CHEMISTRY

77th Class, 21-12-2021

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Last class

- ❑ Module-5, Polymers

Last class…

- Introduction to concept of macromolecules
- DP and Functionality
- Classification – Tacticity
- Classification and properties of polymers - Thermoplastics, Thermosets and Elastomers

In this class…

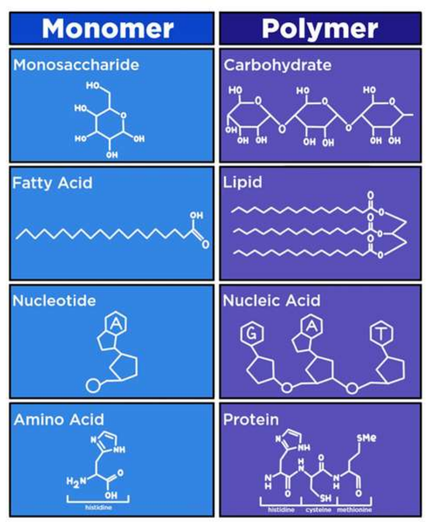
- Classification and properties of polymers - Thermoplastics, Thermosets and Elastomers
- Types of polymerization - Addition and condensation polymerization

Module – 5, Contents

- ❑ Introduction to concept of macromolecules
- ❑ Classification and properties of polymers - Thermoplastics, Thermosets and Elastomers
- ❑ Types of polymerization - Addition and condensation polymerization
- ❑ Polypropylene, polystyrene, PVC, Teflon, Nylon, PET, Polyurethane, Synthetic rubber – Synthesis, properties and applications
- ❑ Conducting polymers
- ❑ polyacetylene and P3HT – synthesis, properties and applications

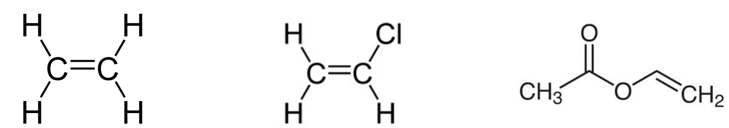
Macromolecules

- ❑ A macromolecule is a very large molecule, such as protein, commonly created by polymerization of smaller subunits (monomers).
- ❑ Four types of macromolecules in the body
  - monosaccharide -- for carbohydrate
  - nucleotide -- for nucleic acids
  - amino acid -- for proteins
  - fatty acid – for lipids



Monomers

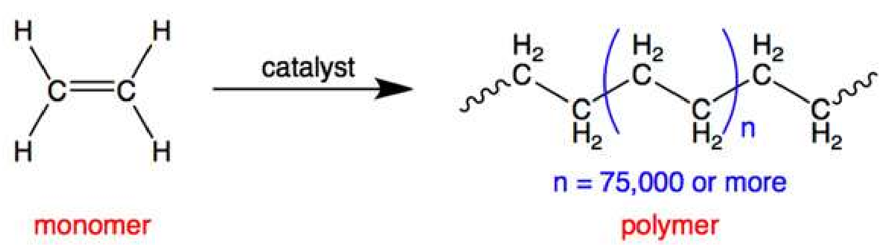
- A monomer is a type of molecule that has the ability to chemically bond with other molecules in a long chain.
- Building blocks of polymers, which are more complex type of molecules. Monomers—repeating molecular units.
- Monomers form polymers by forming chemical bonds or binding supramolecularly through a process called **polymerization.**



Ethylene **Vinyl chloride** **Vinyl acetate**

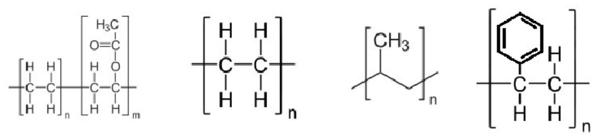
Polymer

- A polymer is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits.
- Polymerization is the process by which monomers (smaller chemical units) are combined to form a polymer.



