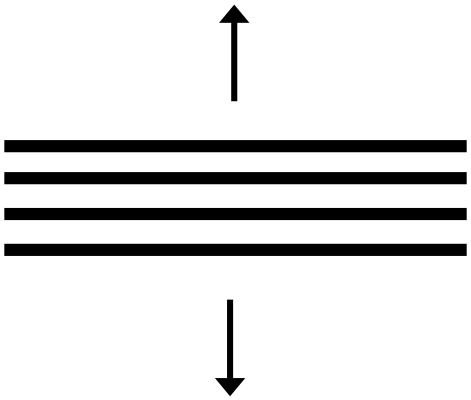
Therefore:

- the resistance of a fiber to the stretching is given by the strength of the covalent bonds of the polymer chain;
- the stability of the structure depends on the intermolecular forces of attraction (hydrogen bonds, dipole-dipole forces, Van der Waals forces) which prevent the folding of the extended chains.

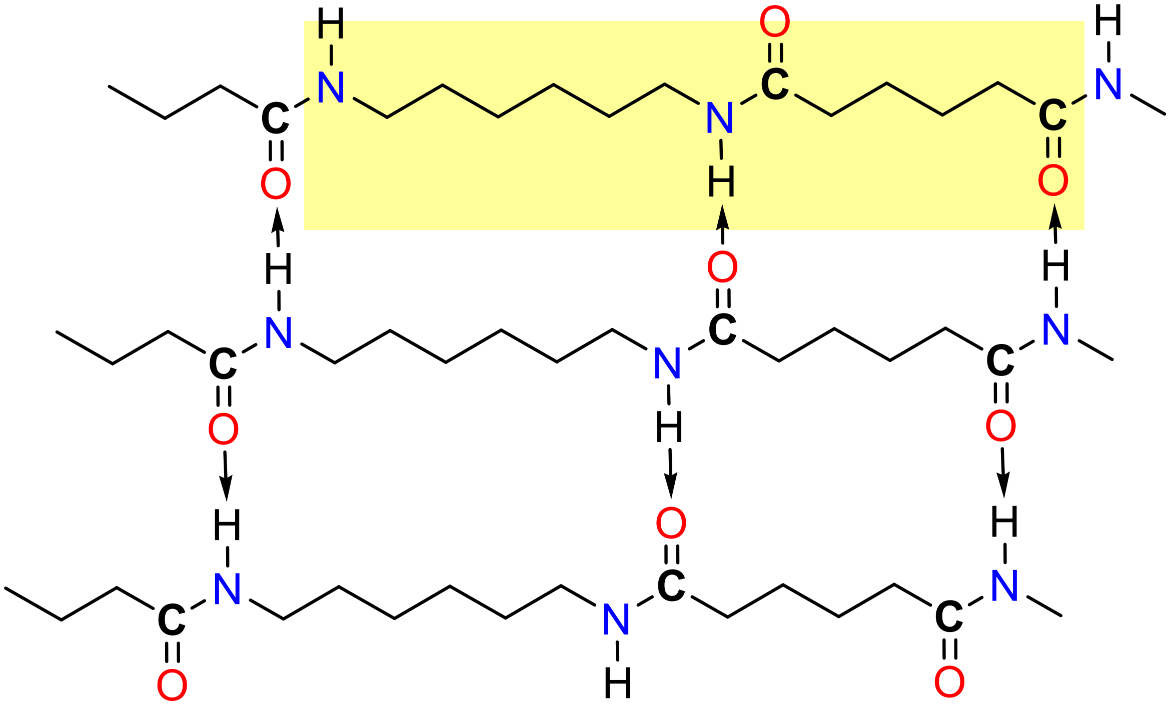
Fibers (2).

High resistance to the extension in the direction of the fiber.

Low tensile strength in the direction perpendicular to the fiber itself.



Fibrous Polymers.

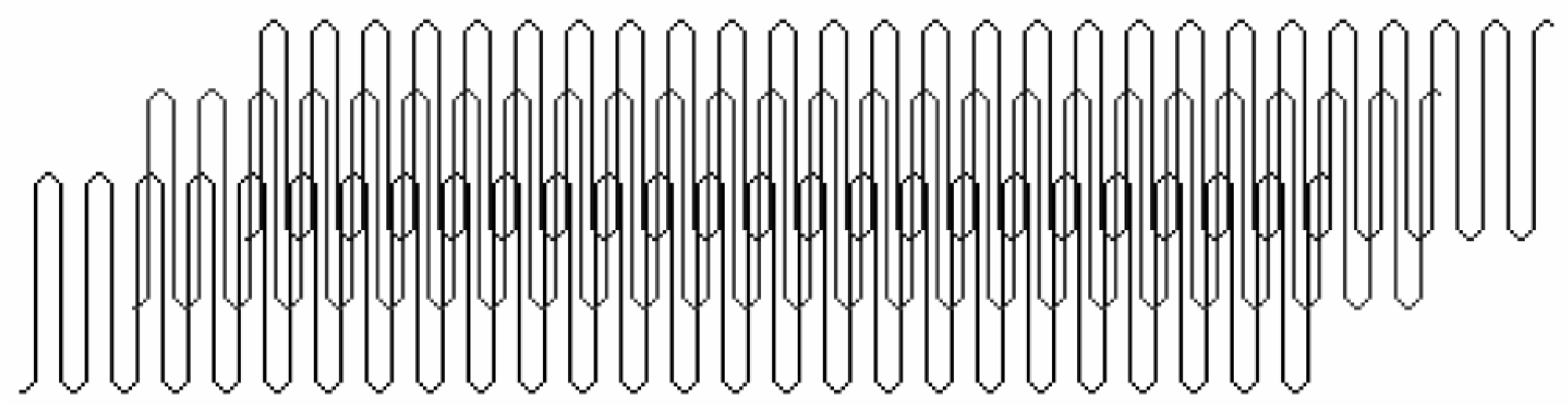


Nylon-6,6

Main Fibrous Polymers.

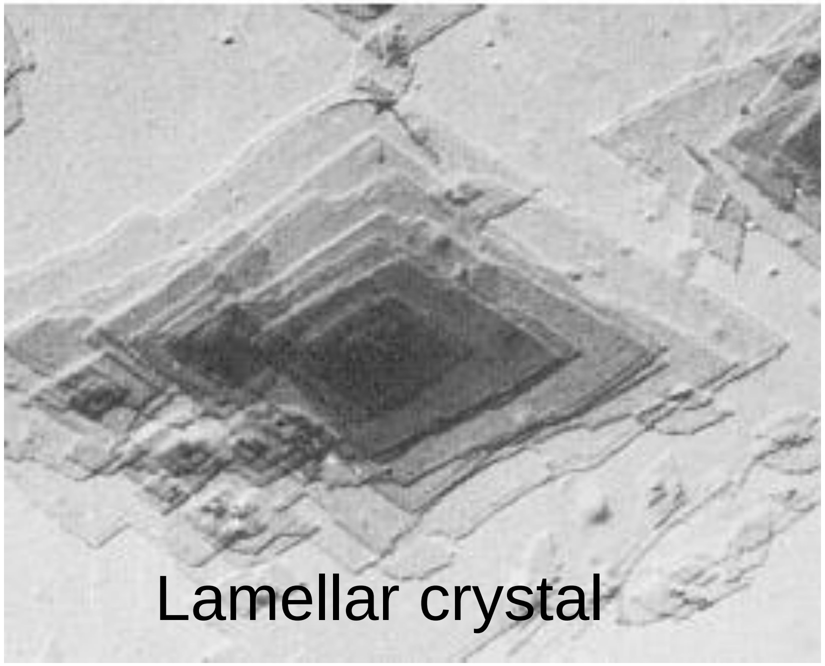
- Polyamides (Nylon, Kevlar)
- Polyethylene (HDPE, UHMWPE)
- Polypropylene isotactic
- Polyesters (poly-ethylenterephthalate)
- Polyacrylonitrile
- Cellulose
- Polyurethanes

Crystalline Polymers: Lamellar Structure.



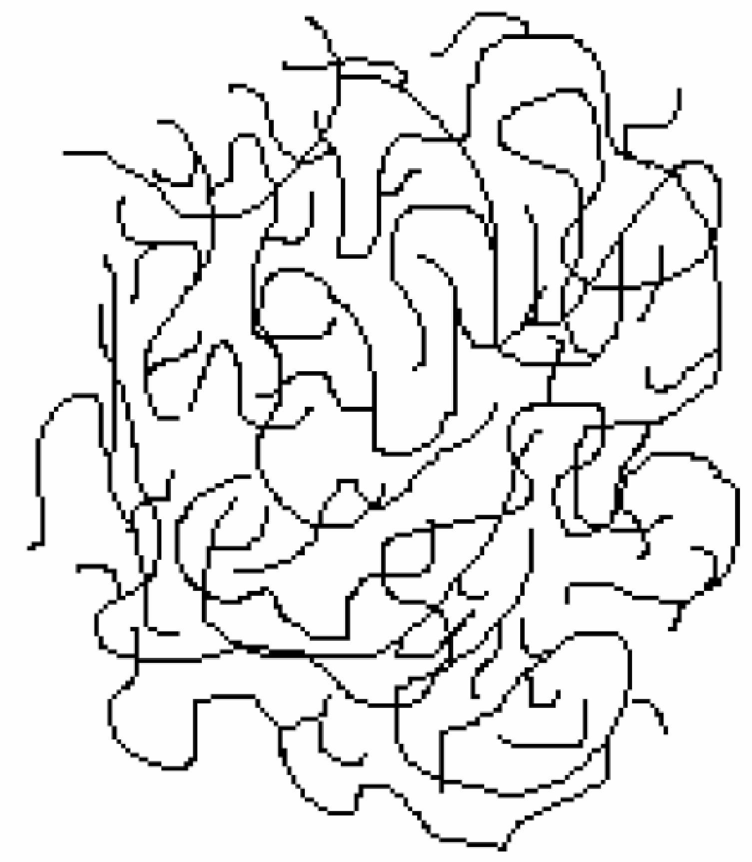
Regular polymers can form lamellar crystals with thickness of 10-20 nm in which the parallel chains are perpendicular to the crystal face.

Crystalline Polymers: Lamellar Structure (2).



- ➢ Syndiotactic Polystyrene
- ➢ Nylon
- ➢ Kevlar
- ➢ Polyketons

Amorphous Polymers.



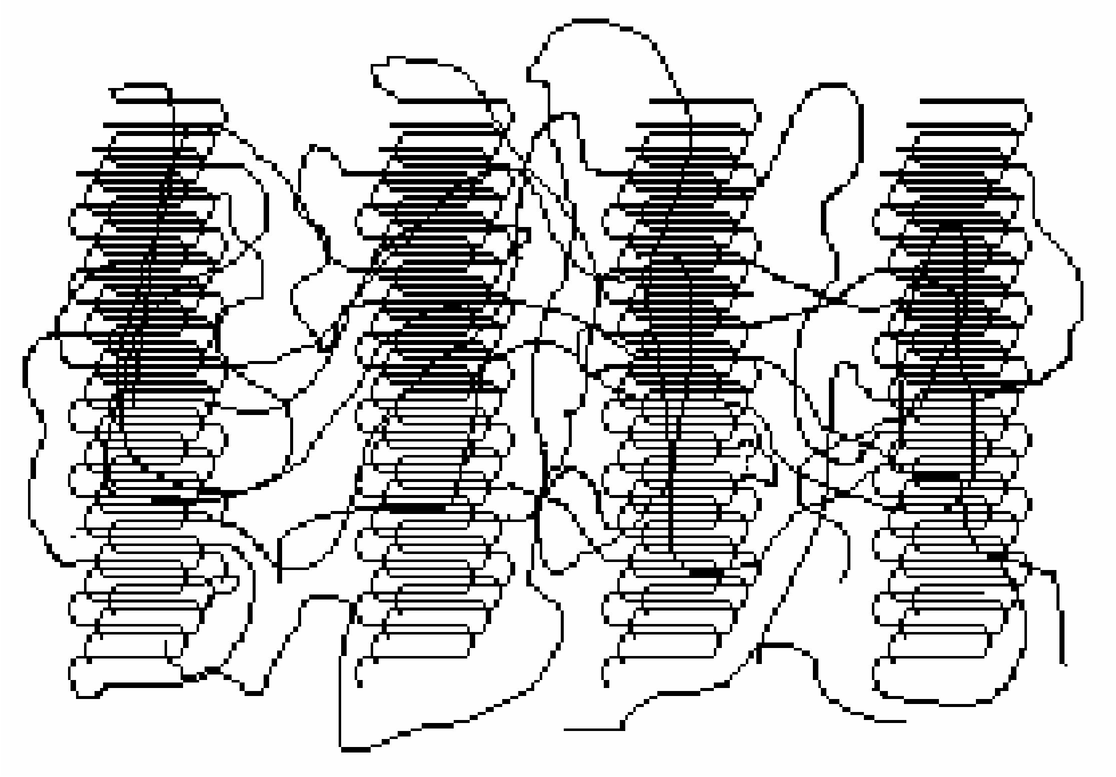
The polymeric chains with branch or side groups irregularly arranged are unable to wrap with a sufficient order to form a crystal.

Highly Amorphous Polymers:

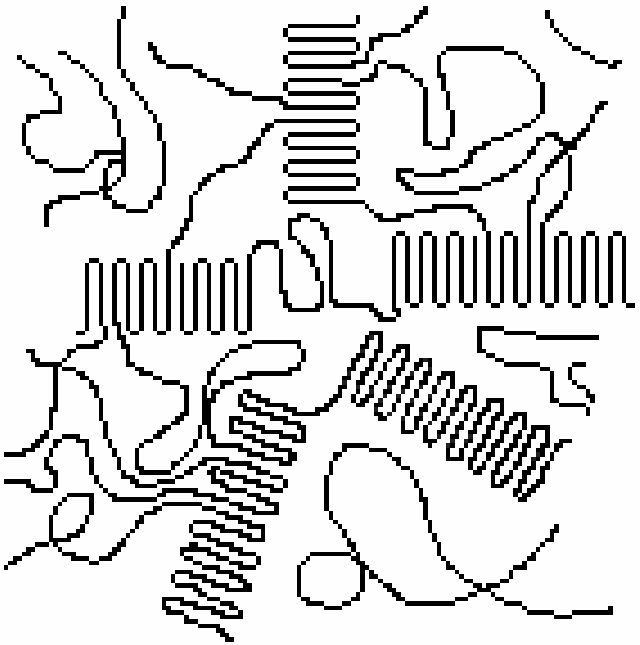
- Poly-methylmethacrylate
- Polystyrene atactic
- Polycarbonates
- Poly-isoprene
- Poly-butadiene

Semi-Crystalline Polymers.

They assume structure in which are present crystalline (lamellar) zones, called crystallites, inserted in amorphous zones.



Semi-Crystalline Polymers and Crystallinity Degree.



Spherulites (from Greek sphaira = ball and lithos = stone): the lamellar regions develop in three directions.

Crystallinity degree is defined as the weight percent of the crystalline state matter to the overall weight.

It depend on the:

- structure of composing molecules;
- mechanical and thermal history of the material.

Crystallinity Degree of a Polymer.

In general, the degree of crystallinity:

- is very high in polymers having non-branched linear structure;
- decreases dramatically for strongly asymmetrical or highly branched monomers, or in polymers with frequent interconnections, i.e. crosslinked.

A high degree of crystallinity end up in a higher packing of the chains resulting in increased density, stiffness, hardness, resistance to friction, to wear, to environmental aggression and to creep, i.e. to a slow and progressive deformation of the material exposed to constant stress.

Elastomers.

As the fibers they are formed by long and thin molecules.

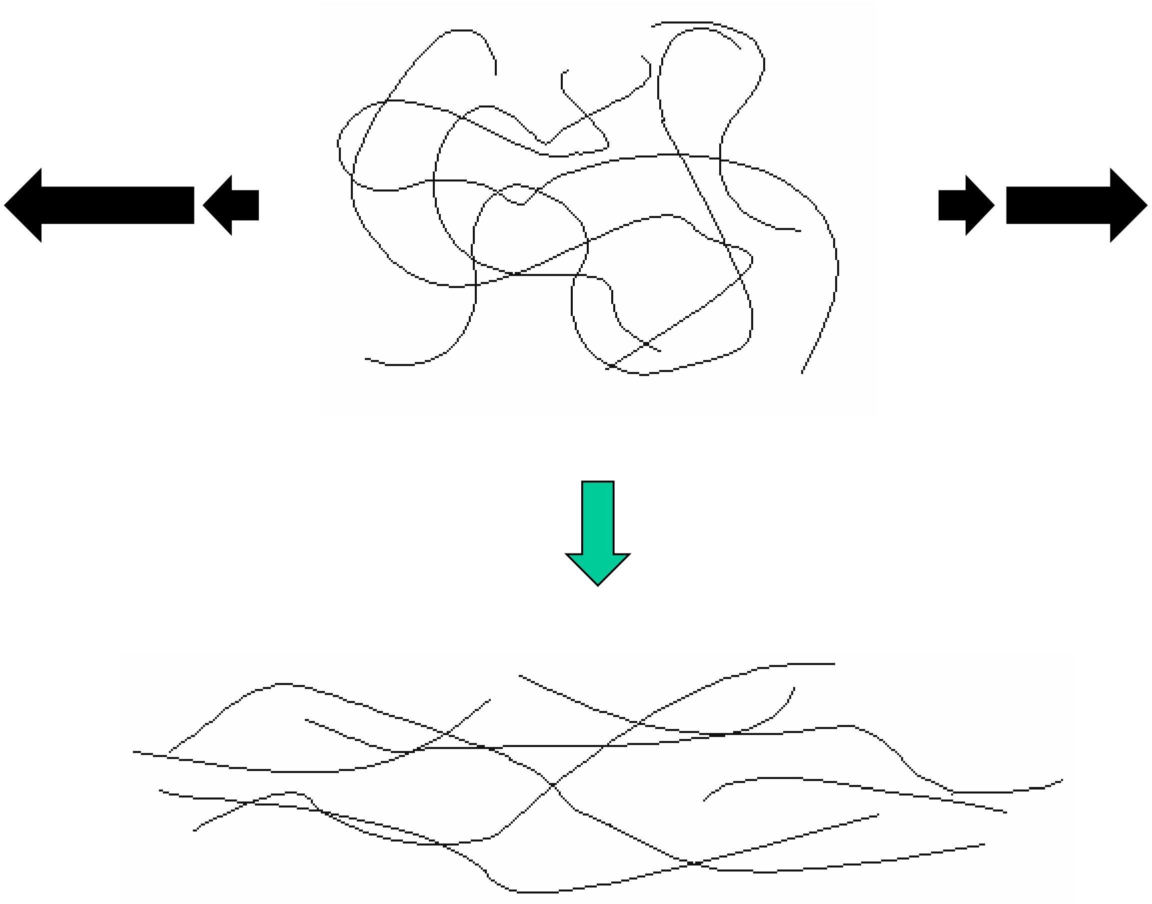
However, they are aligned only when the material is stretched.

Unlike fibers, an elastomer subjected to a force undergoes a deformation and then return to its original shape, once ended the action of the force.

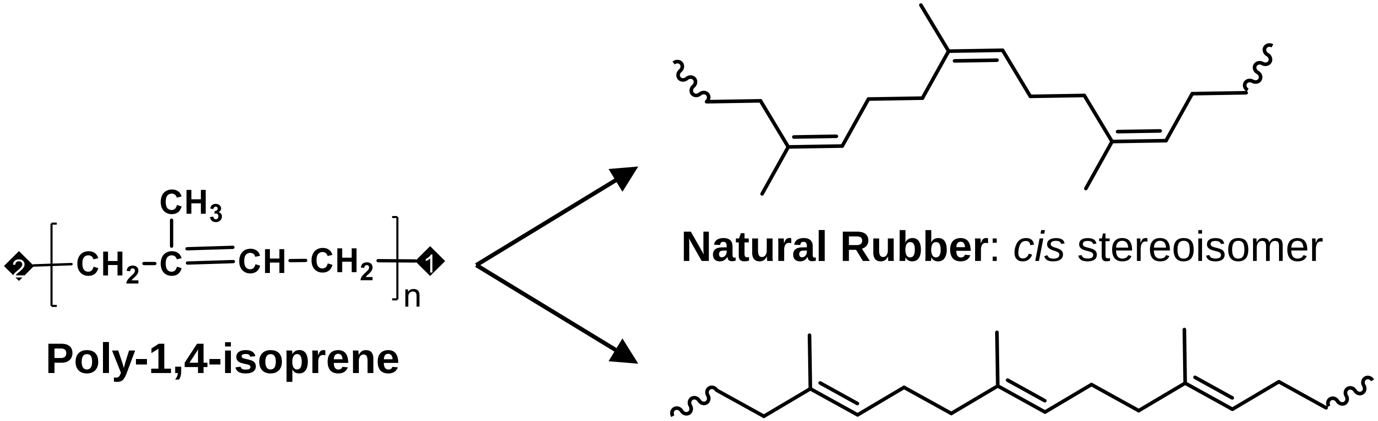
In fact, the polymer chain, finished the stretch, are not extended, but will fall back randomly into their original shape.

This behavior is due to the lack in the molecules of highly polar groups or groups appropriate to form hydrogen bonds.

Elastomers (relaxed and oriented states).



Elastomers.



$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \right]_n$$

Poly-1,4-isoprene

Natural Rubber: *cis* stereoisomer

Gutta-percha: *trans* stereoisomer

A typical example of elastomer: Natural Rubber (NR) for which the intermolecular interaction is due only to weak Van der Waals forces, due to the all *cis*-configurations of double bonds.

In the *trans* isomer of 1,4-polyisoprene, available in gutta-percha, the chain arrangement is instead very smooth; gutta-percha is in fact very crystalline and not at all elastic.

Thermoplastic and Thermoset Polymers.

Plastics can be allocated in two main categories:

Thermoplastics

Linear polymers in which the chains are interconnected by Van der Waals forces or by hydrogen bonds.

When enough sufficient thermal energy is provided, chains detach themselves from one another and the material melts.

Single molecules

- Soluble
- Little crosslinking
- Soften on heating
- Polymer worked

Thermosets

They have a crosslinked structure which prevents the chains to detach from each other even at high temperature.

Therefore, if heated they does not melt but burn (if oxygen is present) or decompose (if in an inert atmosphere)..

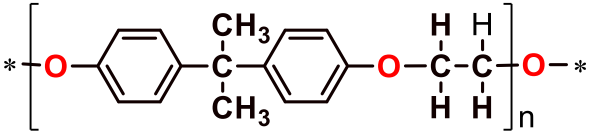
Rigid Network

- Significant crosslinking
- Hard and brittle
- Decompose (do NOT soften)
- Precursor worked

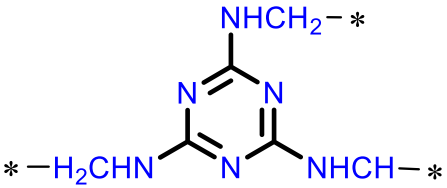
Examples of Plastic Materials.

Thermoset:

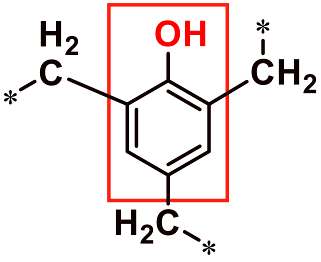
- Epoxide



- Melamine

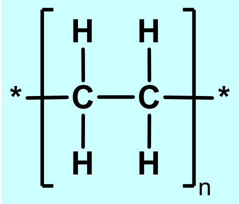


- Phenolic

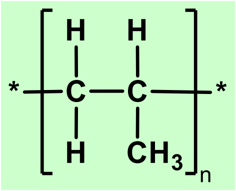


- *Thermoplastic:*

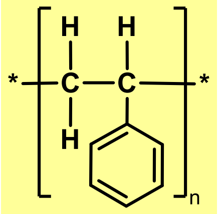
- Polyethylene



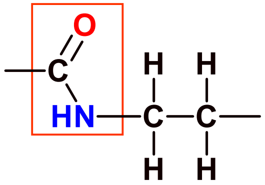
- Polypropylene



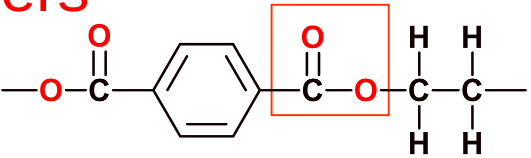
- Polystyrene



- Polyamides



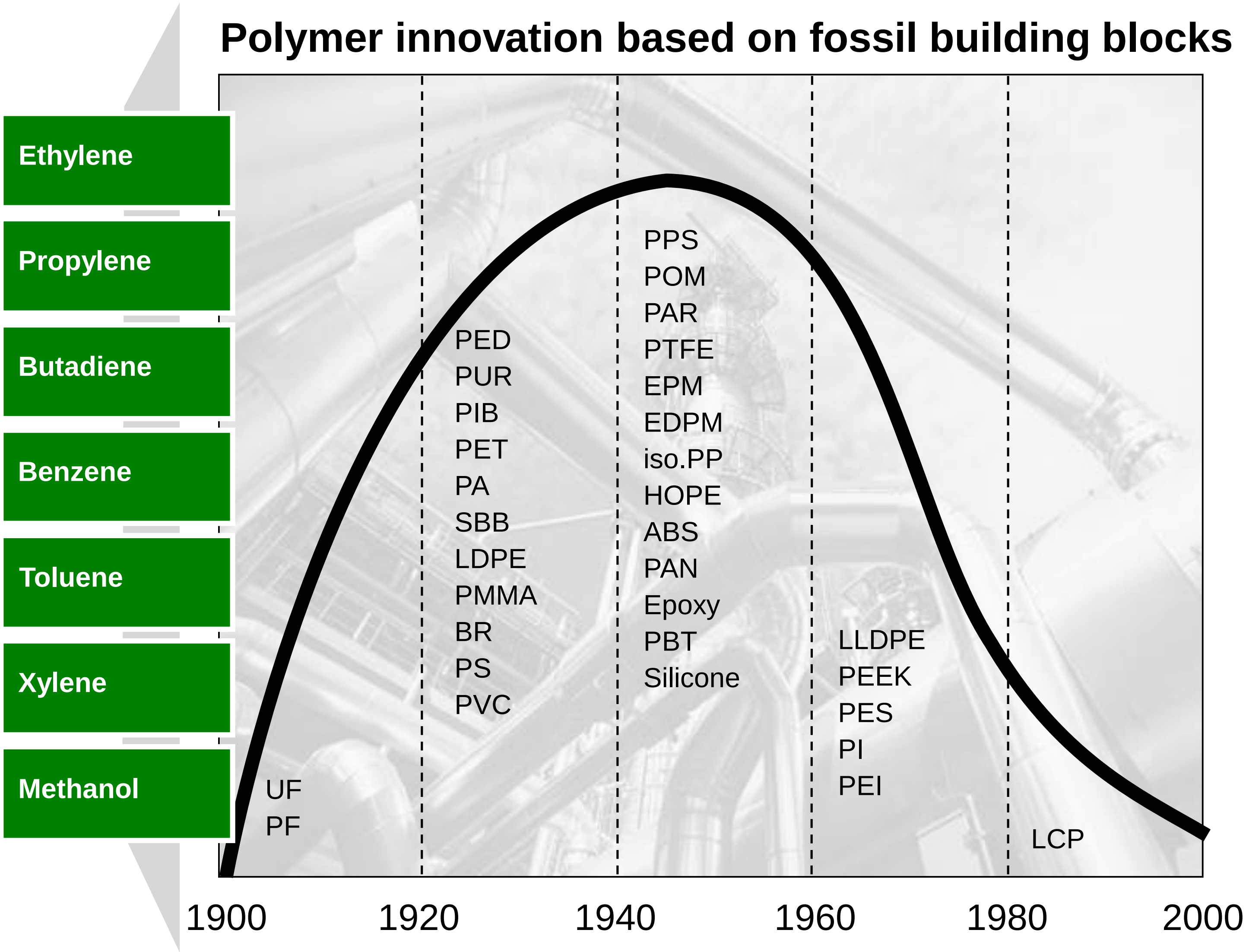
- Polyesters



Some Important Commercial Polymers and Related Introduction Dates.

Date	Polymer	Date	Polymer
1930	Styrene-butadiene rubber	1943	Silicones
1936	Poly(vinyl chloride)	1944	Poly(ethylene terephthalate)
1936	Polychloroprene (neoprene)	1947	Epoxide
1936	Poly(methyl methacrylate)	1948	ABS Resins
1936	Poly(vinyl acetate)	1955	Polyethylene, linear
1937	Polystyrene	1956	Polyoxomethylene
1939	Nylon-66	1957	Polypropylene
1941	Poly(tetrafluoroethylene)	1957	Polycarbonate
1942	Unsaturated Polyesters	1964	Resin monomeric
1943	Polyethylene Branched	1965	Polyamides
1943	Butyl rubber	1970	Thermoplastic elastomers
1943	Nylon-6	1974	Aromatic polyamides

The Innovation Potential of Fossil Building Blocks Appears Largely Exploited.



Polymer innovation based on fossil building blocks

Practical Classification of Polymers.

Based on process determining the properties of an object.
Divided into elastomers, fibres, and plastics depending on mechanical properties: *stress, strain and module*

1. Elastomers

- Full and fast recover after lengthening, deformation strains < 1000%
- Initial modulus is 10^3 psi (7 MN·m^{-2})
- Elastomer Moduli increase increasing temperature
- At temperature sufficiently low, elastomer is glassy and brittle: rubber at LN temp.

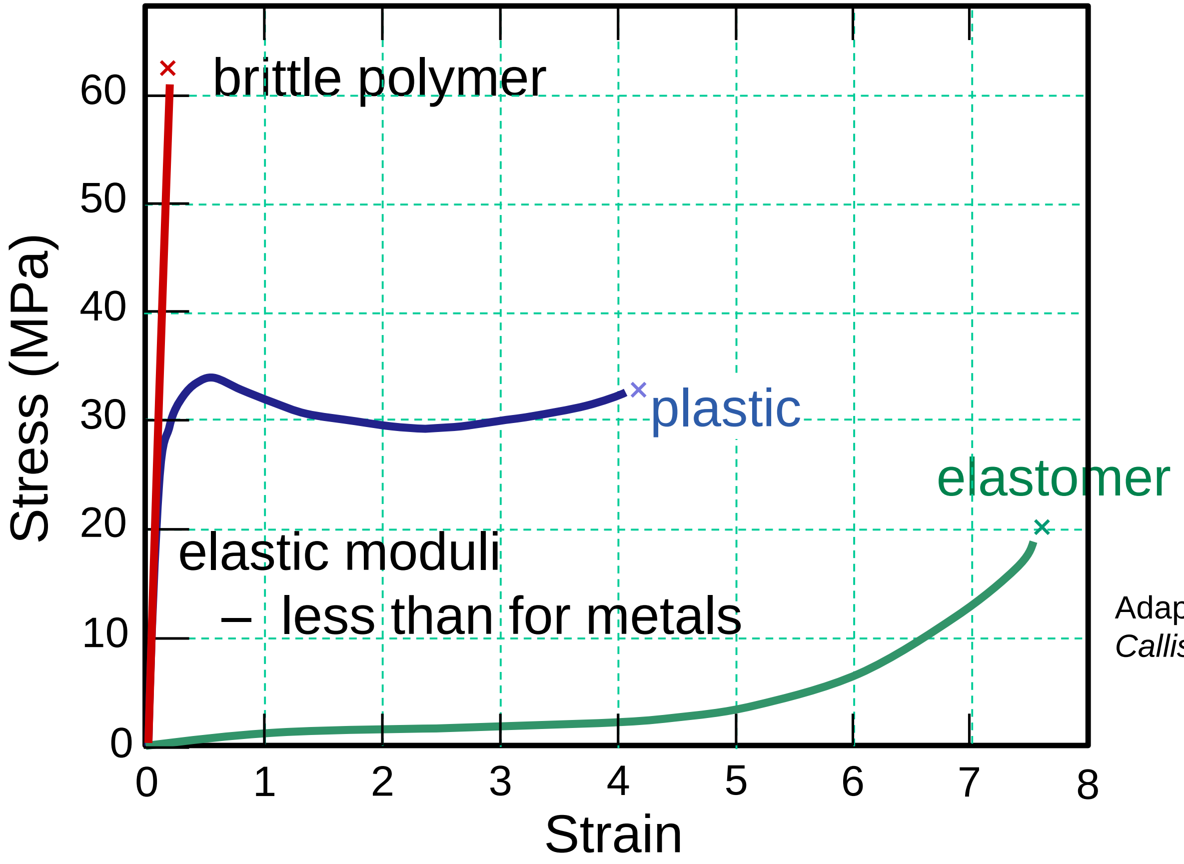
2. Fibres

- Initial modulus: $0.5\times10^6 – 2\times10^6$ psi ($3\times10^3 – 14\times10^6$ MN·m^{-2}), deformation strains less than 20%
- Deformed under beak load and allowed to relax, fibres recover part of deformation, but part remains permanent
- Synthetic commercial fibres do not change their properties in the range –50 - 150°C.

3. Plastics

- Initial Modulus: $0.5\times10^5 – 4\times10^5$ psi ($3.5\times10^2 – 3\times10^3$ MN·m^{-2})
- From minor deformations % (PS) to 400%, semi crystalline (PE)
- A temperature increase produces a rigidity reduction and higher elongation at break.

Mechanical Properties of Polymers – Stress-Strain Behavior.



Adapted from
Callister & Rethwisch 8Ed.

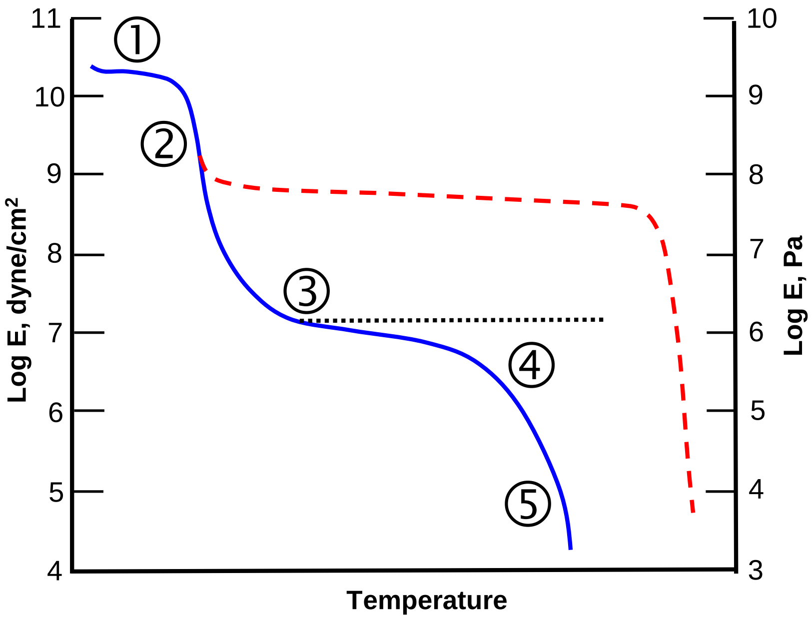
- Load at break of polymers ~ 10% of metals
- Deformation strains for polymers > 1000%
  – for most metals, deformation strains < 10%

Glass-Rubber Transition Behavior.

- The state of polymer depends on the TEMPERATURE and TIME selected
- At enough low temperature, all amorphous polymers are stiff and glassy:

  - called glassy state or vitreous state, especially for inorganic materials.
- On warming, polymers soften in a characteristic TEMPAERATURE RANGE known as GLASS-RUBBER transition region

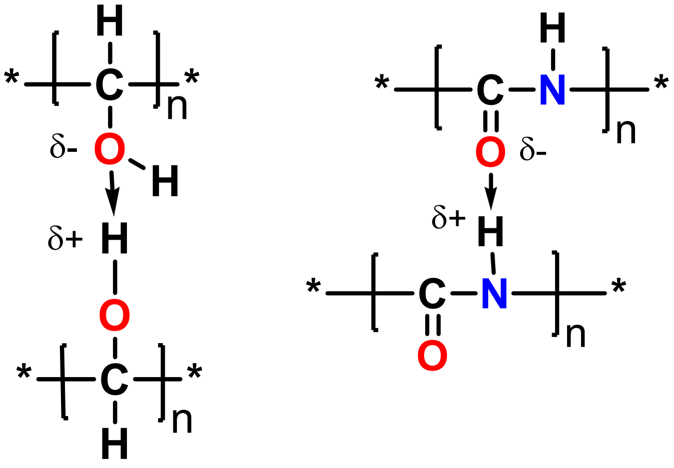
  - behave in a leathery manner
- Eisenberg stated "*The glass transition is perhaps the most important single parameter which one needs to know before one can decide on the applications of …., non-crystalline system…..*"
- For amorphous polymers, T_g constitutes their most important mechanical properties.



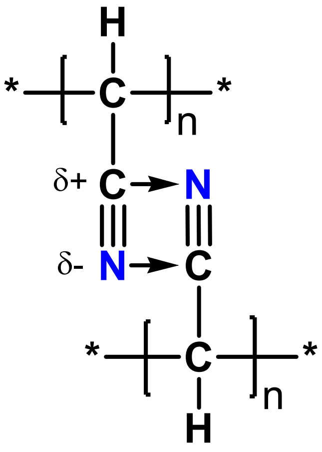
1. Glassy region, 2. Glass transition
3. Rubbery region, 4. Rubbery flow
5. Viscous flow

Intermolecular Forces.

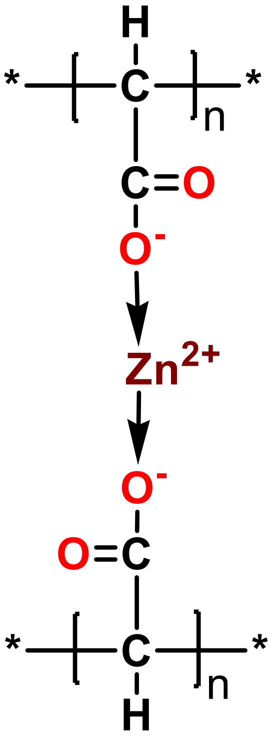
Hydrogen Bond

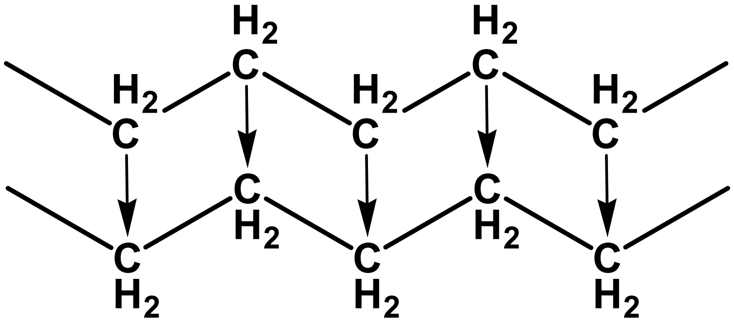


Dipole Interaction



Ionic Bond





Van der Waals interactions

Intermolecular Forces.

Bond type	Interatomic distance r_{m}, Å	Dissociation energy, - E , $kcal \cdot mol^{-1}$	Characteristics
Primary covalent	1 - 2	50 - 200	Occurs between atoms which share electrons; strong strength
Hydrogen bond	2 - 3	3 – 7	Occurs between molecules with O-H, N-H and F-H bonds
Dipole interaction	2 - 3	1.5 – 3	Occurs between polar molecules
Van der Waals	3 - 5	0.5 – 2	Occurs between all molecules; strength depends on size, polarizability.
Ionic	2 - 3	10 – 20	Occurs between ions

Intermolecular Forces.

Solvent	δ_1(cl/cm^3)$^{1/2}$ *	Polymer	δ_2(cl/cm^3)$^{1/2}$*
n-Hexane	14.8	Polytetrafluoroethylene	12.7
Carbon tetrachloride	17.6	Poly(dimethyl siloxane)	14.9
Toluene	18.3	Polyethylene	16.2
2-Butanone	18.5	Polypropylene	16.6
Benzene	18.7	Polybutadiene	17.6
Cyclohexanone	19.0	Polystyrene	17.6
Styrene	19.0	Poly(methyl methacrylate)	18.6
Chlorobenzene	19.4	Poly(vinyl chloride)	19.4
Acetone	19.9	Poly(vinyl acetate)	21.7
Tetrahydrofuran	20.3	Poly(ethylene terephthalate)	21.9
Methanol	29.7	6,6-Nylon	27.8
Water	47.9	Polyacrylonitrile	31.5

Typical Values of the Solubility Parameter δ for some Common Polymers and Solvents

$$(CED)^{1/2} = SP$$

CED = Cohesive Energy Density

$$\delta = \sqrt{c} = \left[\frac{\Delta H_{ev.} - RT}{V_m}\right]^{1/2}$$

Hansen. Journal of Paint Technology
Vol. 39, No. 505, Feb 1967

Solubility Parameter and densities of Common Polymers

Polymer	δ (cl/cm^3)$^{1/2}$	Density (g/mL)
polybutadiene	8.4	1.01
Polyethylene	7.9	0.85 (amorphous)
Poly(methyl methacrylate)	9.45	1.188
Polytetrafluoroethylene	6.2	2.00 (amorphous)
Polyisobutene	7.85	0.917
Polystyrene	9.10	1.06
Cellulose triacetate	13.6	1.28
Cellulose tributyrate	--	1.16
Nylon 66	13.6	1.24
Poly(ethylene oxide)	9.9	1.20
Poly(vinyl chloride)	9.6	1.39

SI Hildebrand values from Barton. Handbook of Solubility Parameters, CRC Press, 1983

http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html

Molar Attraction Constants E.

Group	E [(J·cm^3)$^{1/2}$/mol]	Group	E [(J·cm^3)$^{1/2}$/mol]
$-CH_3$	303	$-NH_2$	463
$-CH_2-$	269	-NH-	368
>CH-	176	-N-	125
>C<	65	C≡N	725
$CH_2=$	259	-NCO	733
-CH=	249	-S-	429
>C=	173	Cl_2	701
-CH=aromatic	239	Cl primary	419
>C=aromatic	200	Cl secondary	425
-O-ether, acetal	235	Cl aromatic	329
-O-epoxide	360	F	84
-COO-	668	Conjugation	47
>C=O	538	*Cis*	-14
-CHO	599	*Trans*	-28
$(CO)_2O$	1159	Six-membered ring	-48
-OH→	462	Ortho	-19
OH aromatic	350	Meta	-13
-H acid dimer	-103	Para	-82

Random Coil (Random Walk) in Polymers.

For a polymer chain model;

- Consider random steps of equal length, **a**, defined by chemical bonds

Complications:

- Excluded volume effects
- Steric limitations

An ideal polymer chain with 106 repeat units (not unusual), each unit of about 6 Å will have:

- a $\underline{R_{ms}}$ end-to-end distance R of 600 nm
- a contour length of 600 µm

The chain end-to-end vector R "describes" a coil made up of N jump vectors $\mathbf{a}_i$.

Random Walk …

$$\bar{\mathrm{R}} = \sum_{i=1}^{N} \bar{a}_i$$

R is made up of N jump vectors **a**$_i$. The average of all conformational states of the polymer is <**R**>=0

$$\left\langle \bar{R}^2 \right\rangle = \left\langle \sum \sum \bar{a}_i \bullet \bar{a}_j \right\rangle$$

The simplest non-zero average is the mean-square end to end distance <R^2>

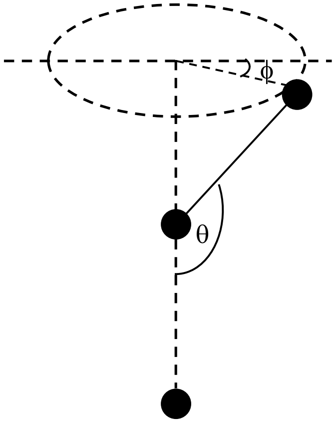
$$\left\langle \bar{R}^2 \right\rangle = Na^2 + 2a^2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \cos\theta_{ij}$$

(A matrix of dot-products where the diagonal represents i=j and off axis elements i≠j)

For a freely jointed chain the average of the cross terms above is zero and we recover a classical random walk: <**R**^{2}>= Na^2

The rms end to end distance <**R**^{2}>$^{1/2}$= N$^{1/2}$a

Real Chains Have Steric Limitations.



$$\langle \bar{R}^2 \rangle = Na^2\sigma^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right)$$

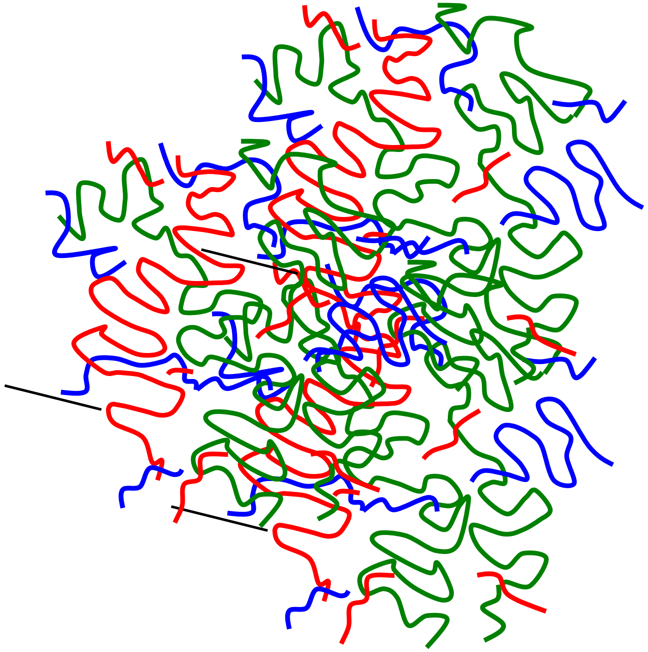
In freely rotating chains ϕ can take any value; $\sigma^2 = 1$.

Polyethylene: θ = 109.5° → $\langle R^2 \rangle = 2Na^2$

With hindered rotation σ^2 depends on the average of ϕ.

σ is experimentally determined.

Space Filling?

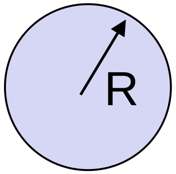


The random walk and the steric limitations makes the polymer coils in a polymer melt or in a polymer glass “expanded”.

However, the overlap between molecules ensure space filling.

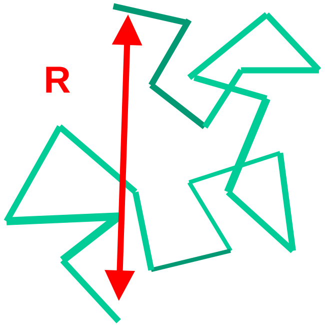
Radius of Gyration of a Polymer Coil.

The radius of gyration R_g is defined as the RMS distance of the collection of atoms from their common centre of gravity.



For a solid sphere of radius R;

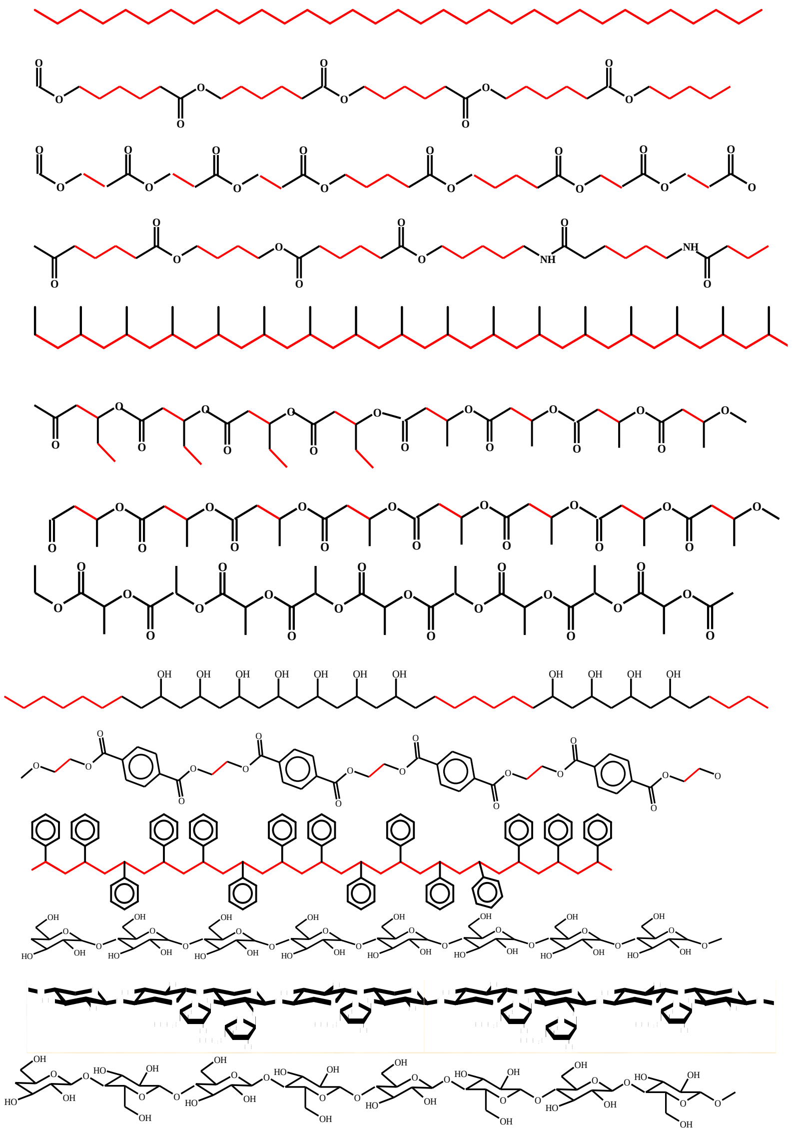
$$R_g = \sqrt{\frac{2}{5}}R = 0.632R$$



For a polymer coil with rms end-to-end distance R ;

$$R_g = \frac{1}{6}\left\langle \bar{R}^2 \right\rangle^{1/2} = \frac{a}{6}N^{1/2}$$

Natural polymers (i.e. starch or proteins) are bad substitutes of plastics (low mechanical properties, hydrophilicity).



PE	Tg = -120°C	Tf = 120°C
PCL	Tg = -60°C	Tf = 60°C
PBSA	Tg = -45°C	Tf = 114°C
PEA	Tg = -30°C	Tf = 112°C
PP	Tg = -15°C	Tf = 165°C
PHBV15	Tg = +5°C	Tf = 145°C
PHB	Tg = +10°C	Tf = 175°C
PLA	Tg = +58°C	Tf = 152°C
EVOH	Tg = 60°C	Tf = 190°C
PET	Tg = 90°C	Tf = 270°C
PS	Tg = 95	
Starch		
Hemicelluloses		
Cellulose		

Tg > 200°C 0% HR

T degradation < Tf

Polymer Synthesis.

Synthetic polymers are produced by chemical reactions of monomers or multimeric sub-units to form bigger molecules.

Modern classification of polymerization is based on polymerization mechanism:

- **Step-growth polymerization**: Condensation reactions
  - bifunctional units of any length connected by a bond formed by a condensed molecule removed (frequently water).
- **Chain growth polymerization**: Addition reactions
  - Monomers are added one by one to existent chains in the polymer
- **Coordination Polymerization**: ionic mechanisms of coordination and ring opening.
- **Ring-opening polymerization**: may be either step or chain reaction.

POLITECNICO DI MILANO

Step-Growth Polymerization.

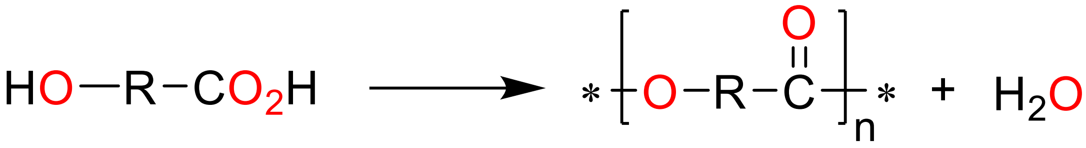
Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
http://iscamap.chem.polimi.it/citterio/education/course-topics/

Step-growth Polymerization - Requirements.