Polymers

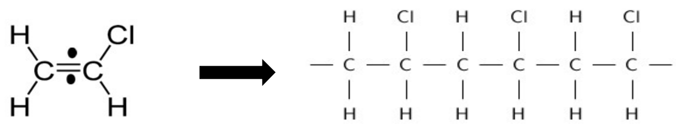
- Polymers are the **high molecular weight compounds** obtained by repeated union of simple molecules.
- Ex: Starch, Polyvinyl chloride, Polyethylene, Nylon 6,6 etc.
- The term polymer is defined as **very large molecules having high molecular mass.**
- These are also referred to as macromolecules, which are formed by joining of repeating structural units on a large scale



Ethylene Vinyl Acetate (EVA) | Polyethylene (PE) | Polypropylene (PP) | Polystyrene (PS)

Basic Concepts - Functionality

- The **functionality of a <u>monomer is the number of sites it has for bonding</u>** to other monomers under the given conditions of the polymerization reaction.
- Thus, a **bifunctional monomer, i.e., monomer with functionality two**, can link to two other molecules under suitable conditions.



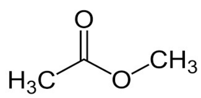
Single Vinyl chloride monomer with bifunctionality

Linked with two vinyl monomers

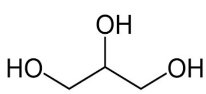
- When the functionality of monomer is two, bifunctional linear (or) straight chain polymer is formed.

Basic Concepts - Functionality

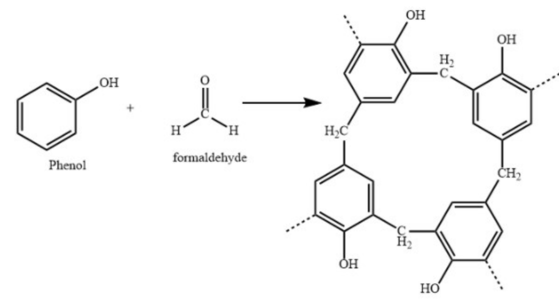
- A **polyfunctional monomer is one that can react with more than two molecules** under the conditions of the polymerization reactions.
- When the **functionality of monomer is three (tri-functional) or more, three-dimensional net work polymer** is formed.



Methyl acetate



Glycerol



Bakelite

Basic Concepts – Degree of polymerization (DP)

- Degree of polymerization is a number, which **indicates the number of repetitive units** **(monomers)** present in the polymer, **represented as 'n'**.
- By knowing **the value of DP, the molecular weight of the polymer** can be calculated.
- [Molecular wt of the polymer] = **DP x Molecular wt. of each monomer.**

Basic Concepts – Degree of polymerization

- **Ex: $(CH_2 – CH_2)_n$ Polythene; Here 'n' is the DP.**
- Calculate the molecular weight of the polythene polymer given DP is 100.
- Molecular weight of the polythene = DP x Molecular weight of Polethylene
- **= 100 X 28 = 2800.**

Molecular weight

- The molecular weight of a synthetic polymer **does not have a single value, since different chains will have different lengths and different numbers of side branches**.
- There will **therefore be a distribution of molecular weights, so it is common to calculate the average molecular weight** of the polymer.
- Several different ways to define the average molecular weight - the **two most common being the number average molecular weight and the weight average molecular weight**.
- Other averages exist, such as the **viscosity average molecular weight.**

Number average molecular weight

The number average molecular weight **is defined as the total weight of polymer divided by the total number of molecules.**

$$\text{Total weight} = \sum_{i=1}^{\infty} N_i M_i$$

where N_i is the number of molecules with weight M_i

$$\text{Total number} = \sum_{i=1}^{\infty} N_i$$

The number average molecular weight is therefore given by:

$$\overline{M_N} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$$

Weight average molecular weight

The weight average molecular weight **depends not only on the number of molecules present, but also on the weight of each molecule**. To calculate this, N_i is replaced with N_iM_i.

$$\overline{M_W} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

This can also be written as:

$$\overline{M_W} = \sum_{i=1}^{\infty} w_i M_i$$

where w_i is the weight fraction of polymer with molecular weight M_i.