Monomer to have difunctional group

1. One having both reactive functional groups in one molecule

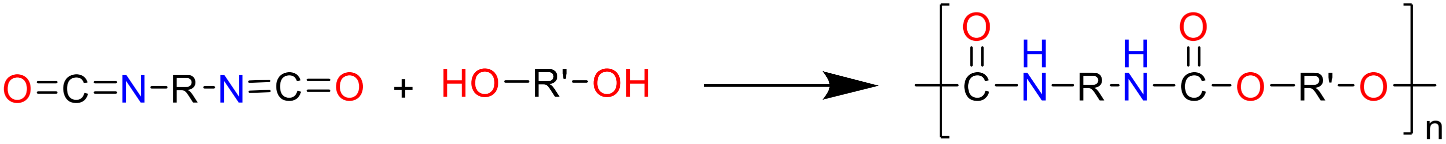
$$A-R-B \longrightarrow *-\left[R-X\right]_n-*$$



$$HO-R-CO_2H \longrightarrow *-\left[O-R-\overset{\overset{O}{\|}}{C}\right]_n-* + H_2O$$

2. Other having two difunctional monomers

$$A-R-A + B-R'-B \longrightarrow -\left[R-X-R'-X\right]_n-$$



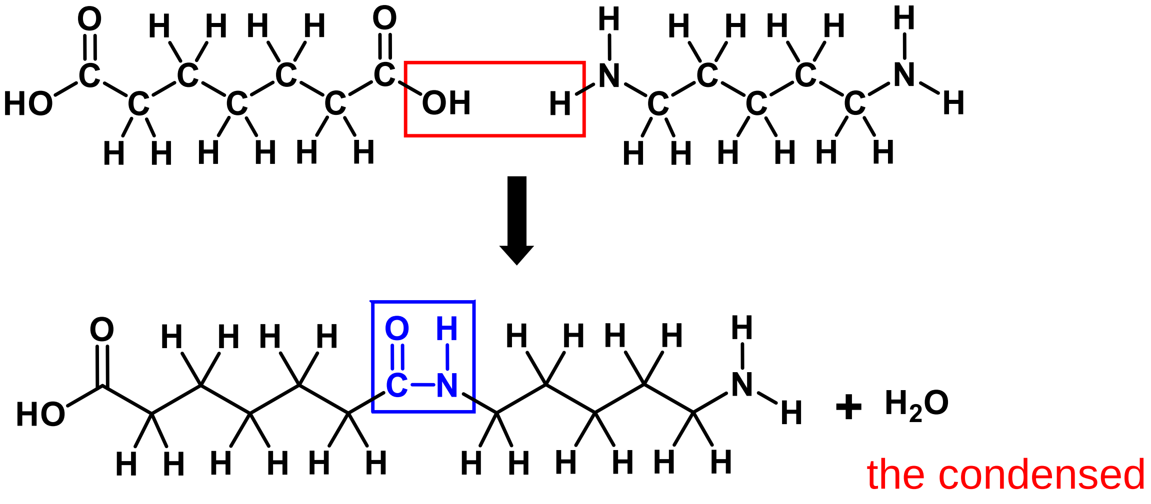
$$O{=}C{=}N-R-N{=}C{=}O + HO-R'-OH \longrightarrow \left[\overset{\overset{O}{\|}}{C}-\overset{H}{N}-R-\overset{H}{N}-\overset{\overset{O}{\|}}{C}-O-R'-O\right]_n$$

Step-growth Polymerization / Condensation.

Reactions of this type bond two molecules by elimination (optional) of a small molecule with bonding all units.

- **Monomer have difunctional groups**
  1. **one having both reactive functional groups in one molecule**
  2. **other having two difunctional monomers**
- **The two reagent molecules can have any length.**
- **Condensation reactions : when elimination occurs.**
- **Depends on functionality of reagent groups.**

Example: Two difunctional monomers

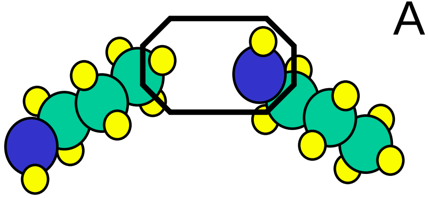


The growing polymer (Nylon 75)

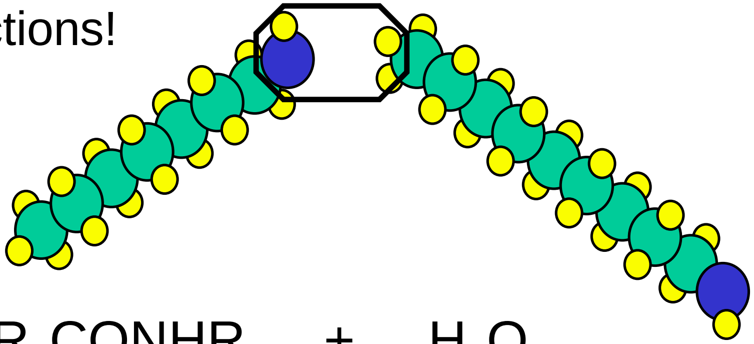
Peculiarity of Step-growth Polymerization.

Aspects of Step Polymerization or Condensation:

- Monomers disappear readily in the reaction!
- Any couple of molecules with 2 functional groups can react.
- The polymer mean MW grows rapidly during the reaction.
- Long reaction times are essential to form extended molecules.
- The molecular weight distribution for molecule length can be readily foreseen.



Are the same reactions!



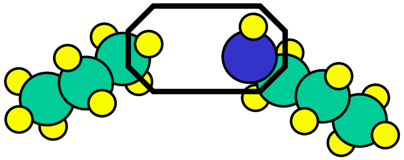
$$R_1\text{-}NH_2 \quad + \quad R_2COOH \longrightarrow R_2CONHR_1 \quad + \quad H_2O$$

Amine — Carboxylic acid — Amide — Condensation molecule

Monomer Nature in Step-growth Polymerization.

Types of monomeric units:

- Monofunctional: give dimers

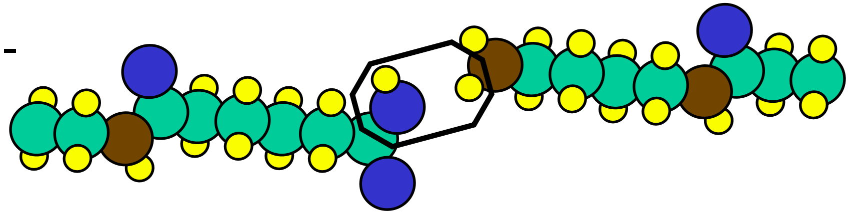


- Bifunctional: give polymers

-A-A- + -B-B- → -A-A-B-B-…

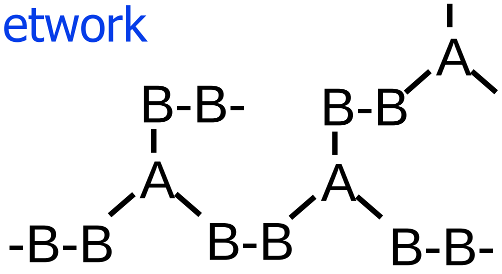
o

-A- + -B- → -A-B-A-B-…

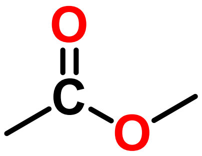


- Trifunctional (or more): give network

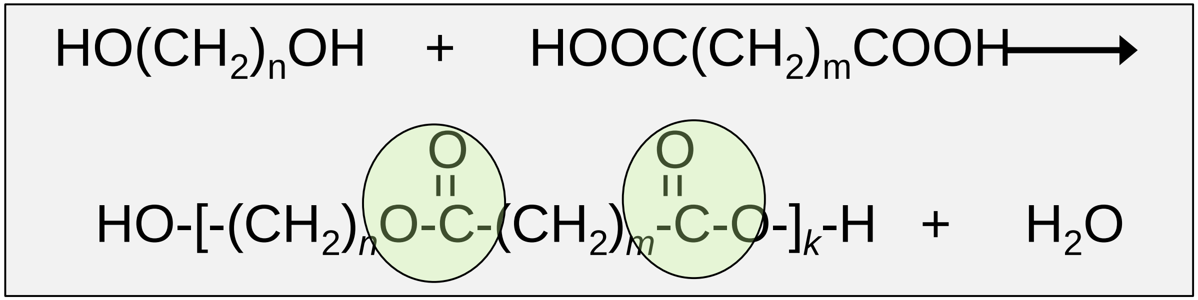
A_3 + -B-B- ⇨



Two Typical Functional Groups Involved in Step-Growth Polymerization.



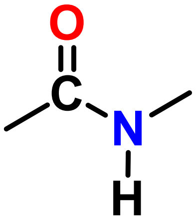
Ester bond



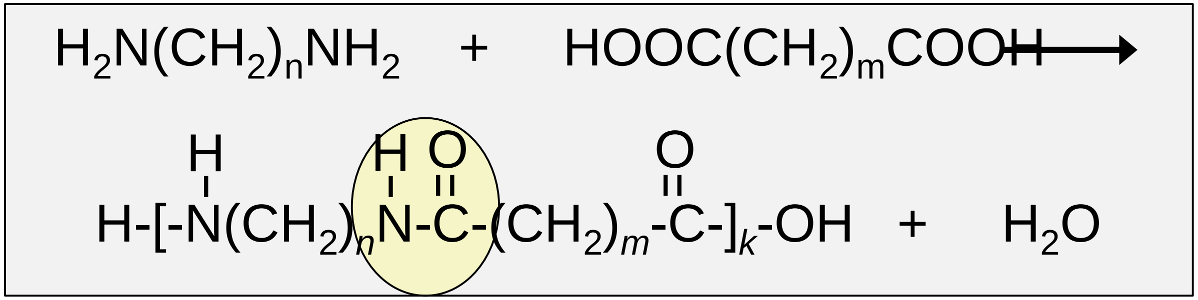
$$HO(CH_2)_nOH \quad + \quad HOOC(CH_2)_mCOOH \longrightarrow$$

$$HO\text{-}[\text{-}(CH_2)_n O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_m\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}]_k\text{-}H \quad + \quad H_2O$$

Polyester



Amidic bond



$$H_2N(CH_2)_nNH_2 \quad + \quad HOOC(CH_2)_mCOOH \longrightarrow$$

$$H\text{-}[\text{-}\overset{H}{\overset{|}{N}}(CH_2)_n\overset{H}{\overset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_m\text{-}\overset{O}{\overset{\|}{C}}\text{-}]_k\text{-}OH \quad + \quad H_2O$$

Polyamide

Aspects of Step-growth Polymerization.

Consideration on step polymerization:

- Typically have relatively high activation energy .
- Typically are only slightly exothermic.

Most step polymerizations are carried out at high temperatures.

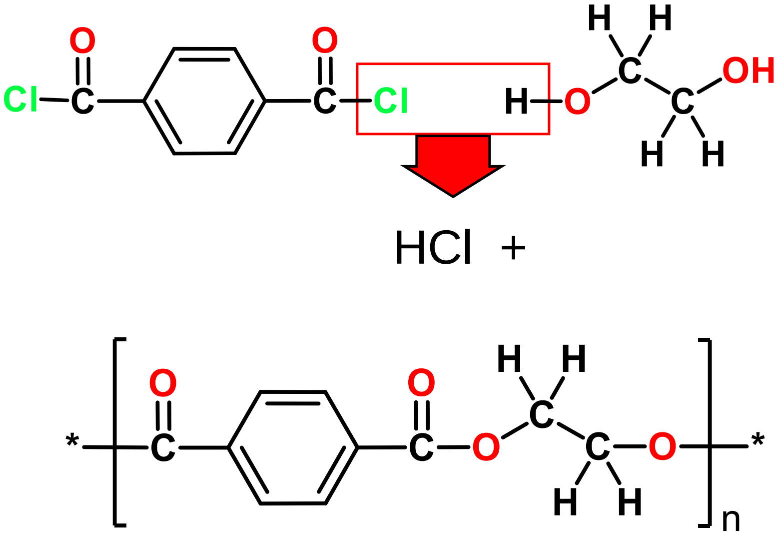
Manufacturing techniques:

- Bulk reactions - homogeneous without solvent.
- Solution reactions - homogeneous in a solvent.
- interfacial reactions - heterogeneous at the interphase of a liquid-liquid system.
- Etc. .....

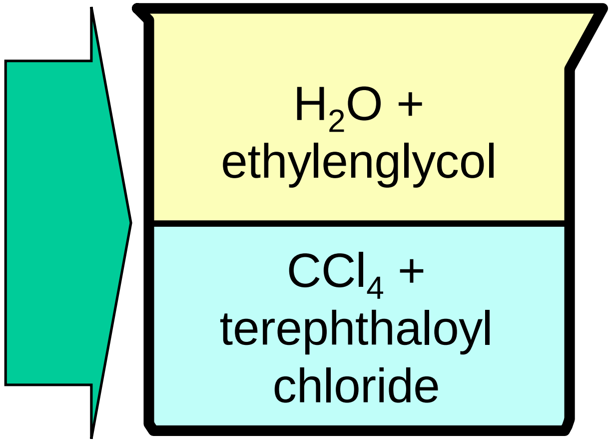
Interfacial Step-growth Polymerization.

Example: Polymerization of polyethylene terephthalate (Ester Bond):

- Option 1: Interfacial condensation



Polyethylene terephthalate
(PTE: Mylar, Dacron,...)



H_2O +
ethylenglycol

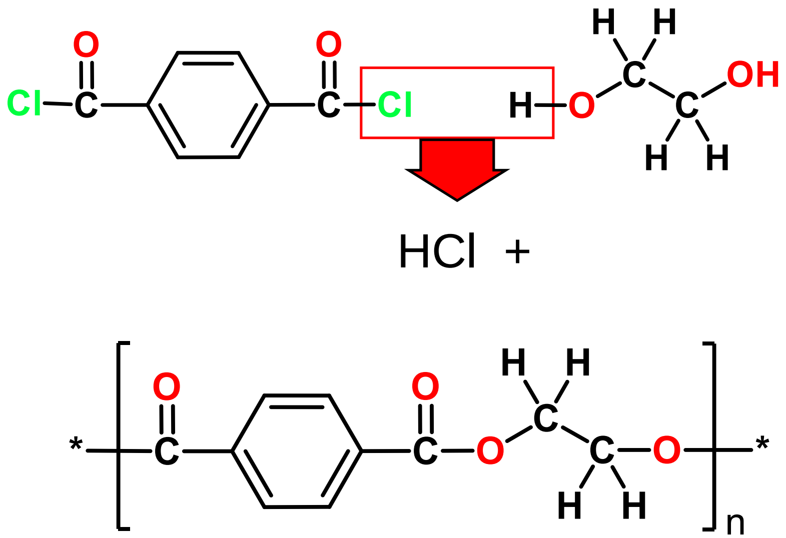
CCl_4 +
terephthaloyl
chloride

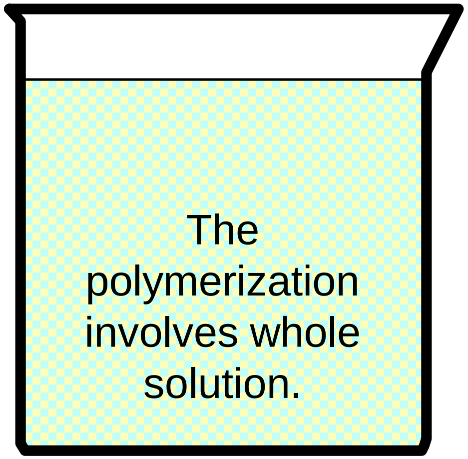
Problem: terephthaloyl chloride is very expensive.

Step-growth Polymerization in Solution.

Example: Polymerization of polyethylene terephthalate:

- Option 2: Polymerization in solution





The polymerization involves whole solution.

Problems:

the process is slow,
terephthalic acid is insoluble in common organic solvents,
terephthalic acid presents an high melting point (>300°C).

Issues in Step-growth Polymerization.

Example: Polymerization of polyethylene terephthalate:

- Option 2: Polymerization in solution

Problem: the reaction is too slow.
Solution: Use of a two-step process:

- Step 1: carry out the polymerization with glycol in excess. This accelerates the '"esterification" [-COOH → -COO-] adding more reagent. Moreover this:
    - a) decreases the polymerization degree and
    - b) terminates all molecules with hydroxyethyl groups.
- Step 2: the reagents ratio is reduced to stoichiometric. Then, the polymerization continues through reaction of (new relatively big) molecules to obtain high PM molecules.

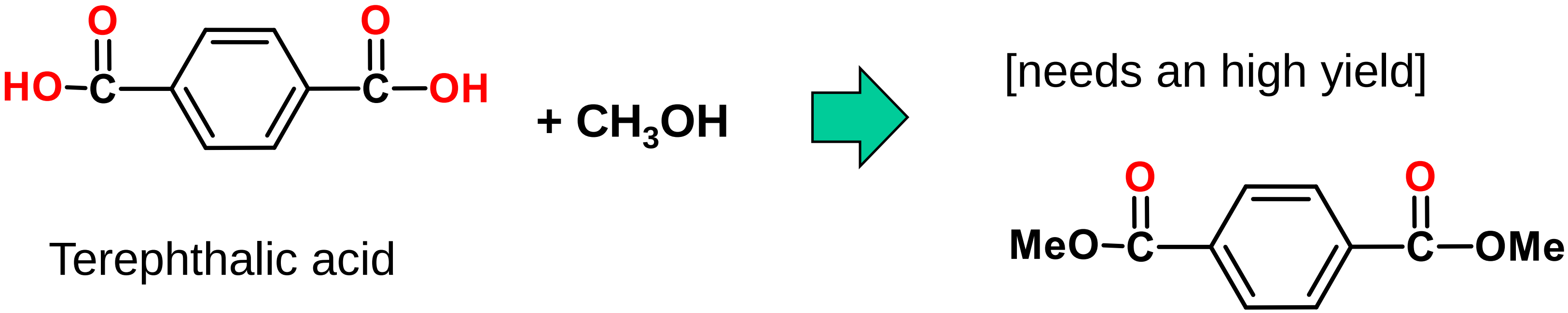
Bulk Step-growth Polymerization.

Example: Polymerization of polyethylene terephthalate:

- Option 3: Bulk condensation (only fused reagents)

Analogous to condensation in solution but without solvent. The problems are the same. We can also use a further approach:

Step 1: Esterification with a small molecule, methanol.



[needs an high yield]

Terephthalic acid

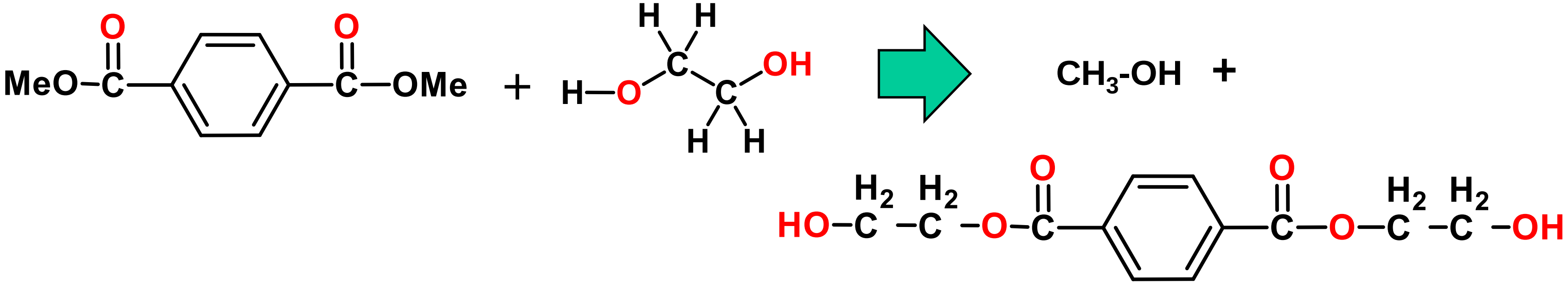
Dimethyl terephthalate

Stages in Step-growth Polymerization.

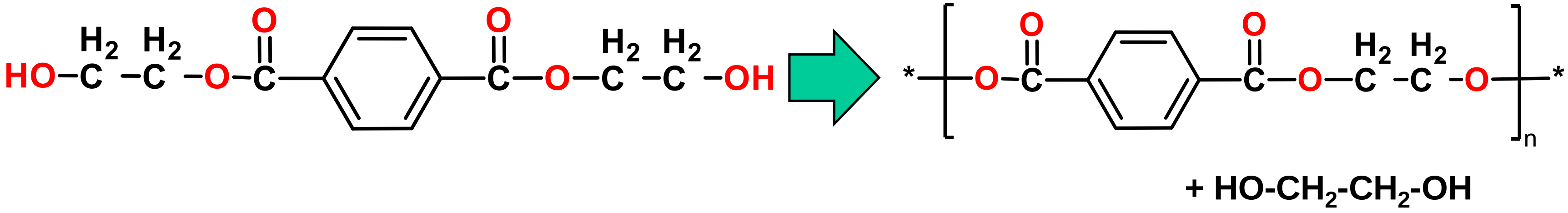
Example: Polymerization of polyethylene terephthalate:

- Option 3: Bulk condensation

Phase 2: Trans esterification - substitute the glycol for methyl groups.



Phase 3: Polymerization by elimination of glycol (condensation):



Step-growth Polymerization (Comparison of Methods).

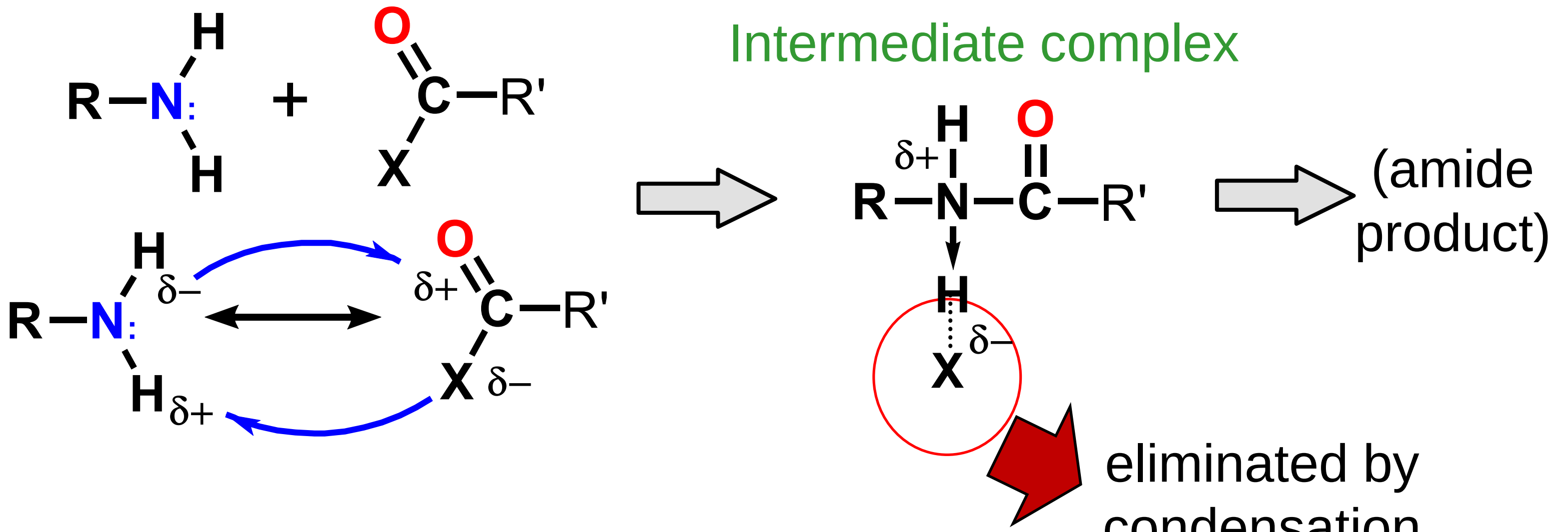
Example: Polymerization of poly(ethylene terephthalate):

Requirements	**Bulk / Fused**	**Solution**	**Interface**
Temperature	High	Low	Low
Thermodynamics	Equilibrium	Equilibrium	Non-equilibrium
Reaction time	hours-days	Min -1 hour	Min - 1 hour
Reagent ratio	Critical	Significant	unimportant
Purity requirements	Critical	Significant	Significant
Pressure	High/Low	Atmospheric	Atmospheric

Mechanism in Step-growth Polymerization.

Mechanisms of polycondensation reactions:

- Synthesis of Nylon (polyamides):



Intermediate complex

(amide product)

eliminated by condensation

Nucleophile

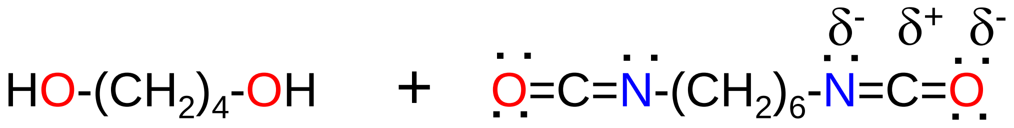
Electrophile

The reaction is similar to esterification with $\underset{\mathrm{H}}{\underset{|}{\ddot{\mathrm{O}}}}$: substituting $\ddot{\mathrm{N}}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$

Step-growth Polymerization in Polyurethanes.

Mechanism of polycondensation reactions :

- Formation of Polyurethane:

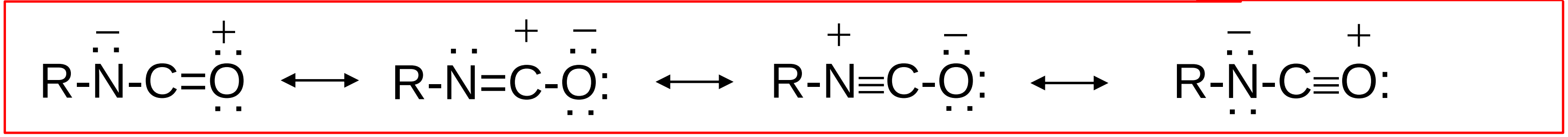


$$HO-(CH_2)_4-OH \; + \; O=C=N-(CH_2)_6-\overset{\delta^-}{N}=\overset{\delta^+}{C}=\overset{\delta^-}{O}$$

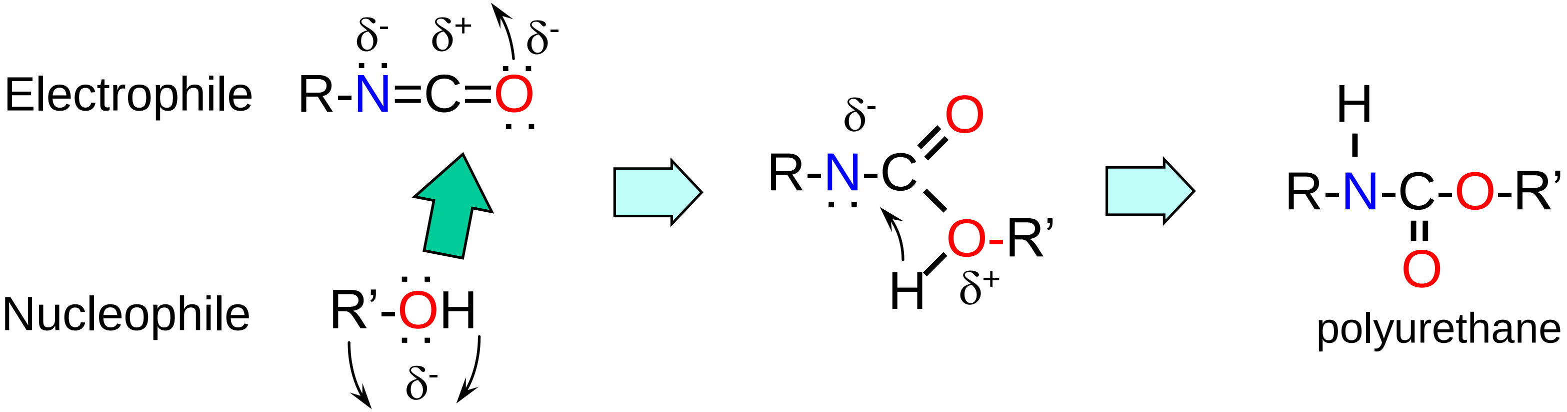
1,4-butandiol

hexamethylene diisocyanate

The isocyanate structure shows several resonance forms



$$R-\overset{-}{N}-C=\overset{+}{O} \longleftrightarrow R-N=\overset{+}{C}-\overset{-}{O}: \longleftrightarrow R-\overset{+}{N}\equiv C-\overset{-}{O}: \longleftrightarrow R-\overset{-}{N}-C\equiv \overset{+}{O}:$$



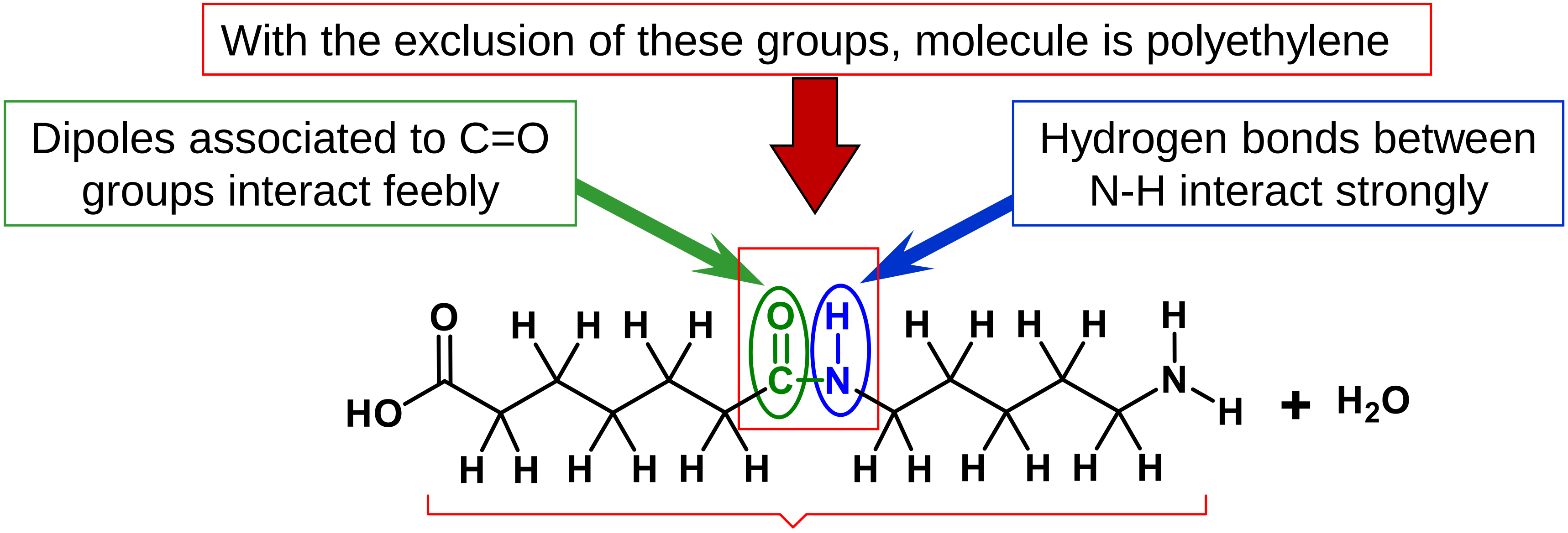
Control in Step-growth Polymerization.

Synthesis and properties:

- The aim of the synthesis of new structures is to change the properties of the material.

Example: melting point of nylon.

Interchain interactions influences the melting point.



With the exclusion of these groups, molecule is polyethylene

Dipoles associated to C=O groups interact feebly

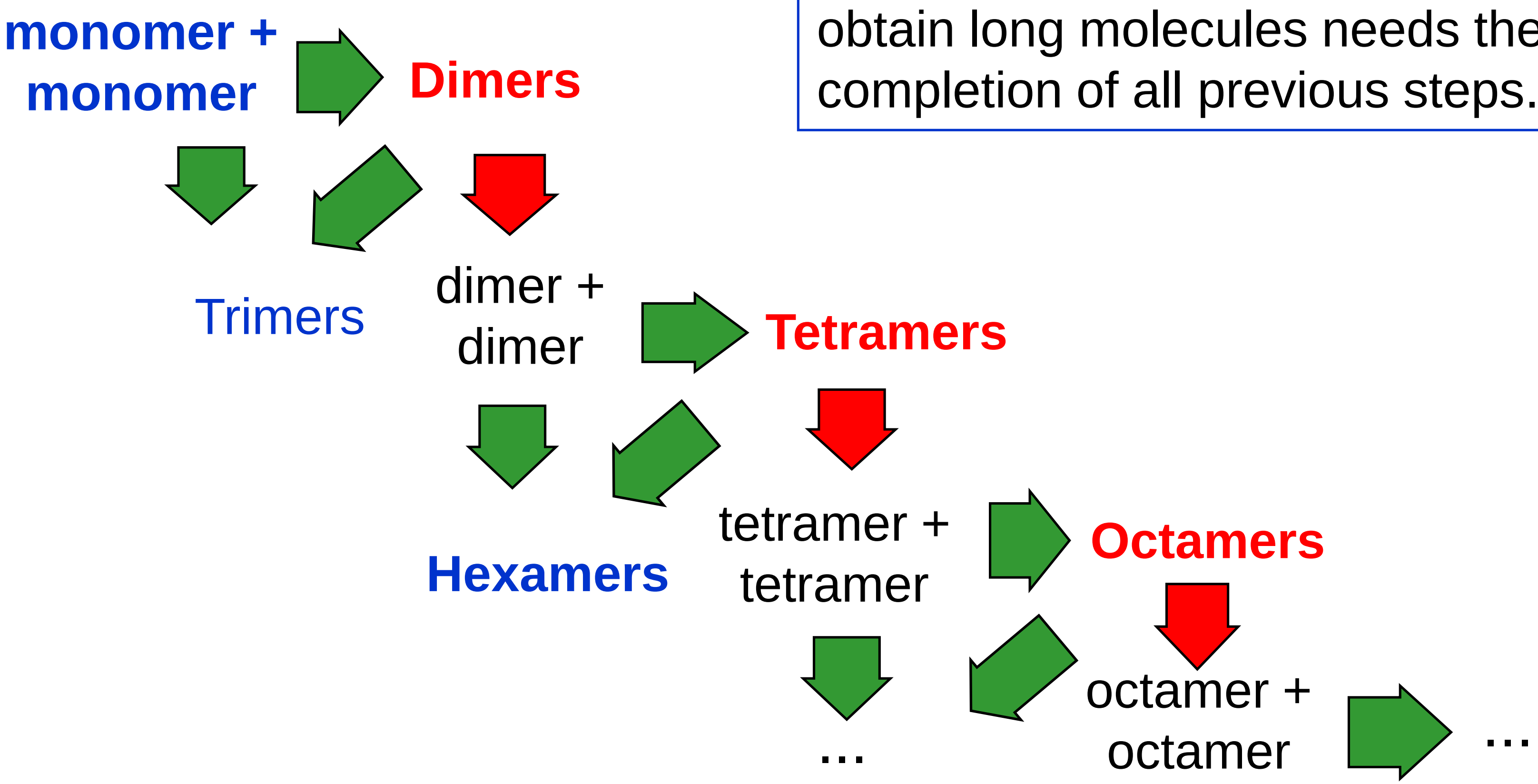
Hydrogen bonds between N-H interact strongly

Chain length influences the melting point.

Step-growth Polymerization - Kinetics.

Kinetics:

Monomers are readily lost but to obtain long molecules needs the completion of all previous steps.



monomer + monomer

Dimers

Trimers

dimer + dimer

Tetramers

Hexamers

tetramer + tetramer

Octamers

…

octamer + octamer

…

Step-growth Polymerization – Kinetics (2).

It is difficult to model system because rates depend on size – it is better to analyze the system by a numerical approach.

- We assume:
  - The reactivity of functional group does not depends on size
  - The reaction rate does not depends on diffusion or viscosity (properties variable during real reactions).
- A simple reaction could be:

$$\text{A} + \text{B} \rightleftharpoons \text{AB} + \text{condensed (C)}$$

Notice: A and B refer to functional groups, therefore they indicate molecules.

Direct rate $R_f = k_f\,[A]\,[B]$

Reverse rate $R_r = k_r\,[AB]\,[C]$ if the condensed is taken off $R_r \sim 0$.

Step-grown Polymerization – Kinetics of m-mers.

- Therefore: $-\frac{d[\mathrm{A}]}{dt} = k_f[\mathrm{A}]\cdot[\mathrm{B}]$
- For monomers, [A]=[B] then: $-\frac{d[1]}{dt} = k_1[1]^2$

  or: $$\boxed{\frac{1}{[1]_t} = k_1 t + \frac{1}{[1]_{t=0}}}$$

- For dimers:

$$-\frac{d[2]}{dt} = k_f^{1}[1]^2 - k_f^{n,2}[2]\sum_{n}[n] + k_r^{n}\sum_{n>3}[n]$$

monomers to dimers **dimers to (2+n)-mers** **n-mers to dimers**

- For m-mers

$$-\frac{d[\mathrm{m}]}{dt} = k_f^{i,j}\sum_{\mathrm{i+j=m}}[\mathrm{i}][\mathrm{j}] - k_f^{n,m}[m]\sum_{n}[n] + k_r^{n}\sum_{n>m}[n]$$

i & j-mers to m-mers **m-mers to (m+n)-mers**

Step-reaction Polymerization – (DP and PM vs. time).

All functional groups are accounted for, i.e. all molecules!

- Defining the polymerization degree as: $\overline{DP} = \frac{[\mathrm{A}]_{t=0}}{[\mathrm{A}]}$

This is the ratio of initial number of molecules (of monomer) on current number of molecules.

- and: $p = 1 - \frac{[\mathrm{A}]}{[\mathrm{A}]_{t=0}}$ is the reaction degree
- By substitution: $$\frac{1}{[\mathrm{A}]_{t=0}(1-p)} - \frac{1}{[\mathrm{A}]_{t=0}} = k_{pol}t$$
- or using: $\overline{DP} = \frac{1}{1-p}$ we obtain: $\boxed{\overline{DP} = [\mathrm{A}]_{t=0} k_{pol} t + 1}$

The mean polymerization degree (and mean molecular weight) increases linearly with time!

Step-growth Polymerization – Time Dependence of n-mer Distribution.

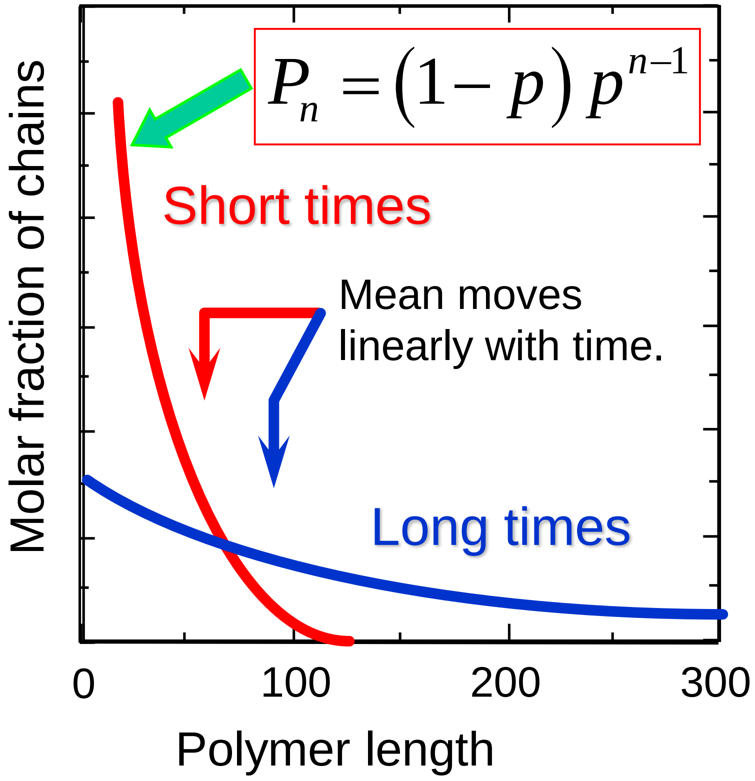
Probability to form a n-mer:

The probability of n-1 reactions is p^{n-1}.

The probability that a certain monomer has not reacted is 1-*p*.

Therefore, the probability to form an n-mer is:

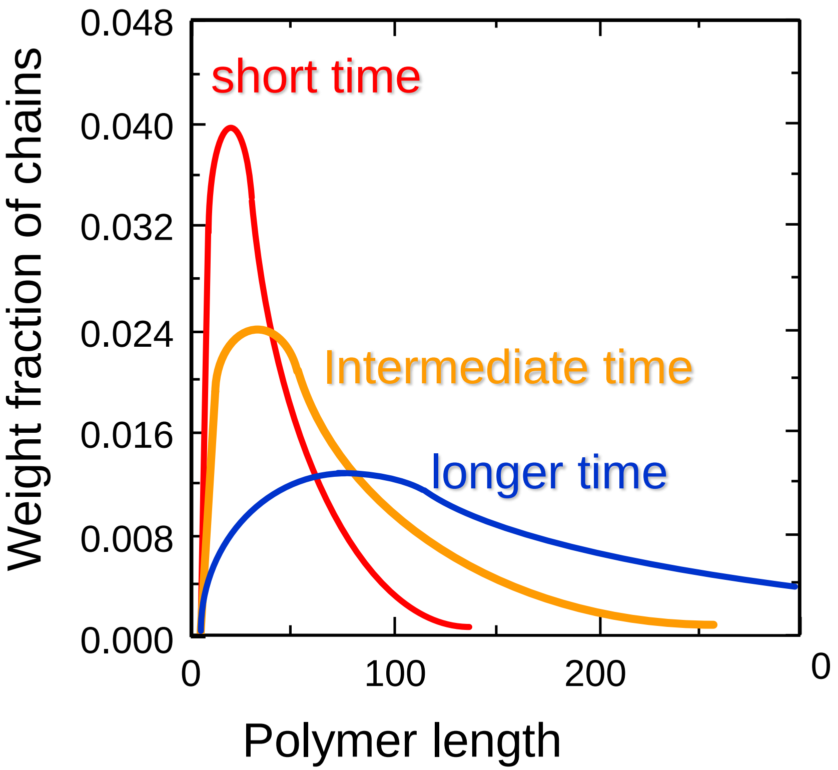
$$\boxed{P_n = (1-p)\, p^{n-1}}$$



Time Dependence of Weight Fraction of Chains on Polymer Length.

Weight fraction (distribution different from numerical fraction!).

Monomer weight = W_0.



Weight fraction = Y_n:

$$Y_n = \frac{\text{weight of n-mer}}{\text{total weight}}$$

$$Y_n = \frac{nW_0N_n}{N_0W_0}$$

$$Y_n = \frac{nN_n}{N}$$

$(1-p)\,p^{n-1}$

$1/(1-p)$

$$\boxed{Y_n = np^{n-1}(1-p)^2}$$

Step-growth Polymerization – PM control.

To obtain high MW, well controlled ratios of reagents are required!

- we define the reagent ratio as:

$$r = \frac{[\mathrm{A}]_{\mathrm{t=0}}}{[\mathrm{B}]_{\mathrm{t=0}}}$$

with A and B so that r < 1.

the chain termination number is:

$$[\mathrm{terminations}] = [\mathrm{A}]_{t=0}\left(1-p\right) + [\mathrm{B}]_{t=0}\left(1-rp\right)$$

When all defect reagent, A, was reacted, p=1 but:

$$\overline{DP}_{\mathrm{max}} = \frac{1+r}{1-r}$$

If r = 0.98, then $\overline{DP}_{\mathrm{max}}$ = 99!

If reagent ratio differs by 2%, the mean molecular weight $\boxed{M = M_0\,DP}$ will be only 100 times the monomer weight!

[This can be used to control final MW]

Disadvantages of Step-growth Polymerization.

- The main disadvantage is related to the difficulty to obtain products of high molecular weight because all reactions are in equilibrium and, therefore, above a certain threshold, additional monomers cannot be inserted in the same chain.
- A quite wide molecular weight distribution is observed and this accounts for the poor physical properties of the material.
- Nylon is an exception because, giving sufficiently long chains, shows quite good physical properties.

$$p = \frac{N_0 - N}{N_0} \quad \textbf{\textit{Or}} \quad N = N_0\left(1 - p\right)$$

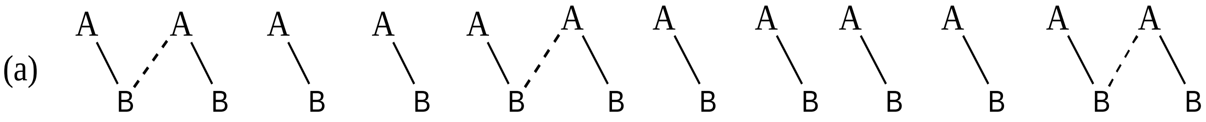
($\boldsymbol{N_O}$: number of molecules
$\boldsymbol{N}$: total molecules after a given reaction period.
$\boldsymbol{N_O - N}$: The amount reacted
$\boldsymbol{p}$: The reaction conversion)

($\overline{\mathbf{DP}}$ is the average number of repeating units of all molecules present)

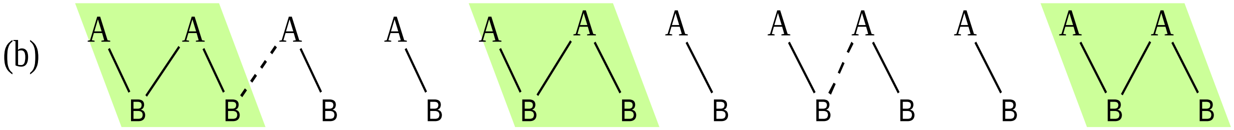
$$\overline{\mathbf{DP}} = N_O/N \qquad \overline{\mathbf{DP}} = \frac{1}{1 - p}$$

Carothers Equation (monomer conversion and DP).

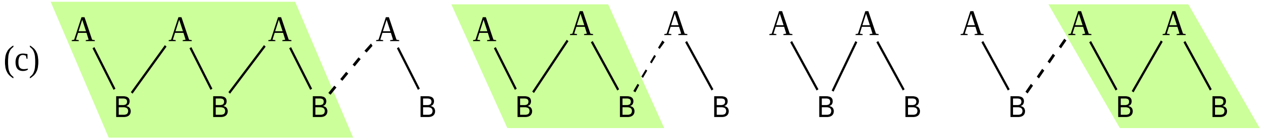
(A) Unreacted monomer



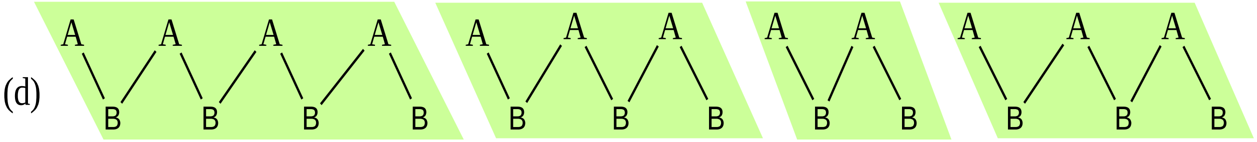
(B) 50% reacted, $\overline{DP}$ = 1.3



(C) 75% reacted, $\overline{DP}$ = 1.7



(D) 100% reacted, $\overline{DP}$ = 3



$$X_n = \frac{1}{1-p}$$

Conversion	X_n
– 50%	2
– 80%	5
– 90%	10
– 95%	20
– 99%	100
– 99.5%	200

POLITECNICO DI MILANO

Chain-growth Polymerization per (Addition).

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

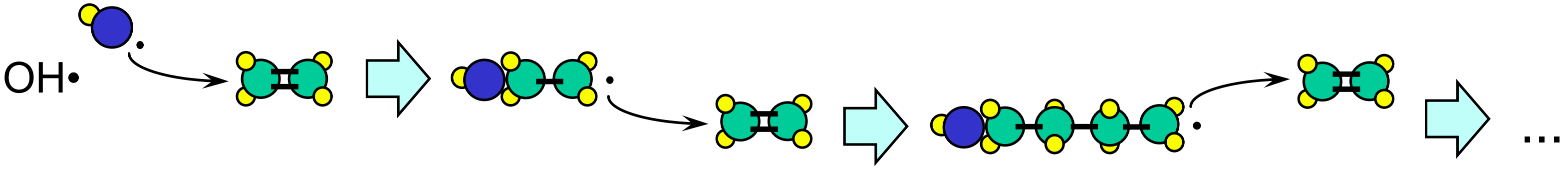
http://iscamap.chem.polimi.it/citterio/education/course-topics/

Chain-growth (Addition) Polymerization.

These reactions involve the addition of small molecules at the end of a big molecule once at a time.

Peculiarity of Addition Polymerization:

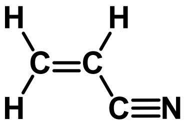
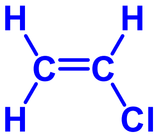
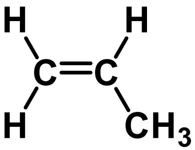
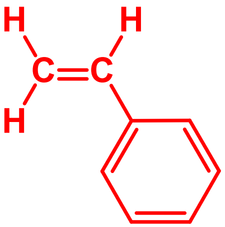
- Monomers fall during the reaction.
- High molecular weight products are readily formed.
- The yield increases with time but the polymer chain lengths remain constant.
- The reaction mixture contains the monomer, long chains and ~ 10 ppb of growing chains. The main IS STATIC!



Addition Polymerization for polyethylene

Chain-growth (Addition) Polymerization (2).

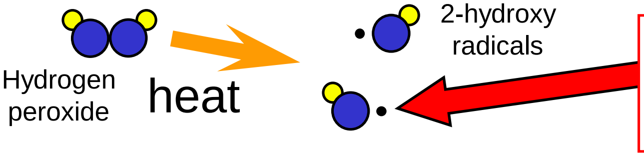
Note: addition polymerizations (except the ring opening ones) involve monomers containing a C=C group (vinyl).

Monomer	Polymer	Applications
	poly(acrylonitrile)	Acrylic carpets, clothes ...
	poly(vinyl chloride)	pipelines, raincoat, insulating, umbrella...
	poly(propylene)	Yarn: ropes, fabrics, carpets household items, ...
	poly(styrene)	Plastic optical components, electrical equipment, ...

Chain-growth Polymerization.

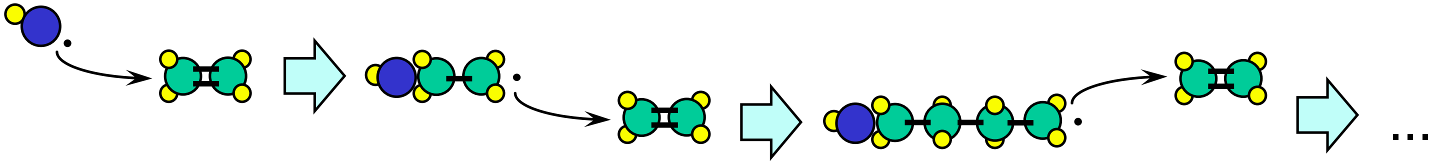
Step in the chain-growth Polymerization:

- **Initiation**: formation of a reactive intermediate (slow).

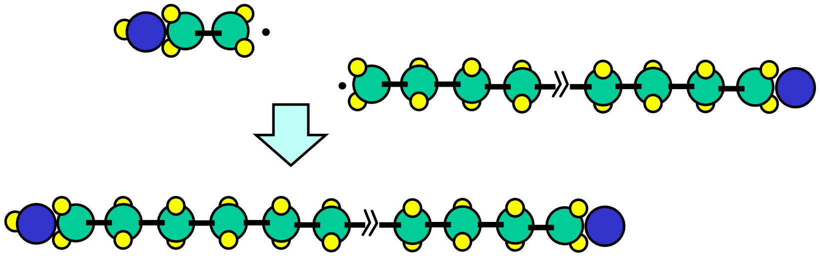


Free radicals have unpaired electrons (very reactive species).

- **Propagation**: by addition of the monomer to intermediate (fast).



- **Termination**: the reactive site is lost.



The chain length depends on relative rates of initiation, propagation, and termination!

Chain-growth Polymerization (2).

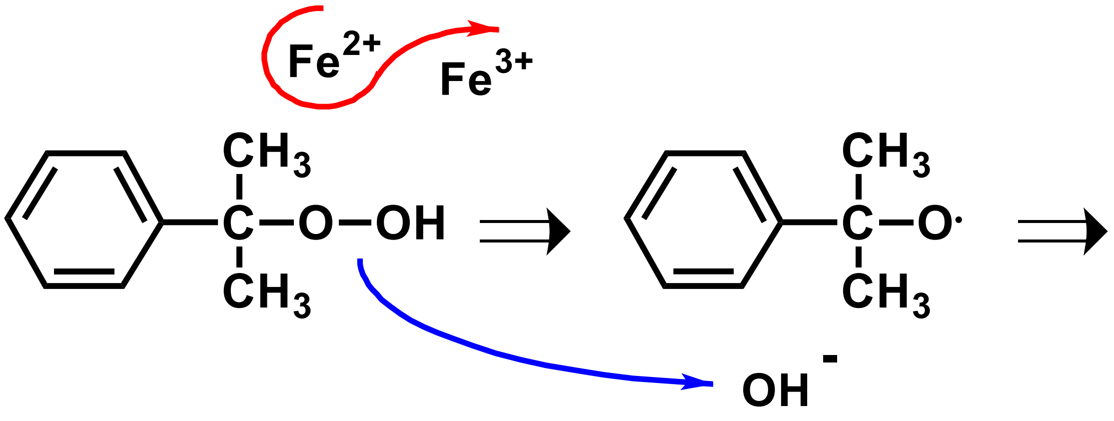
Type of chain-growth polymerization (partitioned according to the formation mechanism of reactive site):

- Free-Radical Polymerizations: The initiator is a free radical. The propagating site is transferred to different sites as polymerization proceeds.
- Ionic Polymerizations: instead of a radical an ion is promoting the formation of the active site.
- Complex coordination Polymerization: a catalytic complex is involved in the polymerization.