Molecular weight

Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 50.000 g/mol and 9 moles of polymer molecules having molecular weight of 30.000 g/mol.

$$\overline{M}_n = \frac{(9\ \text{mol} \times 30{,}000\ \text{g/mol}) + (5\ \text{mol} \times 50{,}000\ \text{g/mol})}{9\ \text{mol} + 5\ \text{mol}} = 37{,}000\ \text{g/mol}$$

$$\overline{M}_w = \frac{9\ \text{mol}(30{,}000\ \text{g/mol})^2 + 5\ \text{mol}(50{,}000\ \text{g/mol})^2}{9\ \text{mol}(30{,}000\ \text{g/mol}) + 5\ \text{mol}(50{,}000\ \text{g/mol})} = 40{,}000\ \text{g/mol}$$

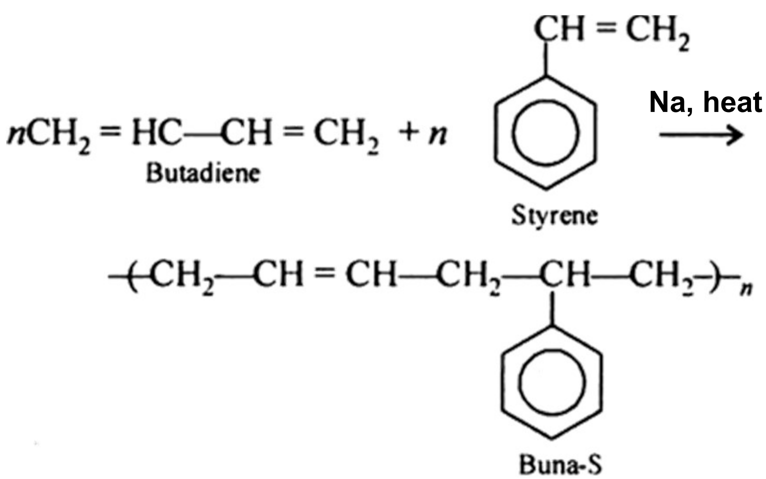
Basic Concepts – Nomenclature of Polymers

- Polymers are classified broadly in to two types

  a) Homo Polymers b) Hetero polymers (Copolymers and Graft copolymers)

- **Homo Polymers :** Polymers made up of with same type of monomers are called homo polymers(A-A-A-A-A-A-A); ex: Poly ethylene, PVC

- **Hetero polymers :** Polymers made up of with different type of monomers are called hetero polymers (A-B-A-B-A-B-A); eg: buna-s rubber

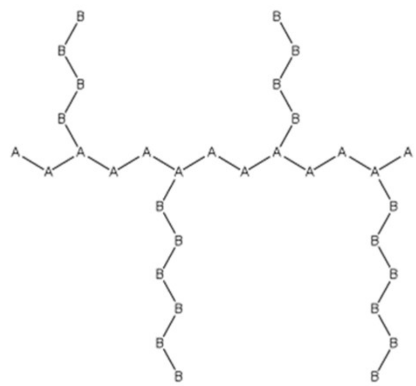


Basic Concepts – Nomenclature of Polymers

- **Copolymers –** a polymer that is made up of two or more monomer species.
- Chain copolymerization (different monomers incorporated during the growth of the polymer chain) can lead to:
  - alternating copolymer – ABABABABABABABABABABABA
  - block copolymer - AAAAAAAABBBBBBBBBBBBAAA
  - random copolymer - BAABBAABABBABABBBAABBAB
  - graft copolymer - branches of a different polymer are attached to a polymer chain AAAAAAABBBBBB (generate reactive site on existing polymer chain, grow new chain)

Basic Concepts – Nomenclature of Polymers

- **Graft copolymers:** If main chain consists of one monomer and branched chain consists of another monomers.



Classification of Polymers

Basis of classification	Polymer type
Origin	Natural, synthetic and semi-synthetic
Structure	Linear, branched and cross-linked
Tacticity	Isotactic, syndiotactic and atactic
Thermal response	Thermoplastics and Thermosets
Crystallinity	Non crystalline (amorphous), semi-crystalline, crystalline
Mode of formation	Addition and condensation
Applications and physical properties	Plastics, rubbers and fibers