Chain-growth Polymerization (3).

Type of chain-growth polymerizations (based on the reactive site generation mode):

- Ring Opening Polymerization: A ring is opened to create a reactive site.
- Redox reactions: Electrons are transferred to a multiple valence metal or to another site generating a radical:



cumyl hydroperoxide

(counter ion in solution)

This represents the terminal functional group of polymer.

Chain-growth Polymerization (4).

Generation of free-radicals (by covalent bond breaking):

- Thermal decomposition of Peroxides: $R_2 \overset{\Delta}{\rightleftharpoons} 2R\bullet$
  - Thermally activated, follow a first order kinetic.

- Photolysis of Halogen derivatives, N-X, O-O, etc.: $X_2 \overset{h\nu}{\rightleftharpoons} 2X\bullet$

  formation rate $\propto$ photonic flow and concentration of X_2

- Decomposition of Azo-compounds:

$$CH_3\text{-}N{=}N\text{-}CH_3 \overset{\Delta}{\rightleftharpoons} N{\equiv}N + 2CH_3\bullet$$

Also this decomposition follows a first order kinetics.

- Several other initiation systems ...

Chain-growth Polymerization

Free-Radical Polymerization: kinetics.

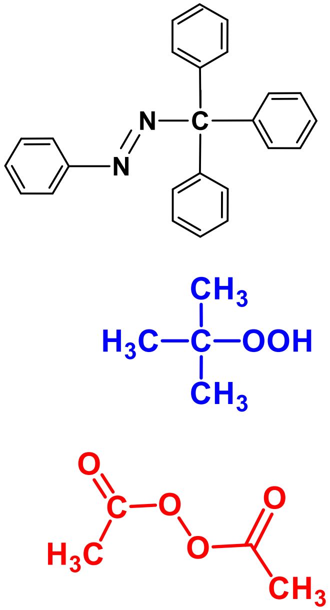
- Activation of initiator: Typically a first order reaction, therefore ...

$$R_2 \rightleftharpoons 2R\bullet$$

With a direct rate constant: $k_d = k_0\, e^{-\Delta E/kT}$

(R_d is influenced by solvents and T)

And overall rate: $\boxed{R_d = k_d\,[R_2]}$



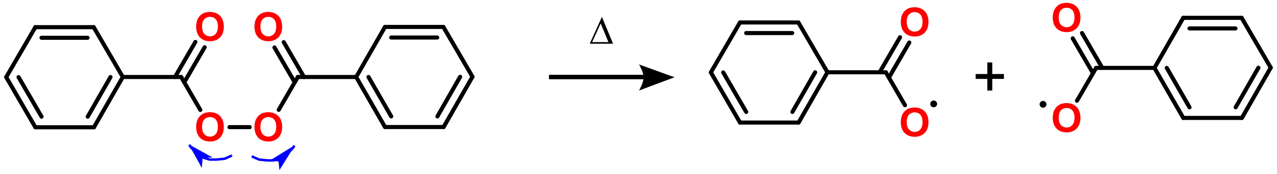
Rate constants for initiation (in benzene)

Initiators	T (°K)	k_d (sec^{-1})	ΔE (kcal/mol)
Phenyl-azo-triphenylmethane	25	4.3×10^{-6}	26.8
tert-butyl hydroperoxide	80	7.8×10^{-8}	34
Diacetyl peroxide	35	9.5×10^{-5}	32.3

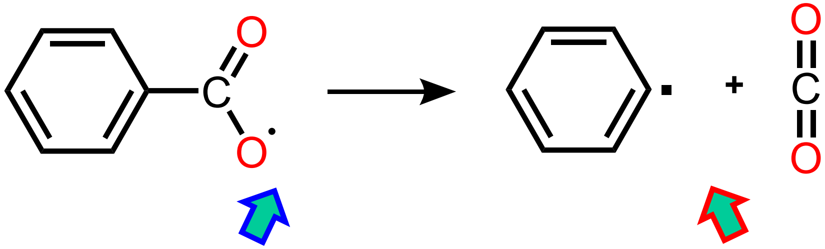
Chain-growth Polymerization

Radical Polymerization: Reactive Intermediates in the Initiator Activation.

In the initiation step, a free radical is formed by homolytic breaking of a bond of reaction initiator, generally a peroxide or azo-compound.



Dibenzoyl peroxide



Fast Irreversible

Benzoyloxy Radical

Phenyl Radical

The relative importance of the two intermediates in the initiation reactions depends on monomer type (if reactivity is low, phenyl radical prevails).

Chain-growth Polymerization

Free-Radical Polymerization: kinetic of Initiation.

- Initiation reaction: occurs when the activated initiator reacts with a monomer

$$R\bullet + M \xrightarrow{k_i} RM\bullet$$

Initiation rate: $R_i = k_i[\mathrm{R}^\bullet]\cdot[\mathrm{M}]\ \boxed{= 2k_d[\mathrm{R}_2]f = \frac{-d[\mathrm{M}^\bullet]}{dt}}$

$$f:\ \text{initiator efficiency} = \frac{\text{radicals initiating polymerization}}{\text{radicals formed by initiator}}$$

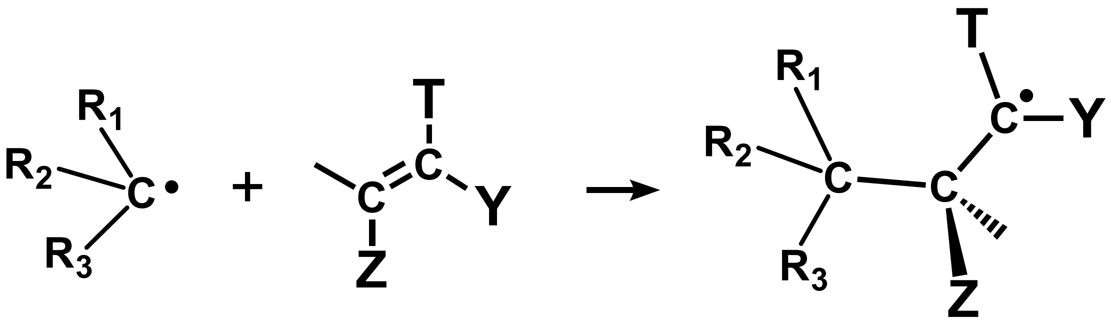
(f typically: 0.3-0.8)

The overall process of initiator activation and reaction starting is the rate determining step of radical polymerization!

Chain-growth Polymerization: Double Bond Radical Addition.

The next step of propagation can be arranged in two parts: the addition and the chain transfer.

In the addition step the radical formed from the initiator adds to a monomer molecule, here represented by an alkene, to form a second free radical, which becomes the start of a growing chain. Substituents on both radical and olefins influence the kinetic of the addition:

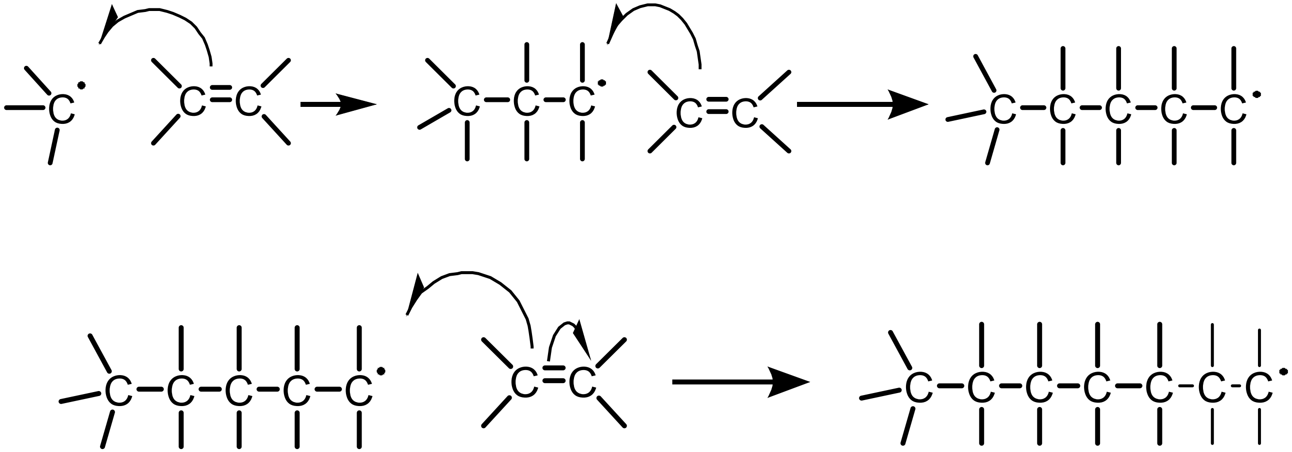


Monomer
(alkene)

Start of the
chain

Chain-growth Polymerization: Radical Propagation.

In the transfer step, the carbon radical reacts with a new monomer molecule providing a new radical:



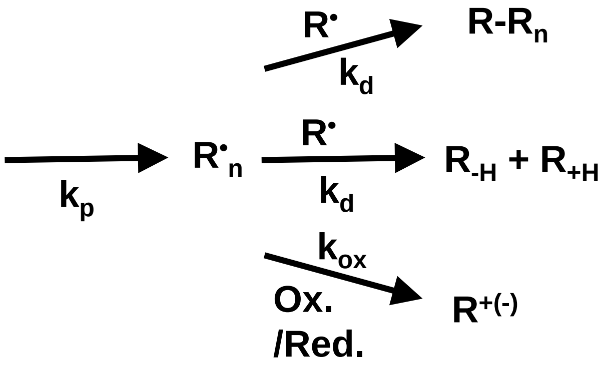
Replication of this step produces the insertion of several monomer molecules forming increasingly longer polymer chains.

Chain-growth Polymerization

Free-Radical Polymerization: Termination and Propagation Kinetics.

Termination reaction: when two radicals interact with disappearance of two active centers. Occurs by:

- dimerization
- disproportionation
- (redox reactions)



$$\xrightarrow[k_p]{} R^\bullet_n$$

$$R^\bullet_n \xrightarrow[k_d]{R^\bullet} R\text{-}R_n$$

$$R^\bullet_n \xrightarrow[k_d]{R^\bullet} R_{-H} + R_{+H}$$

$$R^\bullet_n \xrightarrow[\text{Ox. /Red.}]{k_{ox}} R^{+(-)}$$

Termination rate $R_t = 2k_t[\mathrm{M}^\bullet]^2$

- At the stationary state, $R_i = R_t$ therefore:

$$2k_d[\mathrm{R}_2]f = 2k_t[\mathrm{M}^\bullet]^2$$

e

$$\boxed{[\mathrm{M}^\bullet] = \sqrt{\frac{k_d[\mathrm{R}_2]f}{k_t}}}$$

- then, the propagation rate is:

$$R_t = k_p[\mathrm{M}^\bullet]\cdot[\mathrm{M}]$$

$$\boxed{\mathrm{R_p} = k_p[\mathrm{M}]\sqrt{\frac{k_d[\mathrm{R}_2]f}{k_t}}}$$

Chain-growth Polymerization

Free-Radical Polymerization: Mean Chain Length.

- Mean chain length ν: average number of monomer units polymerized for initiated chain.

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

$$v = \frac{k_p[\mathrm{M}^\bullet]\cdot[\mathrm{M}]}{2k_i[\mathrm{M}^\bullet]^2} = \boxed{\frac{k_p[\mathrm{M}]}{2\sqrt{k_d k_i [\mathrm{R}_2] f}}}$$

The mean chain length can be controlled because it:

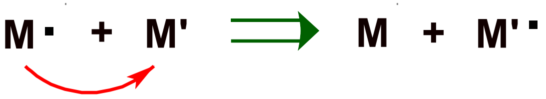
- increases decreasing the initiator concentration.
- increases increasing the polymerization rate.
- Increases increasing the monomer concentration.

Chain-growth Polymerization

Free-Radical Polymerization: More Complex Kinetics.

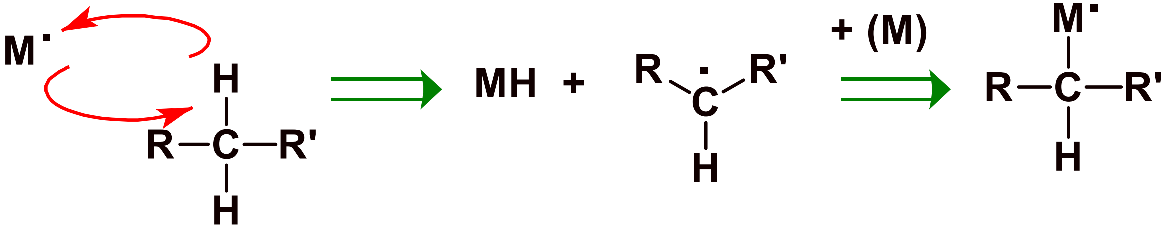
Previous analysis fails when:

- Viscosity of solution changes reducing R_t (because chain terminals are not enough mobile to found termination centers).
- Chain transfer reactions happens (when the active center is transferred to a non reactive molecule).

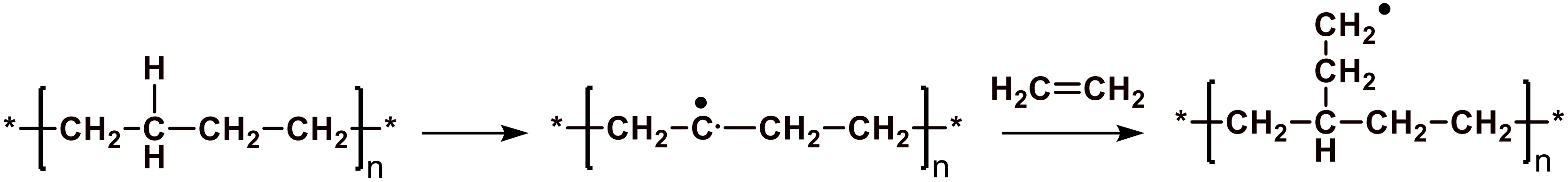


$$M^{\cdot} + M' \Longrightarrow M + M'^{\cdot}$$

molecule-molecule transfer



Hydrogen abstraction (produces branching)



Chain-growth Polymerization

Free-Radical Polymerization: Kinetic Constants.

- Typical values of kinetic constants of radical reactions

k_d	10^{-3} sec^{-1}	ΔE_d	30 - 50 kcal·mol^{-1}
k_i	10^{3} L mol^{-1}sec^{-1}	ΔE_i	5 - 7 kcal·mol^{-1}
k_p	10^{3} L mol^{-1}sec^{-1}	ΔE_p	4 - 10 kcal·mol^{-1}
k_t	10^{7} L mol^{-1}sec^{-1}	ΔE_t	0 - 6 kcal·mol^{-1}

Reminder:

- The increase of T has a strong effect on the **initiation** via k_d.
- Controlling T, we control [M$^\bullet$], the rate, and ν

Chain-growth Polymerization

Free-Radical Polymerization: Influence of the Termination Type.

- The polymerization degree: depends on the termination mechanism.
  - Combination: M• + •M’ ⇨ M-M’ $DP = 2\nu$
  - Disproportionation: M• + •M’ ⇨ M + M’ $DP = \nu$

- Transfer Reactions: they can be changed by addition of molecules which can be involved in transfer reactions but are unable to participate in polymerization (solvent or impurity).

Chain-growth Polymerization

Free-Radical Polymerization: Probability P_p.

Chain fraction of *n length* : X_n

- X_n = product of polymerization probability [P_p] with itself *n*-1 times, multiplied by the termination probability to stage *n* = (1-P_p)

$$\boxed{X_n = P_p^{n-1}(1-P_p)}$$

[Assuming each addition having a constant probability to occur independently from length]

$$P_p = \frac{\text{propagation per time unit}}{\text{reactions per time unit}} = \frac{N_p}{N_p + N_t}$$

$$P_p = \frac{k_p[\mathrm{M}]}{k_p[\mathrm{M}] + 2k_t[\mathrm{M}^\bullet]^2}$$

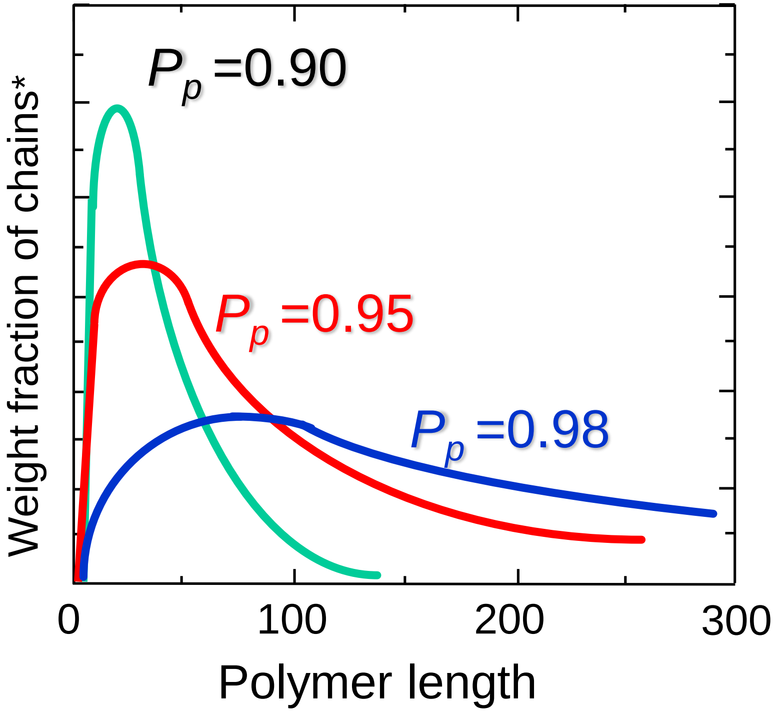
Note: P_p does not change with time.

Chain-growth Polymerization

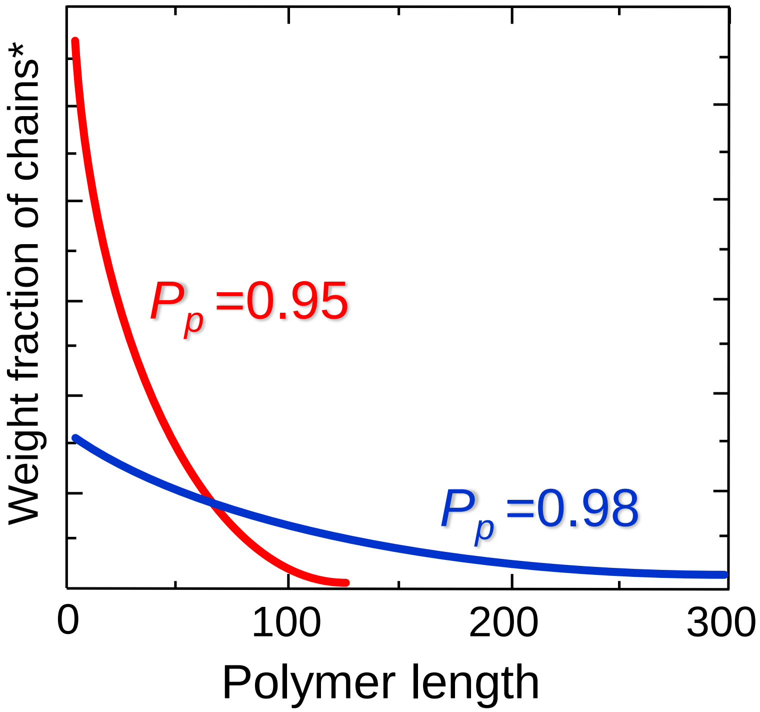
Free-Radical Polymerization: comparison with Step-growth Polymerization.

Distributions are the same of condensation polymerization but does not change with time (P_p = constant).

Step-growth Polymerization



Chain-growth Polymerization



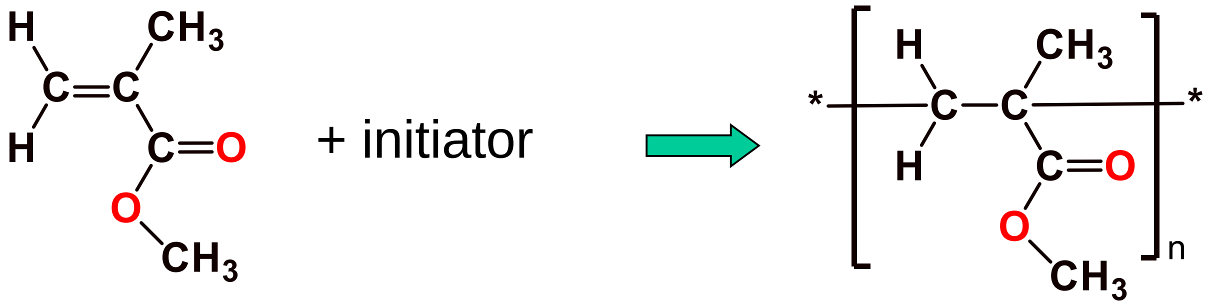
(*Note: monomers are not “chains“ and are not present in the mean)

Chain-growth Polymerization

Free-Radical Bulk Polymerization.

- Bulk Polymerization: initiator and polymer soluble in pure monomer.

Example: poly(methyl methacrylate) (PMMA)



methyl methacrylate

Heating a bottle of methyl methacrylate in the presence of an initiator affords a transparent plastic (PMMA) preserving the shape of container! The volume decreases because the polymer is more dense.

Lucite and Plexiglas are forms of atactic amorphous PMMA.

Bulk Polymerization of PMMA

This system shows auto-acceleration. As the polymer solution becomes more dense, a gel is formed. The reduced mobility of chains decreases the termination rate and the chain length increases. (This is good for fusion, but bad for molding or extrusion).

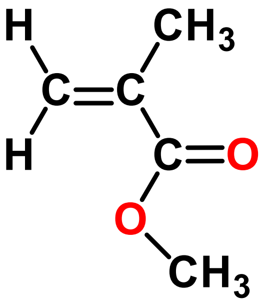
- Large scale bulk polymerizations may threaten to become uncontrollable if heat transfer is impossible due to viscosity increase.
- Still, continuous polymerization of 5 cm thickness strip is feasible.
- The most important commercial applications of bulk polymerizations involve those of
  - polystyrene,
  - methacrylates,
  - low density polyethylene.

Chain-growth Polymerization

Effect of Alkyl Chain in the Free-Radical Polymerization of Methacrylates.

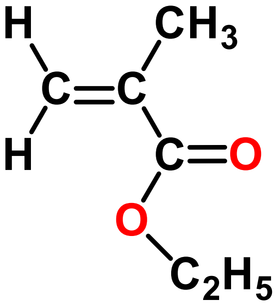
Bulk Polymerization of PMMA

As the molecular weight of side chain of methacrylate monomer increases, the glass transition temperature of polymer decreases:

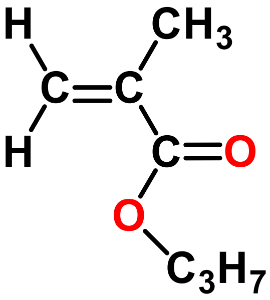


Methyl methacrylate

T_g=105°C



Ethyl methacrylate



n-Propyl methacrylate

T_g=75°C

(but for >10 carbon atoms in side chain, T_g increases by crystallization)

Bulk Polymerization: general behavior

Advantages:

- Simple
- Does not require any isolation or purification of product. Only contains residues of initiator, the remains of monomer and polymer.
- A big object can be directly prepared.
- The product obtained shows high molecular weight.

Disadvantages:

- Wider distribution of molecular weight than normal for addition polymerizations due to:
  - auto-acceleration
  - heating
  - inefficient mixing

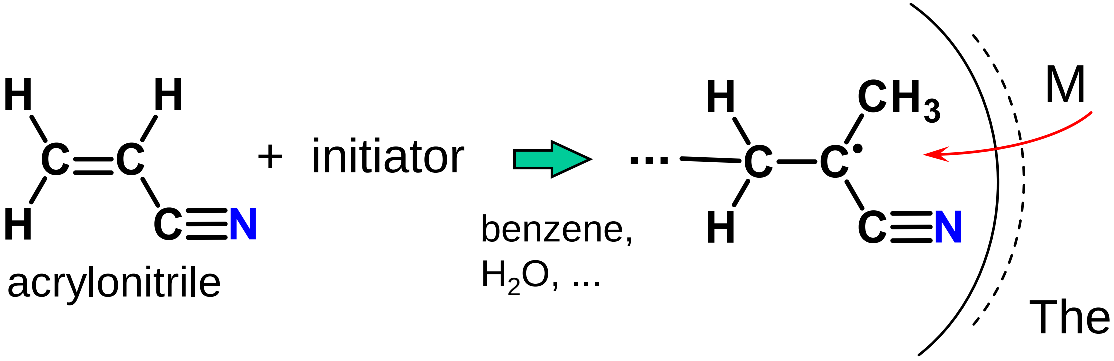
changing P_p with time.

Chain-growth Polymerization

Free-Radical Polymerization in Solution.

Solution Polymerization : a process variant of bulk polymerization but in the presence of a solvent. The reactive polymer precipitates as is formed.

Example: polyacrylonitrile (PAN)



The monomer diffuses in the precipitate and continues the polymerization.

The precipitate increases

The disadvantages are generally::

- Acrylonitrile is carcinogenic. Therefore the acrylic fibers (so made) must not contain monomer in finished products.
- The solvent must be removed from polymer before the use.
- PAN is strongly hydrogen bonded and relatively insoluble, used for C fibers.

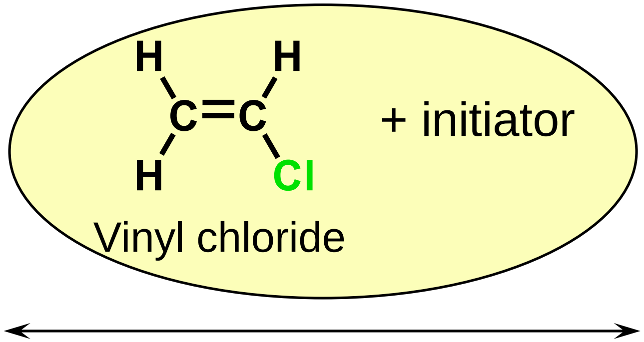
Chain-growth Polymerization

Free-Radical Polymerization in Suspension.

Suspension Polymerization: a process variant of bulk polymerization but with the monomer suspended in drops.

Monomer, initiator and polymer must be insoluble in the suspension media such as water. (O/W and W/O suspension polymerization)

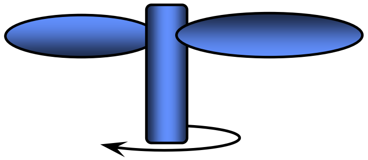
Example: polyvinyl chloride (PVC)



suspension in water (with polyvinyl alcohol to maintain the suspension).

Heat is removed by water.

Drop diameter 10-500 μm



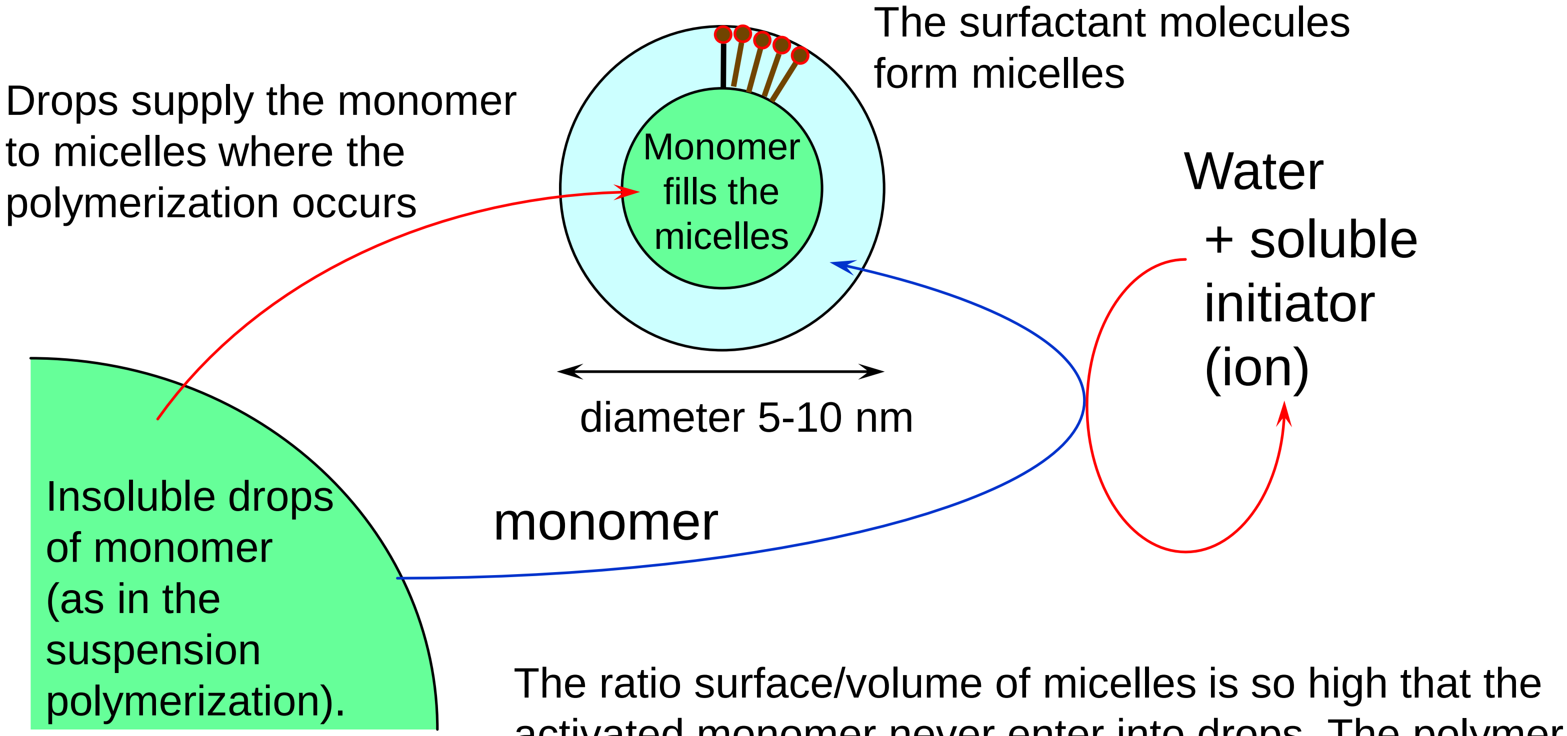
Stirring to maintain the suspension.

A well separated particle suspension is produced. The residual monomer is removed by vacuum evaporation.

Chain-growth Polymerization

Free-Radical Polymerization in Emulsion.

Emulsion Polymerization: a process variant of suspension polymerization except that the initiator is soluble in suspension media and insoluble in the monomer.



The surfactant molecules form micelles

Drops supply the monomer to micelles where the polymerization occurs

Monomer fills the micelles

Water + soluble initiator (ion)

diameter 5-10 nm

monomer

Insoluble drops of monomer (as in the suspension polymerization).

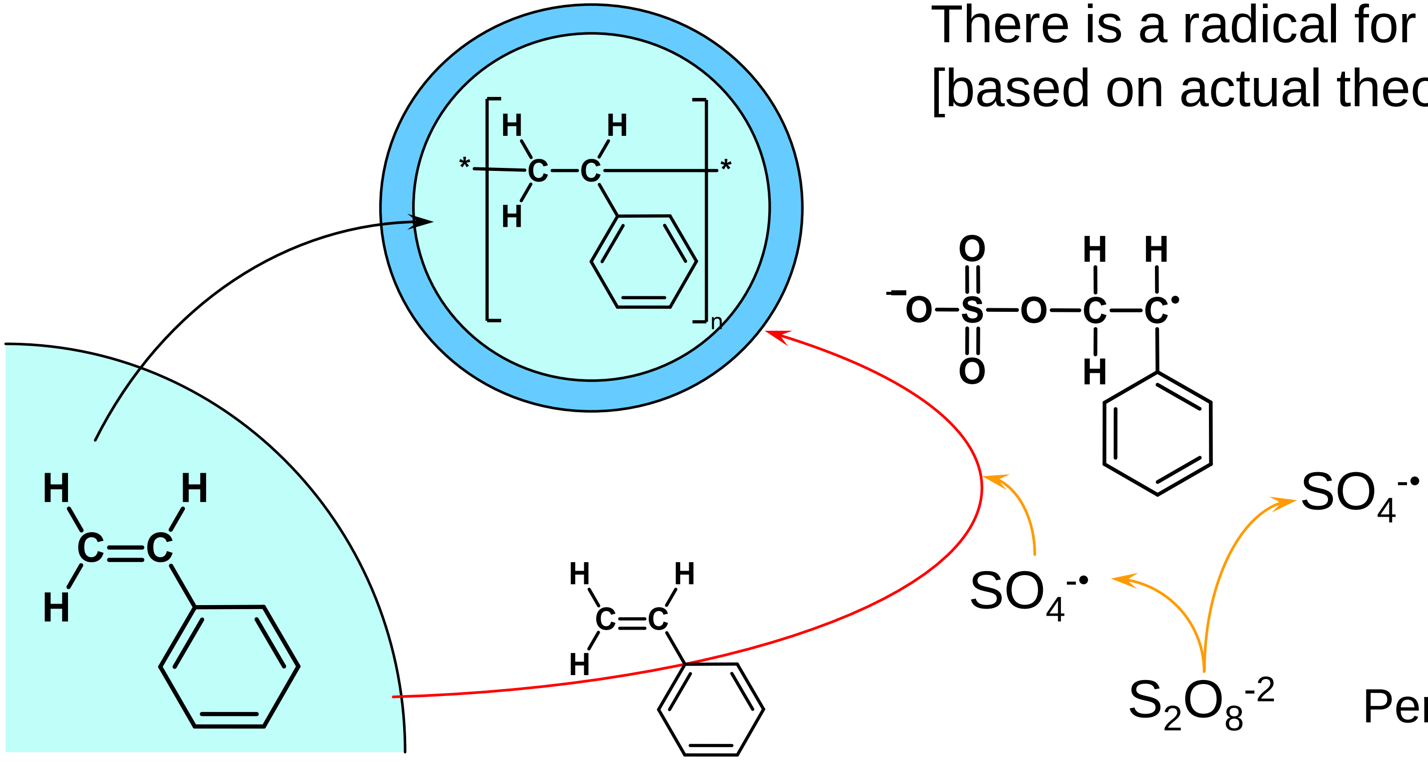
The ratio surface/volume of micelles is so high that the activated monomer never enter into drops. The polymer particles have diameter in the range of 0.05 - 1 μm.

Chain-growth Polymerization

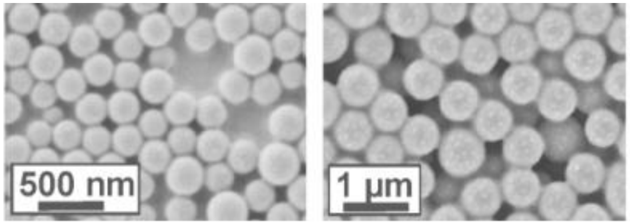
Free-Radical Styrene Polymerization in Emulsion.

Emulsion Polymerization: polystyrene (PS)

There is a radical for a micelle
[based on actual theory]



Persulfate ion

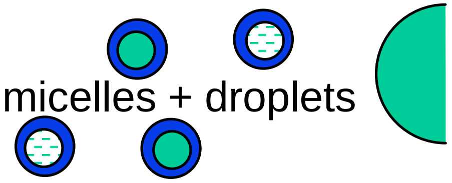


Chain-growth Polymerization

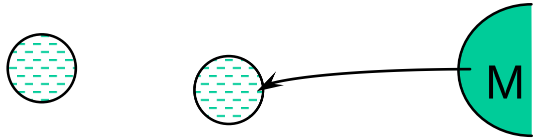
Steps in Free-Radical Polymerization.

Emulsion Polymerization : four steps

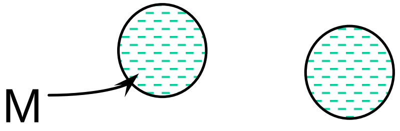
0-20% of monomer consumed:



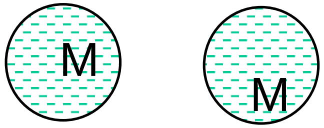
20-30% (form micelles):



30-60% (form droplets):



> 60% (monomer supplied by diffusion into particles).



Emulsion Polymerization: polystyrene (PS)

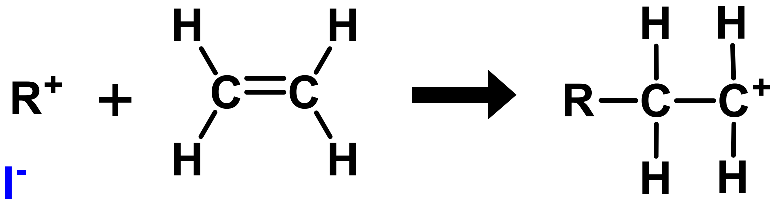
- about half of micelles includes a reactive center.
- The reaction rate depends on micelle concentration which in turn depends on surfactant amount.
- Big micelles take surfactant from smaller (where the polymerization is not started). Finally remain only those where the reaction is taking place.
- The polymerization rate can be increased by addition of Fe^{+2} salts
- This process generates high molecular weight polymers.

Chain-growth Polymerization

Ionic Polymerization.

Similar to radical polymerization. The main differences are:

- The reactive group is charged,
- Counter ions are present.



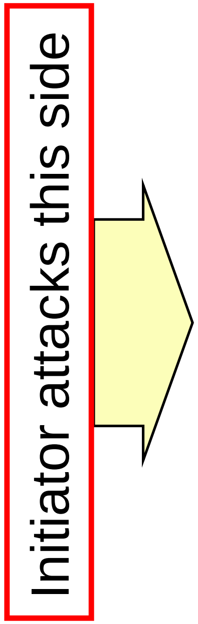
Carbocation

Anionic, cationic, and radical Polymerization:

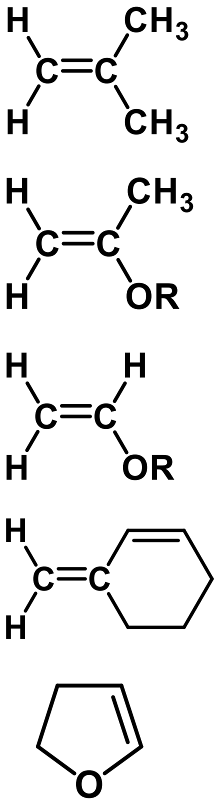
- Depend on substituents bonded to (C=C) vinyl group
- Electron-withdrawing substituents favor anionic polymerization.
- Electron-donor substituents favor cationic polymerization
- Electrophilic and nucleophilic properties of radical intermediates induce discrimination of electron-poor or electron-rich substrates

Chain-growth Polymerization

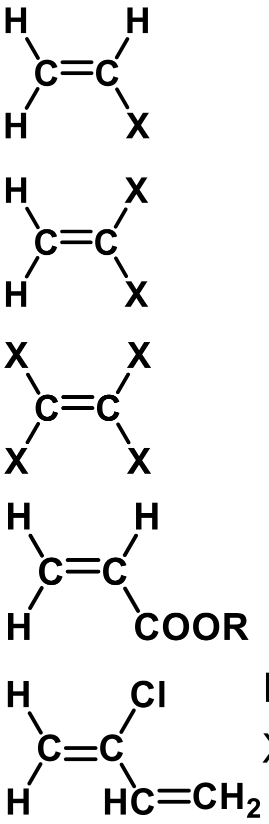
Ionic Polymerization: Effect of Alkene Substituents.



Only cationic:



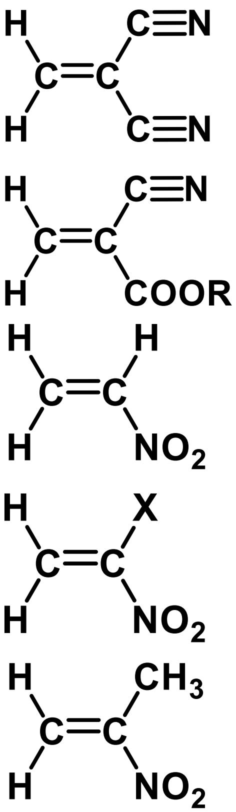
Only radical:



R: alkyl

X: halogen

Only anionic:



Strong e^- donor

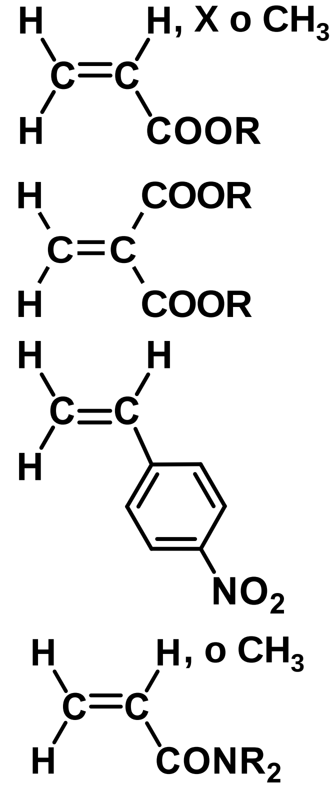
Weak e^- acceptor

Strong e^- acceptor

Chain-growth Polymerization

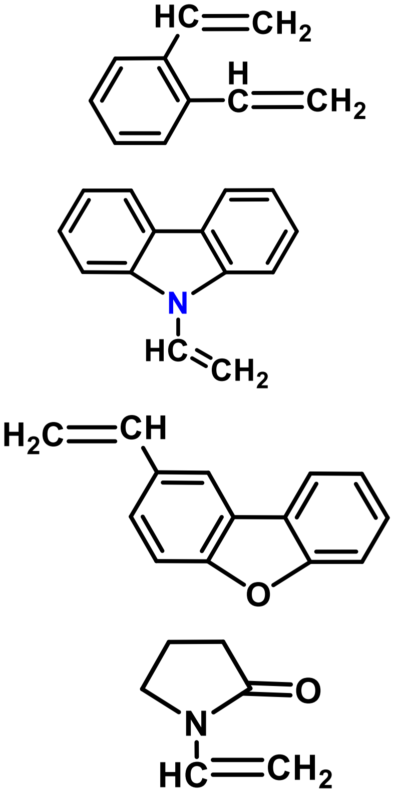
Ionic Polymerization: Effect of Alkene Substituents (2).

Anionic or Radical:



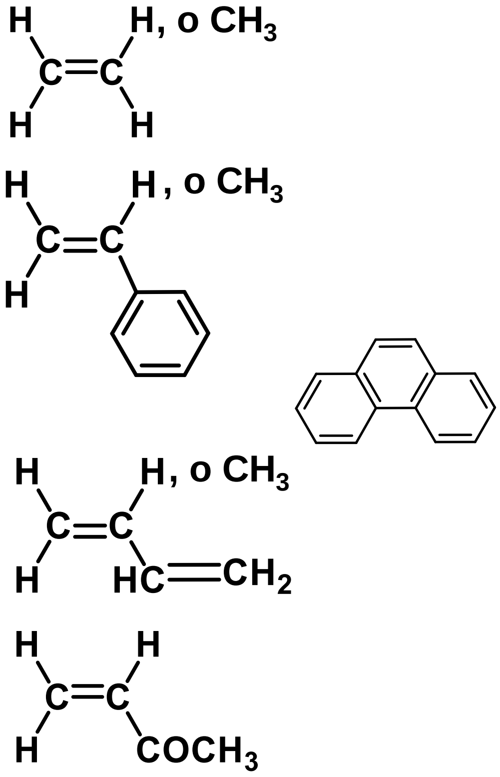
Mild e^- acceptor

Cationic or Radical:



Weak e^- donor

Cationic, Anionic or Radical:



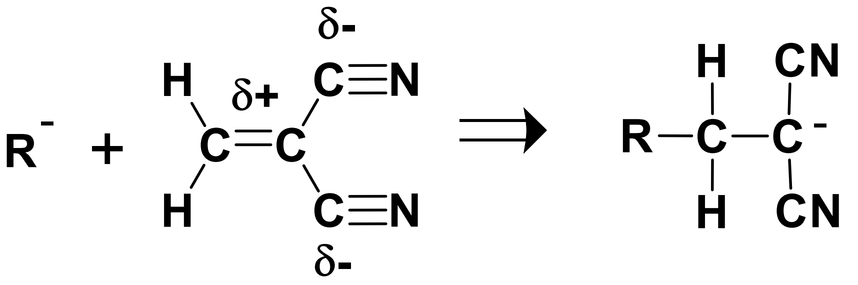
Neutral

Chain-growth Polymerization

Ionic Polymerization: Initiation.

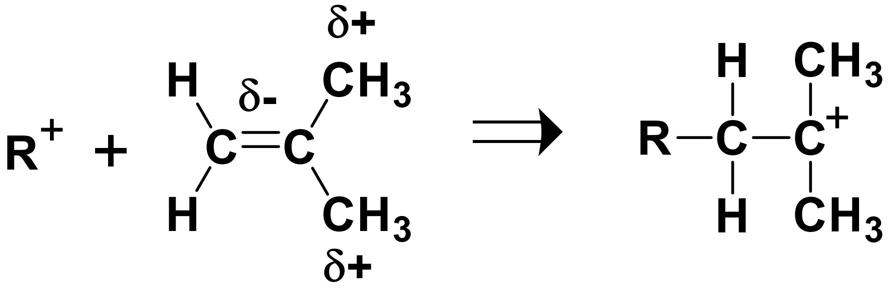
General processes:

Anionic:



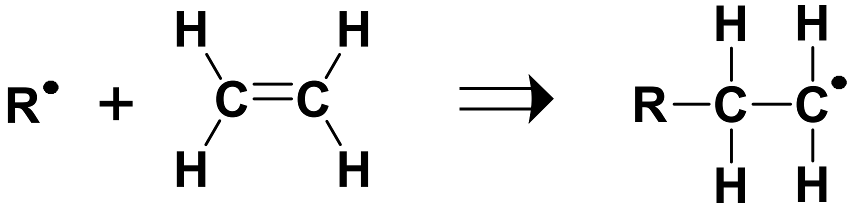
carbanion

Cationic:



carbocation

Radical:

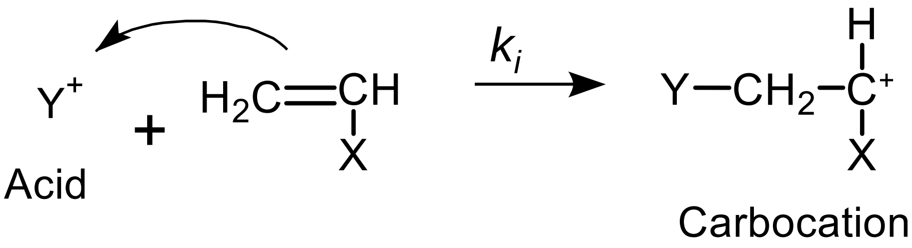


carbon centered radical

Cationic Addition Polymerization.

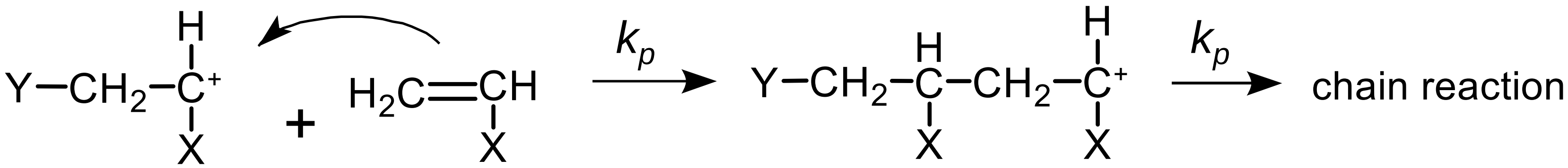
Also the ionic addition polymerization proceeds following a mechanism characterized by an initiation step and a propagation step.

In the case of cationic polymerization, the initiator is an acid, i.e. sulfuric acid, $AlCl_3$ or BF_3 in the presence of traces of water.



X = electron-releasing group

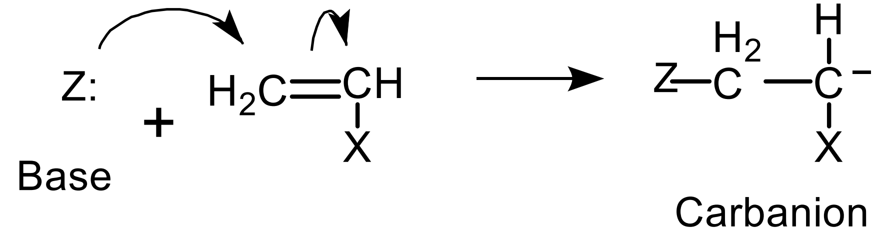
Initiation step



Propagation step

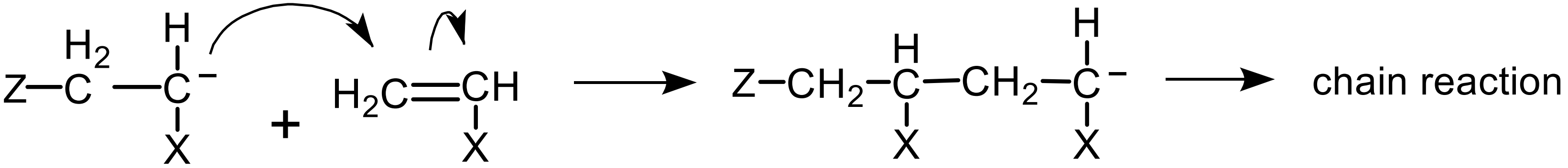
Anionic Addition Polymerization.

In the case of anionic polymerization the initiator is a base, i.e. $LiNH_2$ or organometallic compounds i.e. n-butyl-lithium:



X = electron-withdrawing group

Initiation step



Prpagation step

Chain-growth Polymerization

Cationic Polymerization: DP and Stereochemistry.

- Frequently isotactic or syndiotactic (alternant) structures are observed (reasons are unclear).
- Tacticity becomes more casual with the increase of temperature.
- Change with the initiator and with solvent polarity.

Kinetics:

$$DP = \frac{k_p[\mathrm{M}]}{\underset{\substack{\uparrow \\ \text{Termination rate}}}{k_t}[\mathrm{M}] + \underset{\substack{\uparrow \\ \text{Transfer rate}}}{k_{tr}}}$$

Chain-growth Polymerization

Cationic Polymerization: Initiation.

- The initiator contains an electron-deficient center (electron-acceptor).
- May require a proton donor added to activate the initiator. (e.g.: $R_3Al + H_2O$ [H^+ donor]) or Lewis acids ($AlCl_3$, BF_3).