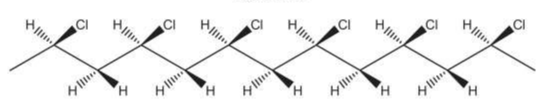
Classification of Polymers -Tacticity

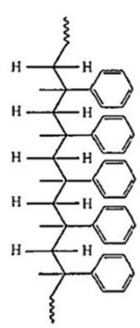
- The difference in configuration due to the orientation of different functional groups with respect to the main chain is called tacticity.
- It is the relative stereochemistry of adjacent chiral centers within a macromolecule
- It is of three types
  - **Isotactic**
  - **Syndiotactic**
  - **Atactic**

Classification of Polymers -Tacticity

- **Isotactic** – All the **functional groups are arranged on the same side of main chain**

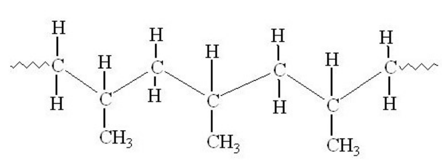
Isotactic PVC





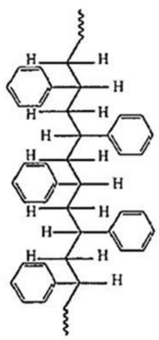
Isotactic Polystyrene

Isotactic Polypropylene



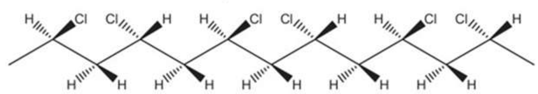
Classification of Polymers -Tacticity

- **Syndiotactic** - All the **<u>functional groups are arranged in the alternative fashion of main chain</u>**

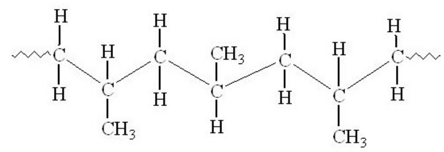


Syndiotactic Polystyrene

Syndiotactic PVC

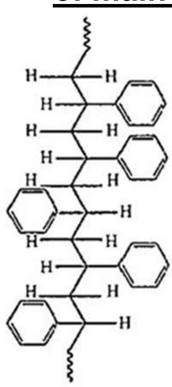


Syndiotactic Polypropylene



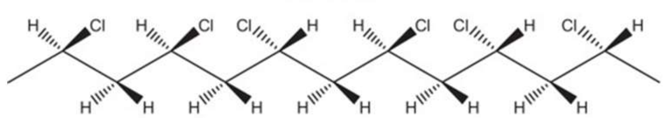
Classification of Polymers -Tacticity

- **Atactic** - All the **<u>functional groups are arranged in random of main chain</u>**

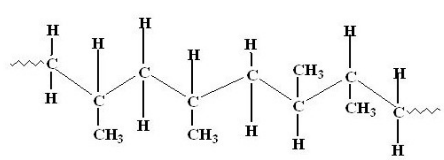


Atactic Polystyrene

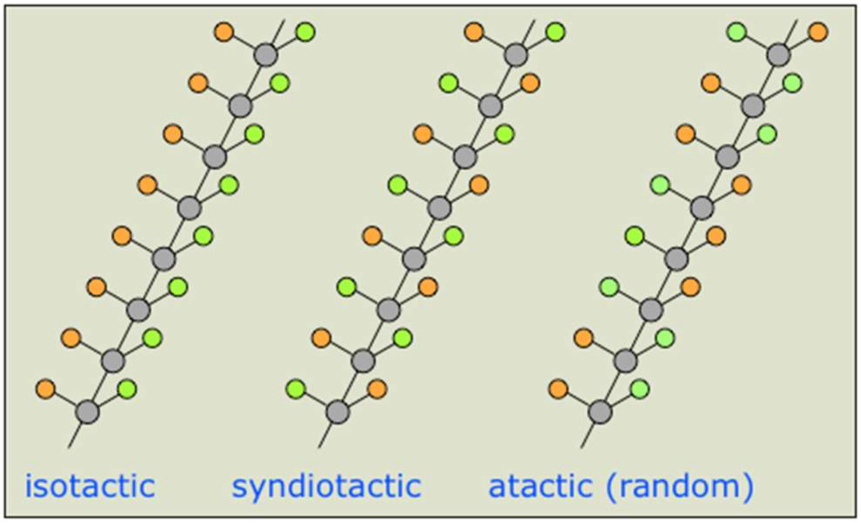
Atactic PVC



Atactic Polypropylene



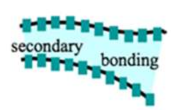
Tacticity



Classification of Polymers - Structure

- **Linear polymers:** Only bifunctional monomers can form linear polymers.
- These polymers have extensive van der Waals attractions keeping the chains together
- They are generally thermoplastic polymers, and except for very high molecular weight materials, they are soluble in solvents.
- Some of the common examples of linear polymers are polyethylene, PVC, polystyrene, and polyamides.
- Linear polymers are generally more rigid.

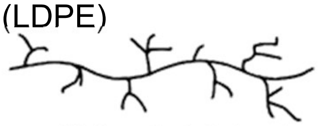

(*a*) Linear polymer



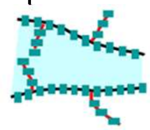
Linear

Classification of Polymers -Structure

- **Branched – chain polymer** : When there is no cross-linking in a polymer molecule, yet **branches arise from the parent polymer chain**, then the polymer formed is called a branched – chain polymer.
- Monomers **with two or more end groups are likely to support branching.** A small amount of trifunctional impurities in a bifunctional monomer may cause branching.
- Branching may lead to decrease of solubility in solvents, rise in the softening point and also the reduction in thermoplastic properties. One of the most common example is low-density polyethylene (LDPE)



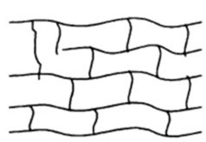
(*b*) Branched chain polymer



Branched

Classification of Polymers - Structure

- **Cross–linked polymers:** These polymers have a 3-D network structure. Only bi-functional and tri-functional monomers can form cross-linked polymers.
- Once the **crosslinks between the chains develop the polymer then becomes thermoset**. Such polymers are characterized by their crosslink density or degree of crosslink which is the indication of number of junction points per unit volume



(c) Cross-linked polymers.

Classification of Polymers - Thermoplastics

- Some polymers **<u>soften on heating and can be converted into any shape that they can retain on cooling</u>**.
- The process of heating, reshaping and retaining the same on cooling can be repeated several times.
- These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling.
- These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres.
- Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers.




Thermoplastics - properties

- The thermoplastics can soften or melt when they heated and returning to solid when they cooled, The process is repeatable and it does not change the chemical nature of the polymer
- Heating provides the thermal energy to allow the long polymer chains to move freely past one another and take on new shapes, cooling reduces molecular motion to the level where the chains no longer move freely.
- Thermoplastics **<u>materials are highly recyclable</u>** and offer aesthetically-superior finishes,
- High-impact resistance, Good chemical resistant
- They have hard crystalline or rubbery surface options and they have eco-friendly manufacturing.

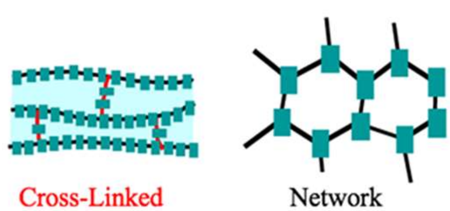
Classification of Polymers - Thermosets

- Some polymers, on the other hand, **undergo some chemical change on heating and convert themselves into complex 3-D** network (cross-linked or branched)
- Such polymers, that **become infusible and insoluble** mass on heating.
- These polymers are **cross linked or heavily branched** molecules, which on heating undergo extensive cross linking in moulds and again become infusible.
- These cannot be reused. Some common examples are **bakelite, urea-formaldelyde resins**, etc

Common thermosets in daily life

Classification of Polymers - Structure

- Thermosetting polymers having **high thermal resistance and mechanical strength** may be formed if the cross-linking among the monomer groups is extensive.
- Common examples include epoxies, bulk molding compounds, rubber, and various adhesives



Thermosets - properties

- Hard and brittle because of crosslinking
- Opaque
- Good electrical resistance – used in electric circuit boards
- Good heat resistance - servicing temperature of a thermoset plastic material is 300°C.
- Resistant to deformation under load
- Low cost
- Good chemical resistant to most solvents and acids

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Classification of Polymers - Elastomers

- These are **rubber – like solids with elastic properties**.
- In these elastomeric polymers, the polymer chains are held together by the **weakest intermolecular forces**.
- These weak binding forces **permit the polymer to be stretched**.
- A **few 'crosslinks' are introduced in between the chains**, which help the polymer to retract to its original position after the force is released as in vulcanized rubber.
- The examples are buna-S, buna-N, neoprene, etc.