Examples of initiators :

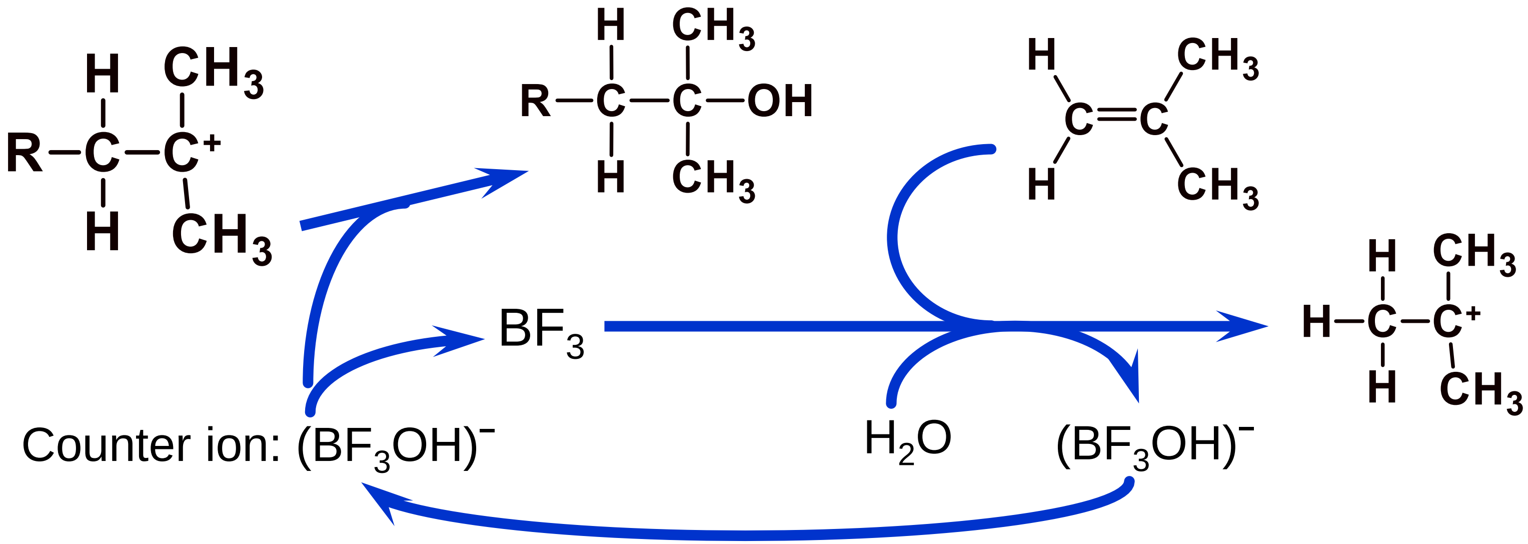
- Strong mineral acids (H_2SO_4, H_3PO_4,...)
- Lewis Acids (e.g.: $AlCl_3$, BF_3, $SnCl_4$, $FeCl_3$)
- Iodine ($2\ I_2 \rightarrow I^+ + I_3^-$)
- Carbocations (carbonium ions C^+) (e.g..: $\phi_3C\text{-}X$, $R_3C^+{:}HgX_3^-$, $RC^+O{:}ClO_4^-$,...
- Coordination complexes ($TiCl_4 + RCl \rightarrow TiCl_5^- + R^+$)

Cationic Polymerization: Termination.

Charge neutralization

- The ion pair rearranges to form a terminated polymer
  - If the initiator can be regenerated, it can be considered a **catalyst**!

Example: [polymerization of dimetyllethylene (isobutene) with BF_3 as initiator]

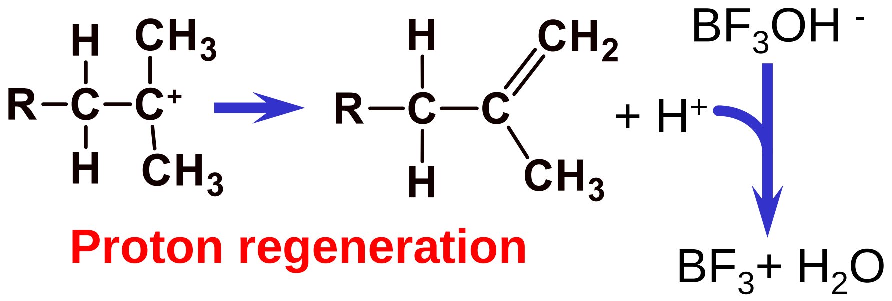


Chain-growth Polymerization

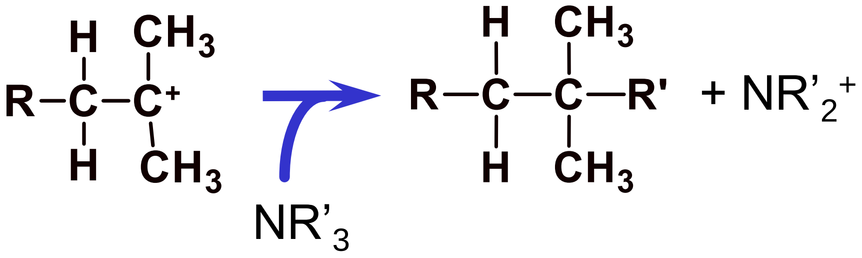
Cationic Polymerization: Termination Types.

Charge neutralization

- Alternative termination processes:



Proton regeneration



Poisoning by contaminants (e.g.: O, N or S compounds)

Charge transfer

To another polymer => a branched polymer

To solvent => dead catalyst

To a monomer => start of a new chain, dead of the old chain.

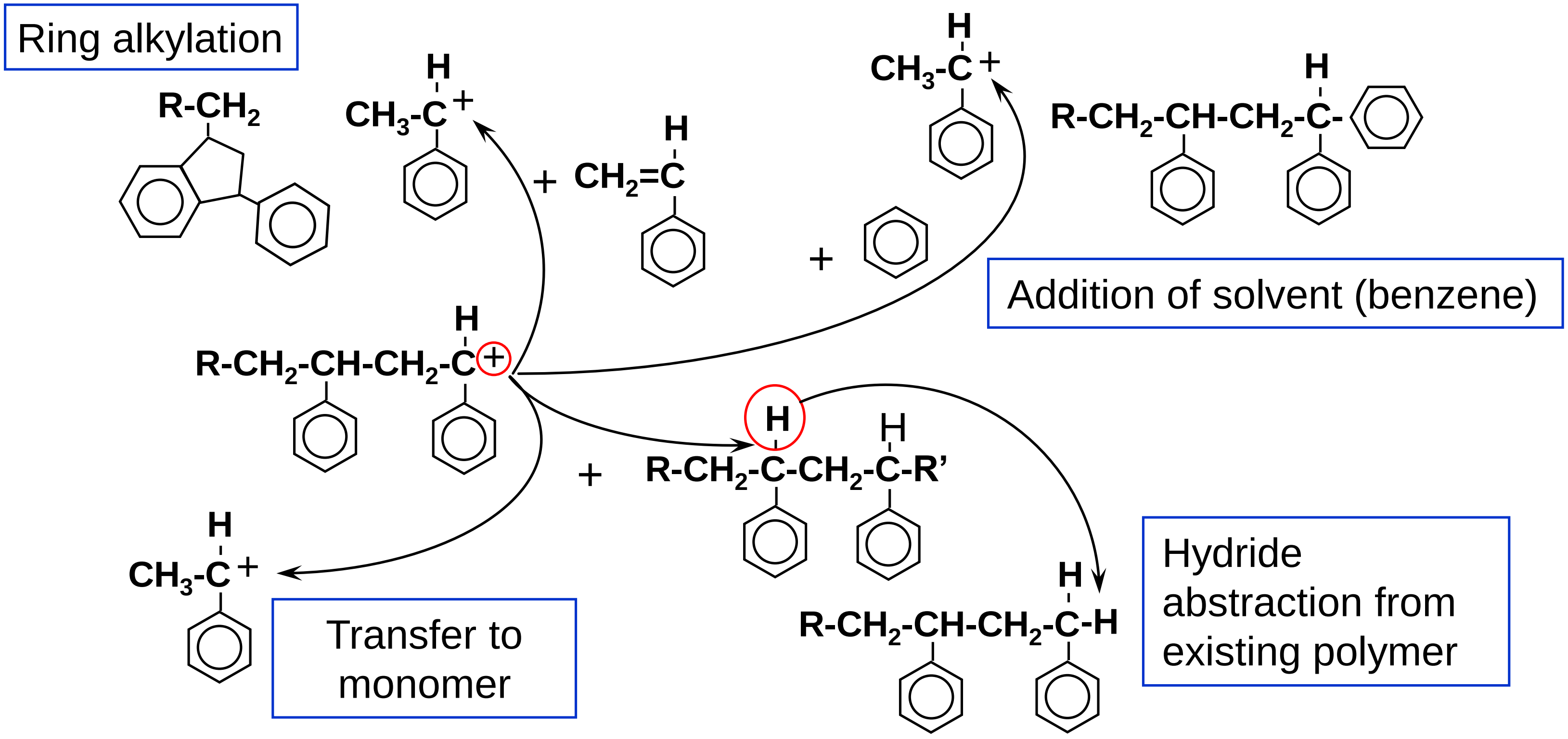
[common with carbocations]

Chain-growth Polymerization

Cationic Polymerization: Termination by Charge Transfer.

Example of charge transfer reaction (most common termination)

Polymerization of styrene with sulfuric acid (H_2SO_4):

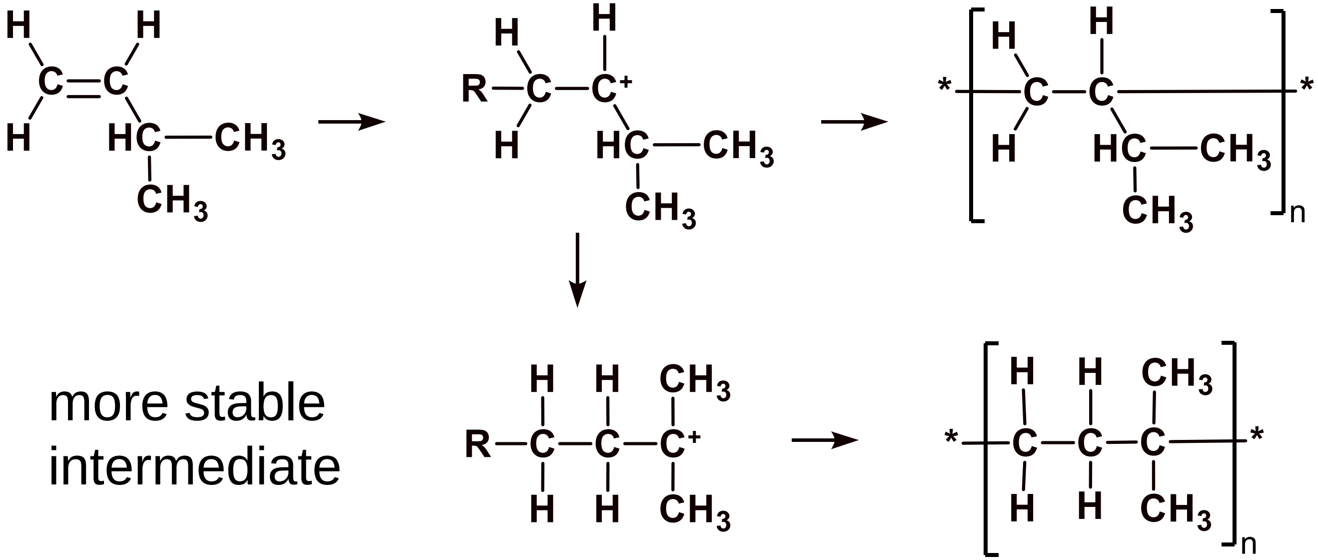


Chain-growth Polymerization

Cationic Polymerization: Mechanism Isomerization / Branching.

In addition to proton abstraction, branching and isomerization can occurs during polymerization with rearrangement of structure.

Example: polymerization of 3-methyl-1-butene :



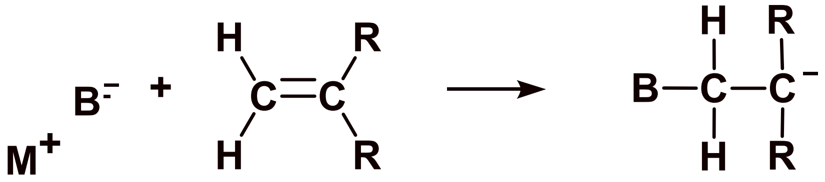
simple

more stable intermediate

rearranged

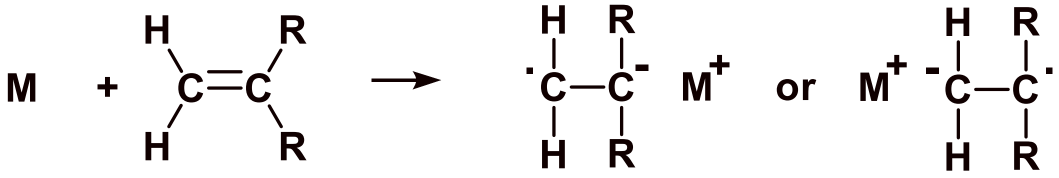
Similar to cationic polymerization. Initiation:

- Substituents on vinyl group must be electron-withdrawing or unsaturated both stabilizing the addition of a base to a carbanion:



B: a base, normally the strongest is better.

- Alkali metal reactions:



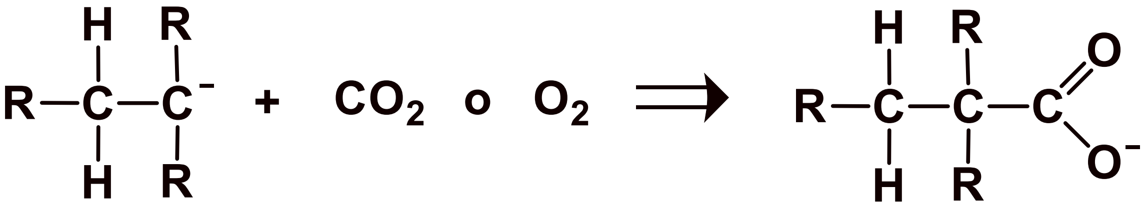
- Propagation is similar to the cationic processes.

Chain-growth Polymerization

Ionic Polymerization: Anionic Termination.

Termination

- Hydrogen abstraction (as before).
- Transfer of reactive center (as before).
- Formation of a stable anion:

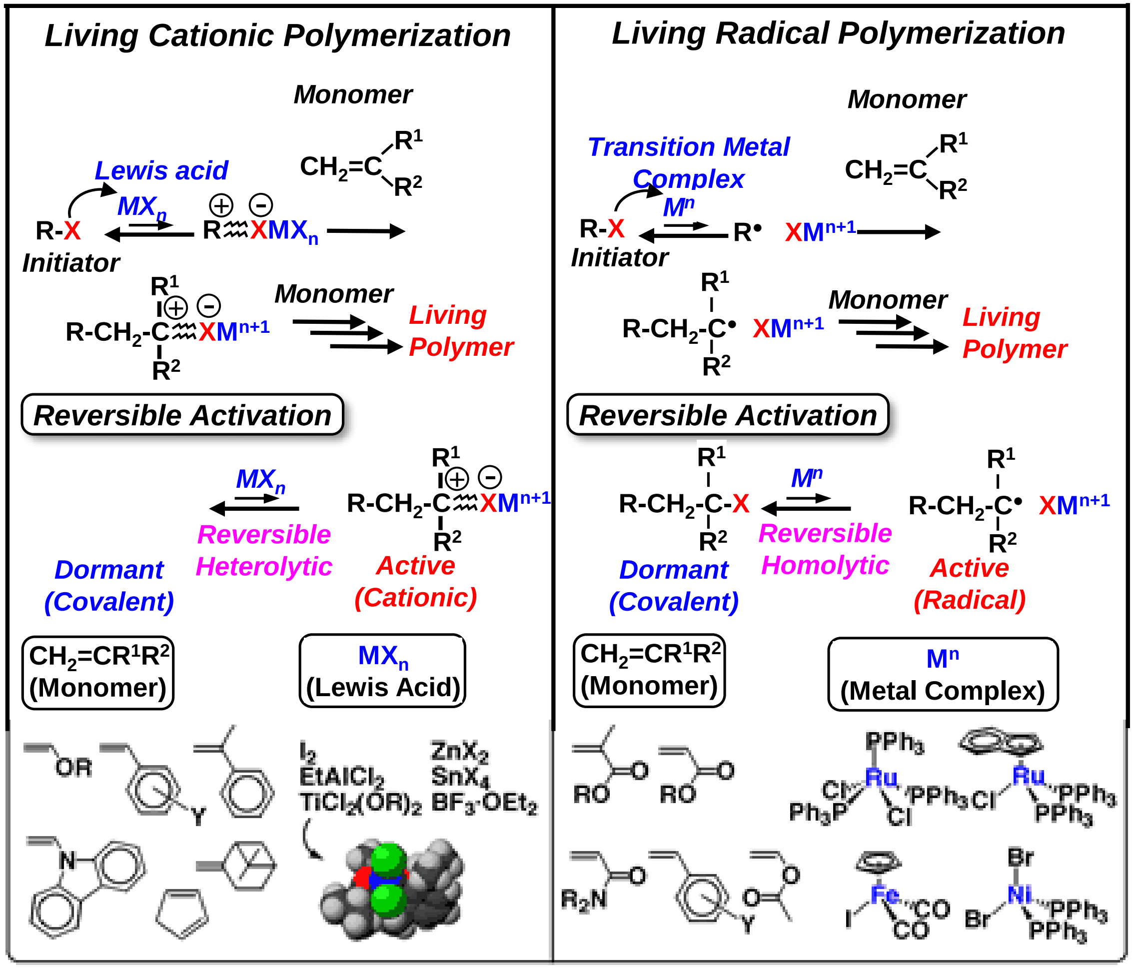


“Living” Polymerization: if free from impurity, the initiation sites are preserved even when all the monomer is consumed. By addition of further monomer other polymer is formed! (Useful for copolymerization.)

Living Polymerization.

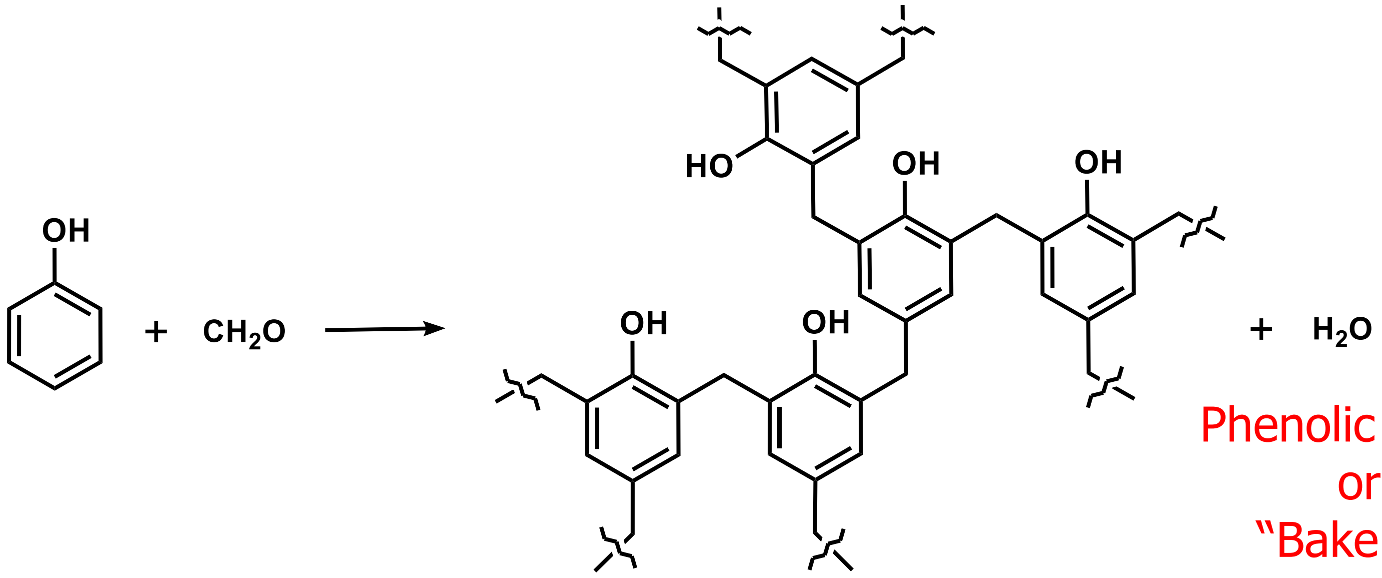
Precision Polymerization

- a) Living cationic polymerization (via designed Lewis acids)
- b) Living radical polymerization (via designed metal catalysts)
- c) Precision polymerization in water
- d) Stereoregular polymerization
- e) Chemistry of reaction intermediates
- f) General principles of precision polymerization control



Phenol-Formaldehyde Resins.

Polymers obtained by polyaddition of formaldehyde to *ortho-para* carbons of phenol. The material has a tridimensional structure (cross linked) owing to the casual involvement of two different positions.

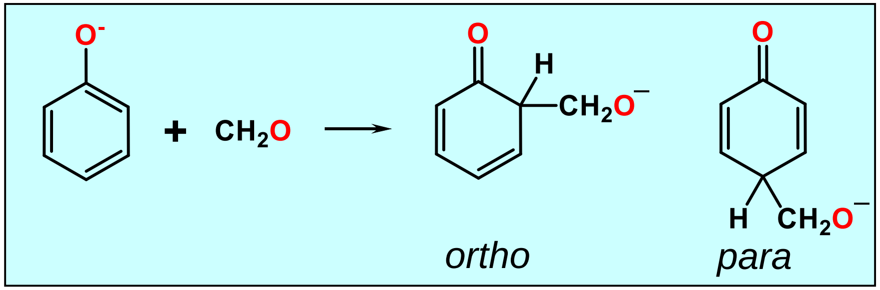


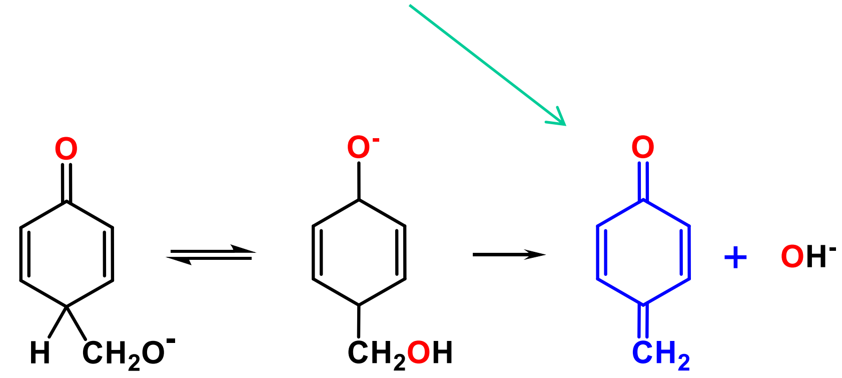
Phenolic Resin
or
“Bakelite”

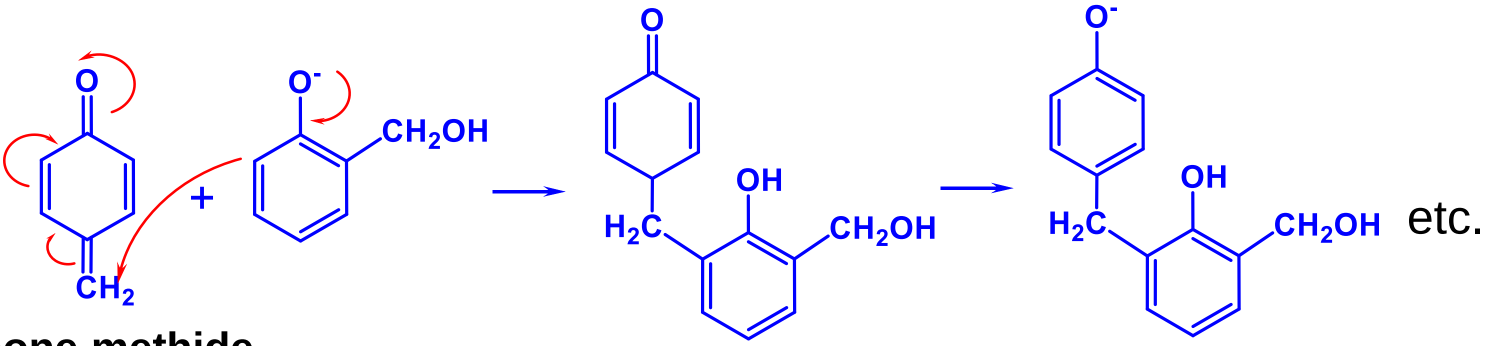
In this polymerization the phenoxide ion (formed from the weak acid phenol) is the reactive specie.

Phenol-formaldehyde Resins – Bakelite.

The electron-poor C of formaldehyde adds to phenol at the positions *ortho* or *para* to oxygen, owing to the high density of negative charge for resonance at these sites. Then, addition to Quinone methide can occurs.







Quinone methide

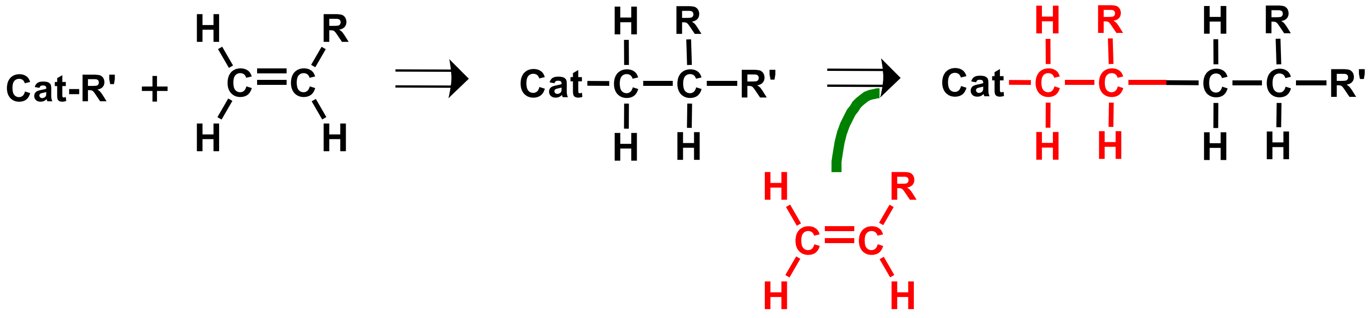
Addition Polymerization

Coordination complex Polymerization.

An example of catalyzed polymerization

- Peculiarity
  - Can be stereospecific
  - Heterogeneous or homogeneous.
  - Chain growth by insertion between the catalyst and the chain residue:

Catalyst



Addition Polymerization

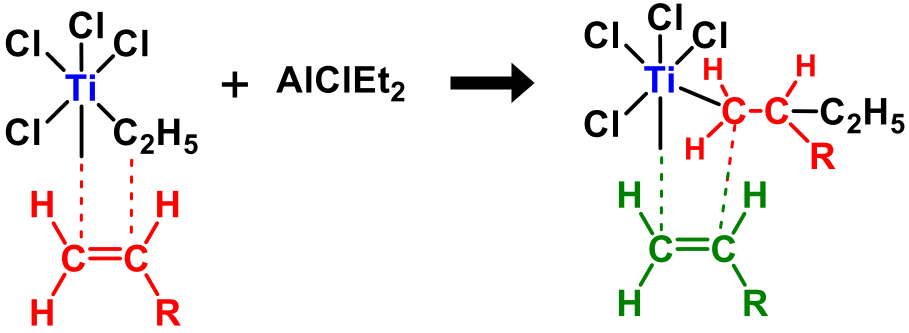
Coordination complex Polymerization (2).

Example: Ziegler-Natta Catalysis (developed in early 1960)

- Catalyst:
  - Transition metal compound (e.g.: $TiCl_3$) - the catalyst
  - Organometallic compound of I or III group [e.g.: $(C_2H_5)_3Al$] - the co-catalyst

Catalytic complex:

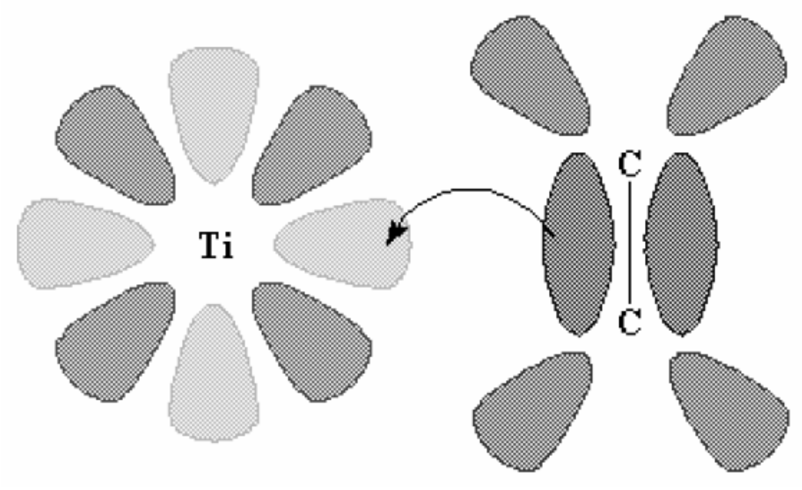
interaction with π bond

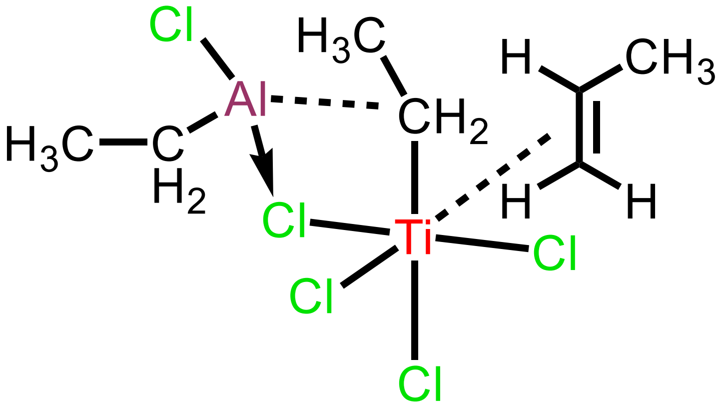


An isotactic polymer is formed.

Mechanism of Coordination Polymerization.

The polymerization reaction occurs with a mechanism which involve a bond between the titanium metal and the alkene (monomer) via a π bond, i.e. with overlapping of the molecular orbital of π bond of alkene to an empty *d* orbital of the metal.

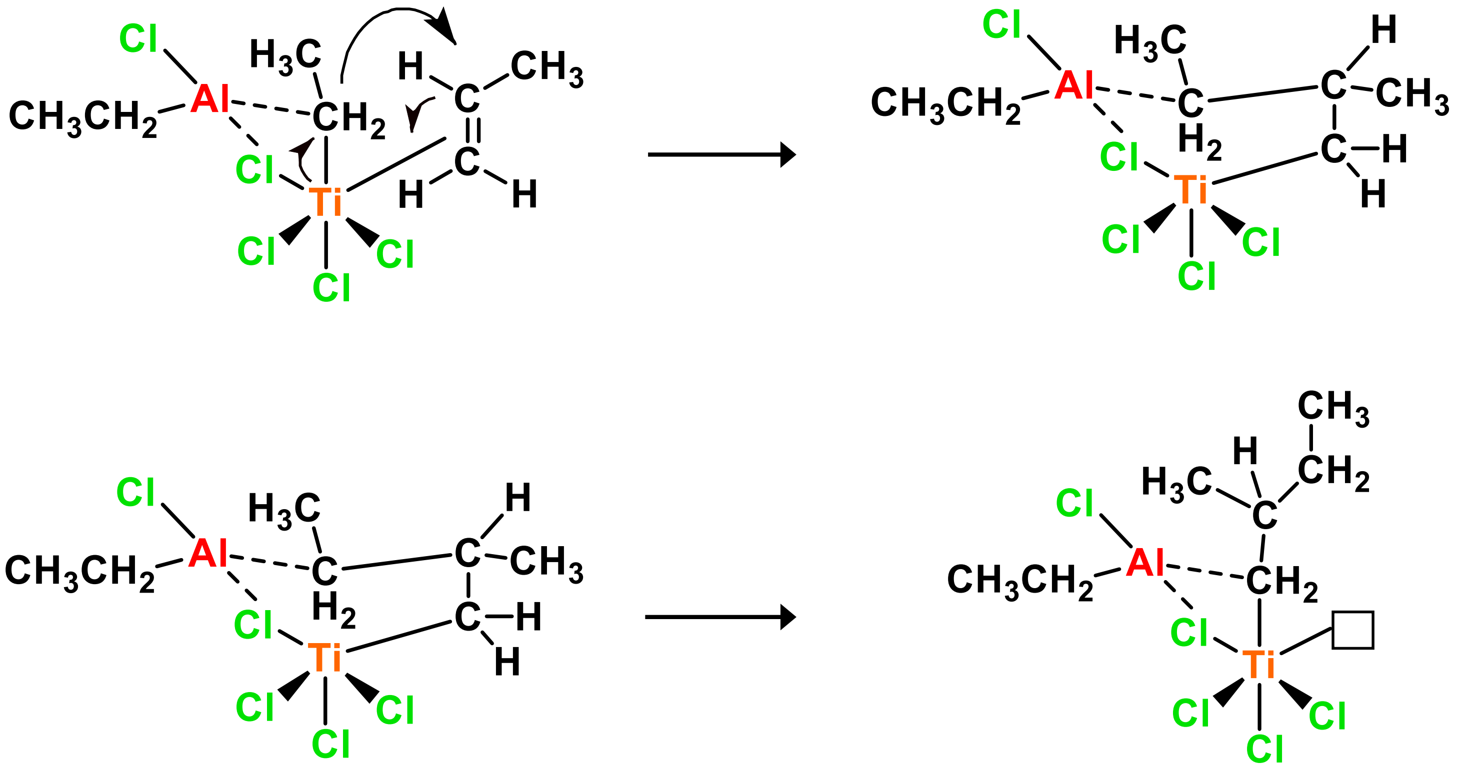




Titanium Complex

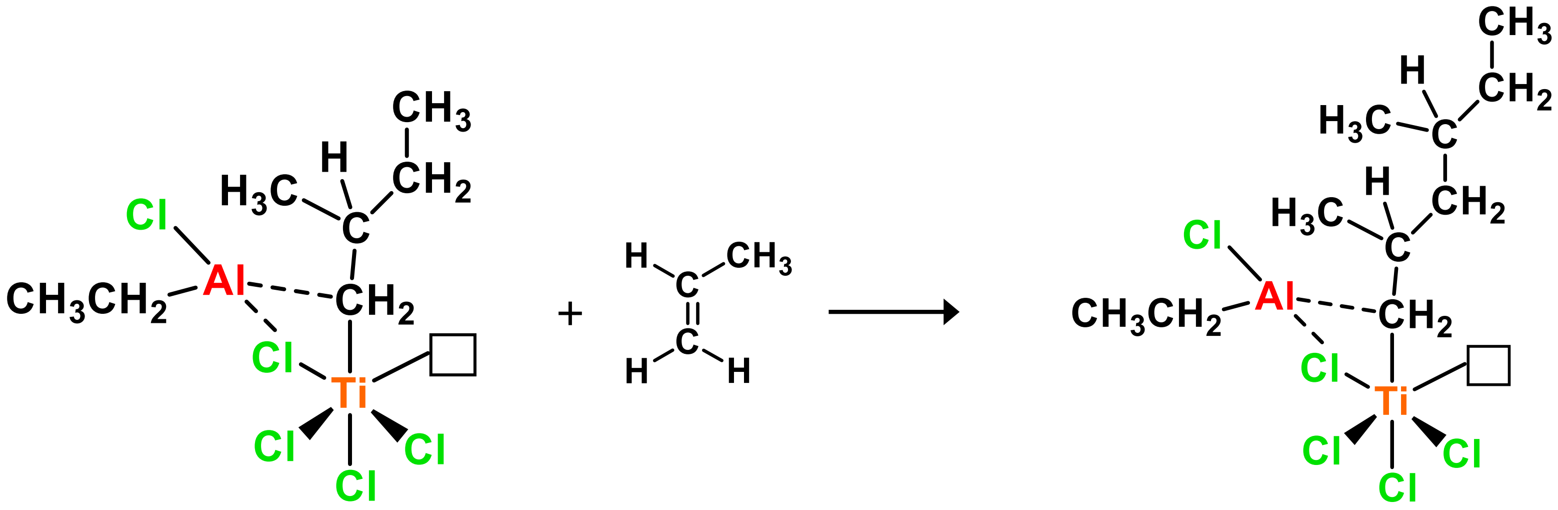
Mechanism of Coordination Polymerization: Alkene Insertion.

Next, the monomeric unit inserts between the metal and the ethyl group to form a butyl group linked to titanium:



Mechanism of Coordination Polymerization: Propagation of Insertion.

At this stage, a new alkene molecule can bound to the titanium starting a new addition process:

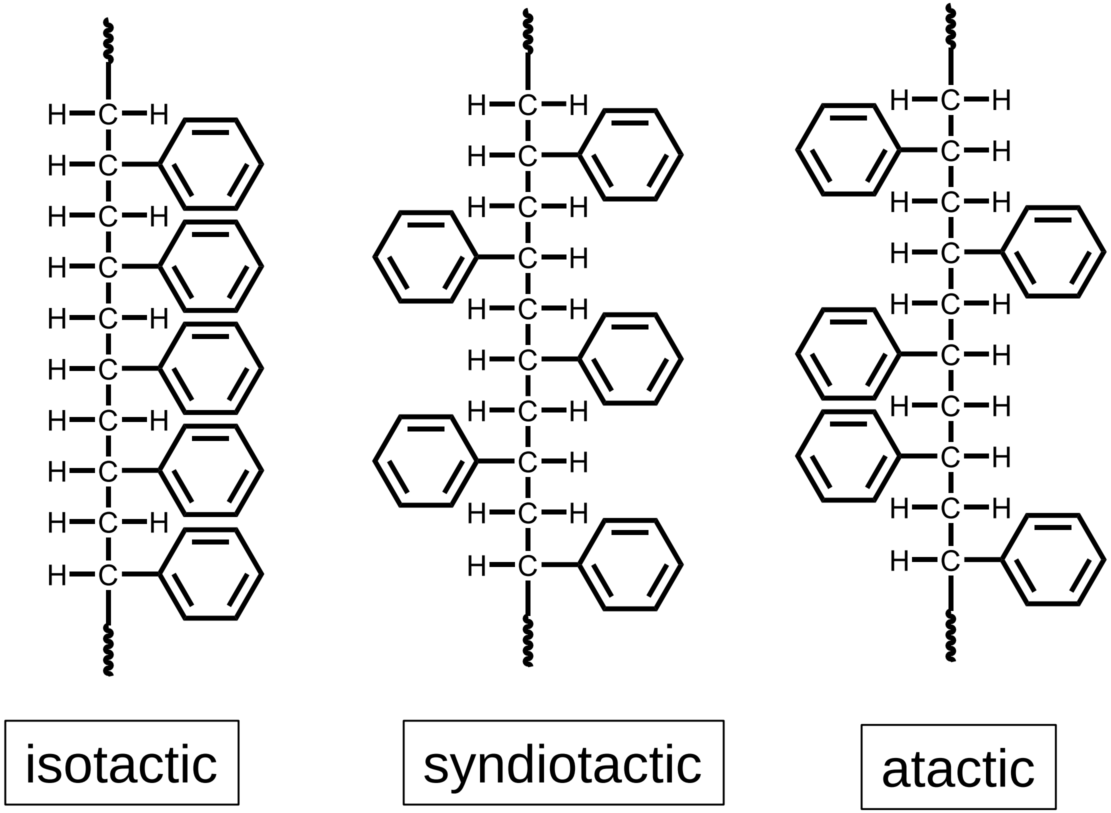


The insertion proceeds further, with the alkyl group bound to titanium growing at each stage by two carbon units.

Finally, perhaps via the insertion of an hydrogen atom, the polymer chain is removed from the metal.

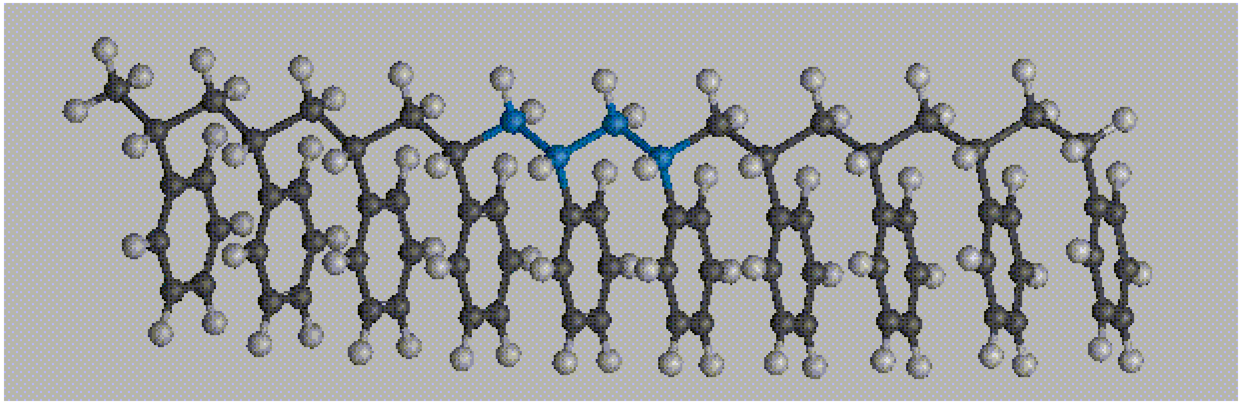
Peculiarities of Coordination Polymerization - Tacticity.

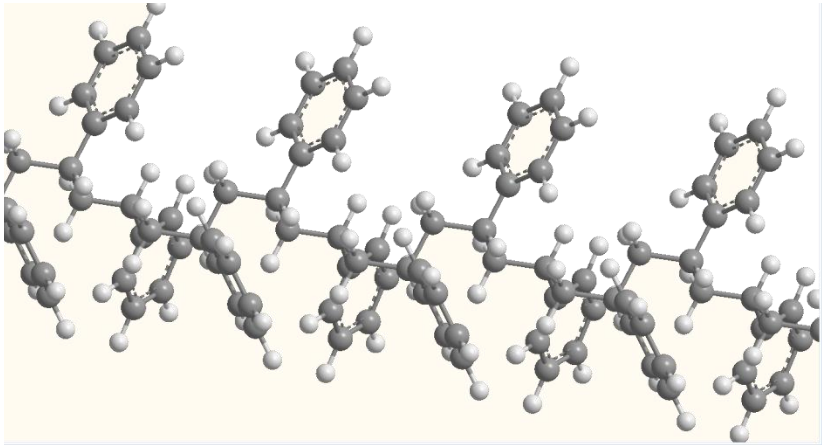
In the polymerization of monosubstituted alkenes the stereochemical control drive the synthesis to form chains which are or isotactic, or syndiotactic, or atactic.



Peculiarities of Coordination Polymerization: Isotactic Polymers.

An isotactic polymer presents the substituent groups (methyl groups in the case of polypropylene, and phenyl group in polystyrene) all chains are sideway lined. Isotactic polymer consists entirely of *meso* diads.

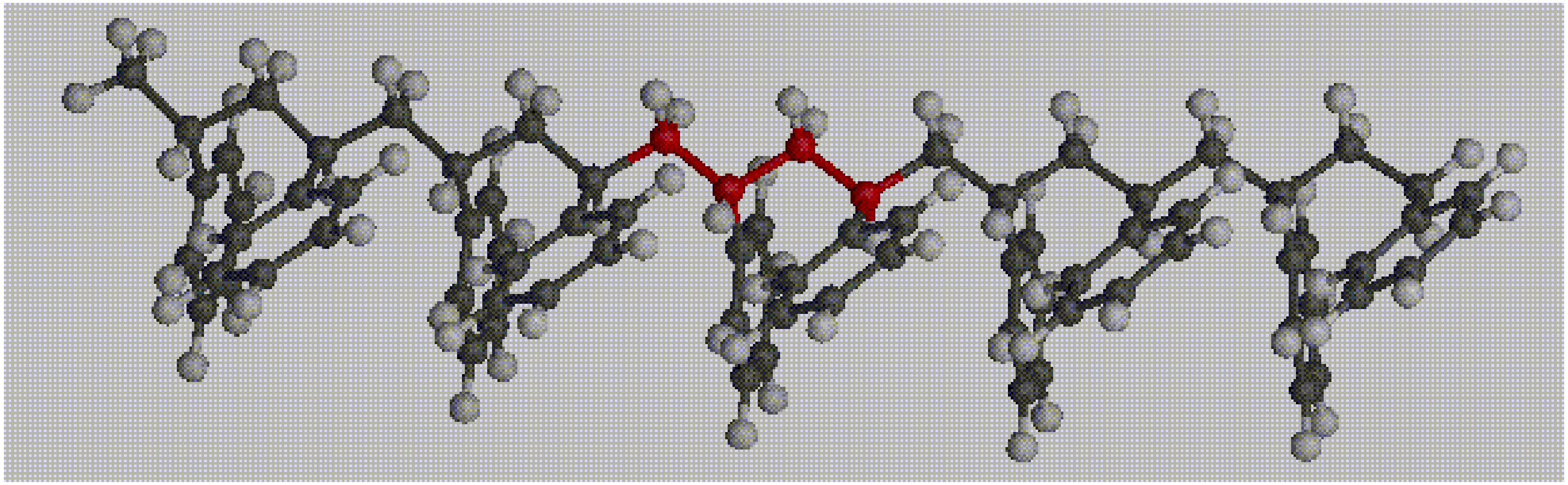




X-ray crystallographic data from G. Natta, P. Corradini, I.W. Bassi, Il Nuovo Cimento (1960), 15 (Suppl. No. 1), 68-82

Peculiarities of Coordination Polymerization: Syndiotactic polymers.

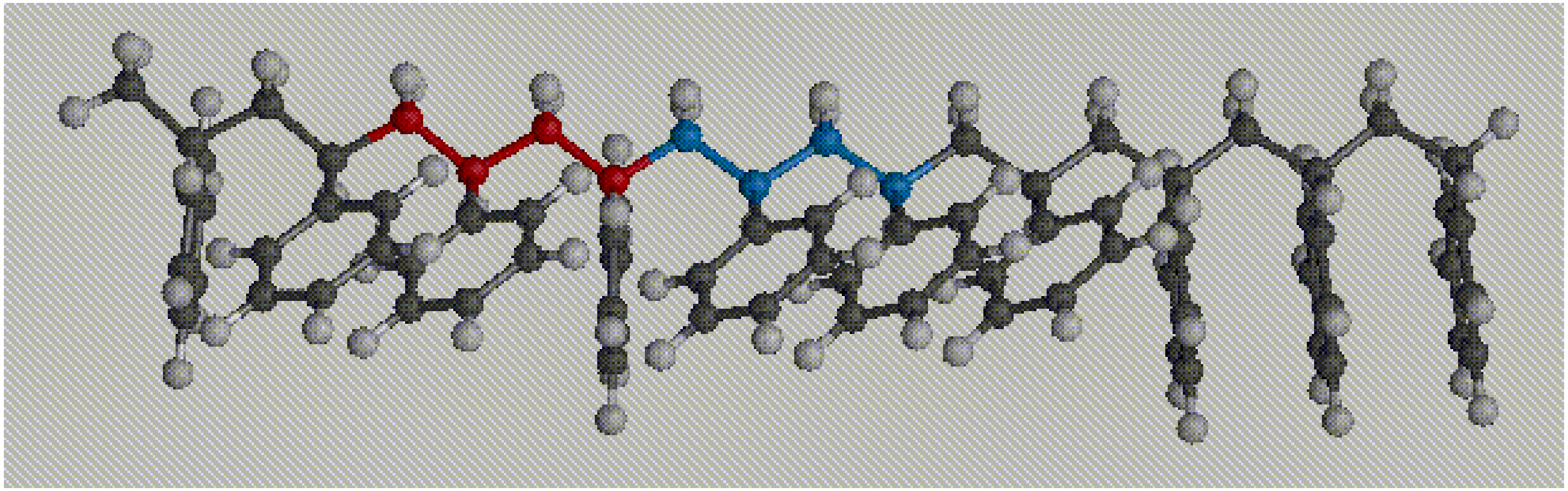
In a syndiotactic polymer the substituents are located alternated from one side and the other. Syndiotactic polymer consists entirely of racemic diads:



The absolute configuration sequence is ...-RSRSRSRS-.... Syndiotactic polymer typically have very different properties from their isotactic analogues.

Peculiarities of Coordination Polymerization: Atactic Polymers.

On the contrary, in an atactic polymer, the orientation of substituent groups is random:



Peculiarities of Coordination Polymerization: Performance Control.

The coordination polymerization with Ziegler-Natta catalysts :

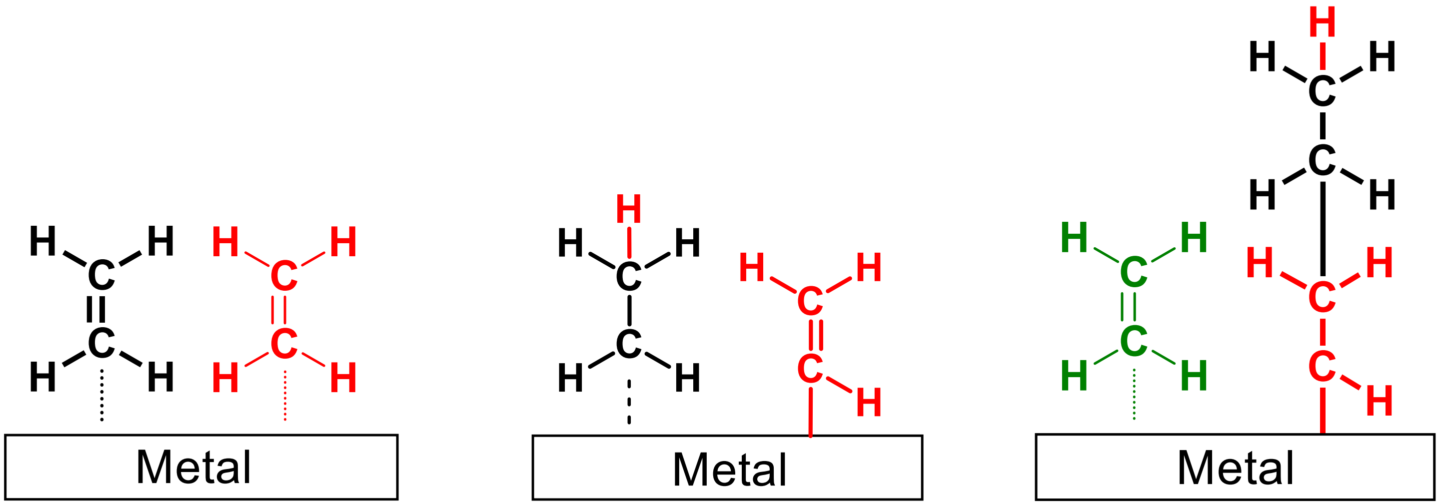
- Affords linear chains;
- Allow the stereochemical control of the process in the presence of asymmetric alkenes.

These peculiar features represent two important advantages on radical polymerization.

Linear polymers, compared with the branched, form in fact materials with high crystallinity, high melting point, higher density and mechanical strength.

Example: Catalyst with Supported Metal

- Similar to heterogeneous reductions



1

Adsorption

2

H Transfer

3

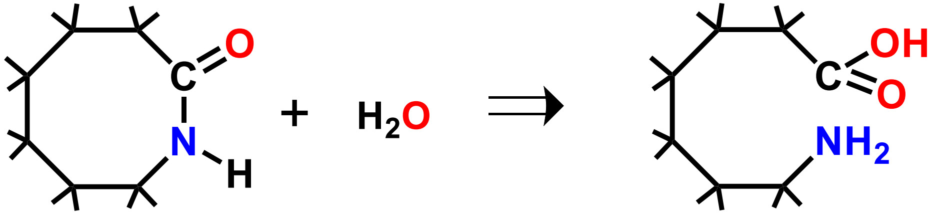
Insertion

Addition Polymerization

Ring Opening Polymerization.

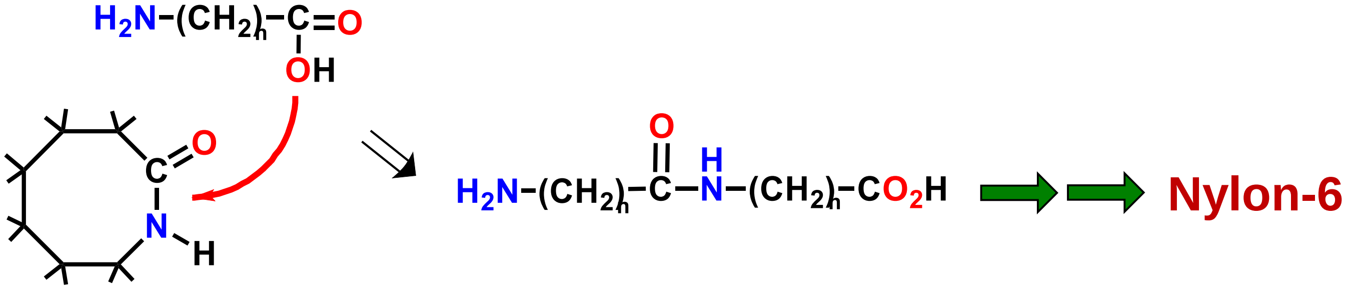
Involve opening of a ring with subsequent interexchange

- Example: formation of polyamide by ring opening



Lactam

Hydration of bond
(6-aminocapronic acid)



[Note: the condensation can occur also within open rings.]