Common elastomers in daily life

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Elastomers - properties

- Elastomers have excellent tensile, elongation, tear resistance resilience.
- They show exceptional resistance to gas and moisture (water and steam) permeation.
- Elastomers provide excellent electrical isolation performance.
- Good resistance to weather aging, ozone and UV exposure.
- Elastomers are flame resistant and will not support combustion.

Types of Polymerization, Addition

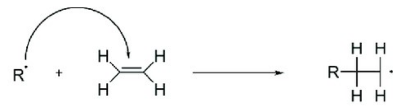
- Molecules of the **<u>same monomer or different monomers add</u>** together on a large scale to form a polymer.
- The monomers normally employed in this type of polymerization contain a **<u>carbon-carbon double bond</u>** (unsaturated compounds, e.g., alkenes and their derivatives) that can participate in a chain reaction.
- A **<u>chain reaction consists of three stages, Initiation, Propagation and Termination</u>**.

$$n\,CH_2{=}CH_2 \xrightarrow{\text{polymerization}} \left[CH_2-CH_2 \right]_n$$

Ethylene — Polyethylene

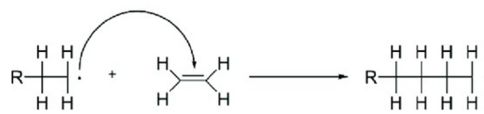
Addition Polymerization

- Initiation - an initiator molecule is thermally decomposed or allowed to undergo a chemical reaction to generate an "**active species**."
  - This "active species," which can be a free radical or a cation or an anion, then initiates the polymerization.



Initiation

- In the Propagation step, the newly generated "active species" adds to another monomer in the same manner as in the initiation step. This procedure is repeated over and over again



Propagation

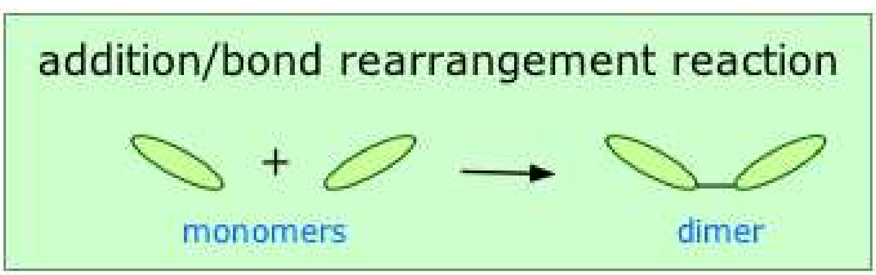
Addition Polymerization

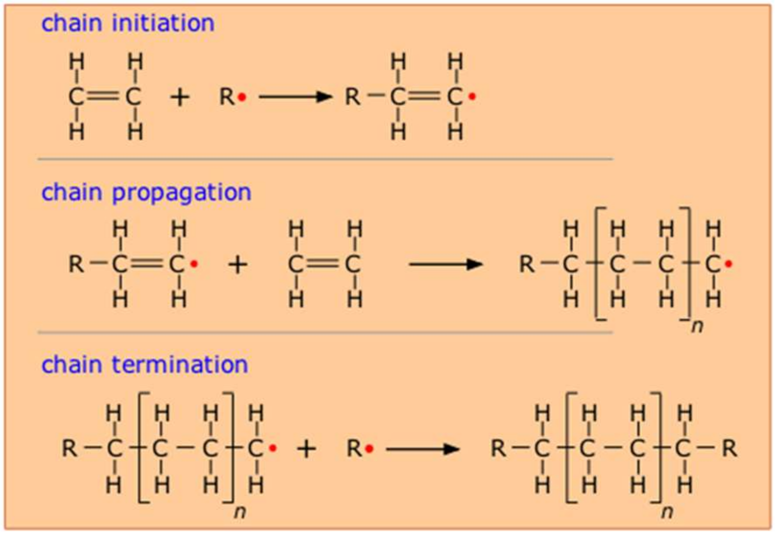
- In the Termination step, the growing chain terminates through reaction with another growing chain, by reaction with another species in the polymerization mixture, or by the spontaneous decomposition of the active site.

Termination

Addition Polymerization, characteristics

- Once initiation occurs, the polymer chain forms very quickly.
- The concentration of active species is very low.
- Hence, the polymerisation mixture consists primarily of newly-formed polymer and unreacted monomer.
- Since the carbon-carbon double bonds in the monomers are, in effect, converted to two single carbon-carbon bonds in the polymer, so energy is released making the polymerization exothermic with cooling often required.





Condensation polymerization

- This type of polymerization generally involves a repetitive condensation reaction **(two molecules join together, resulting loss of small molecules)** between two bi-functional monomers.
- Result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.
- In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on.

Condensation polymerization

- The type of end polymer product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.
- Monomers with only one reactive group terminate a growing chain and thus give end products with a lower molecular weight.
- Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are cross linked.

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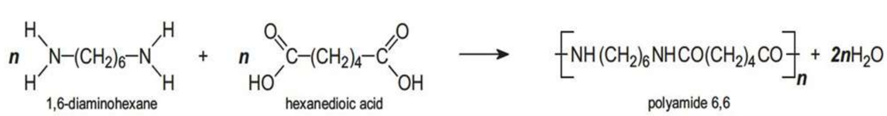
Condensation polymerization

- Polyamide is created through amide linkages between monomers, which involve the functional groups carboxyl and amine (an organic acid and an amine monomer).
- Nylon-6,6 formed by condensation of hexamethylenediamine with adipic acid under high pressure and at high temperature.



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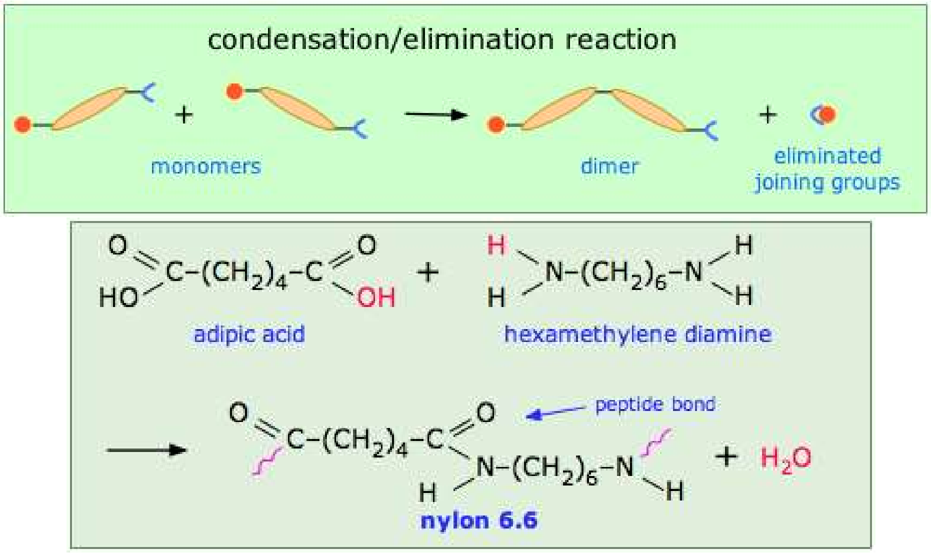

Condensation polymerization, characteristics

- The polymer chain forms slowly, sometimes requiring several hours to several days.
- All of the monomers are quickly converted to oligomers, thus, the concentration of growing chains is high.
- Since most of the chemical reactions employed have relatively high energies of activation, the polymerization mixture is usually heated to high temperatures.

Condensation polymerization

- Step-reaction polymerizations normally afford polymers with moderate molecular weights, i.e., <100,000
- Branching or crosslinking does not occur unless a monomer with three or more functional groups is used.

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.