POLYMER IN VIEW OF CHEMISTRY; SYNTHESIS AND USES

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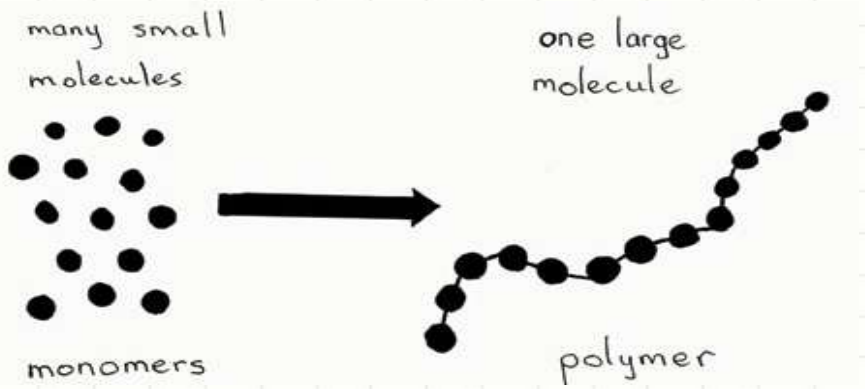
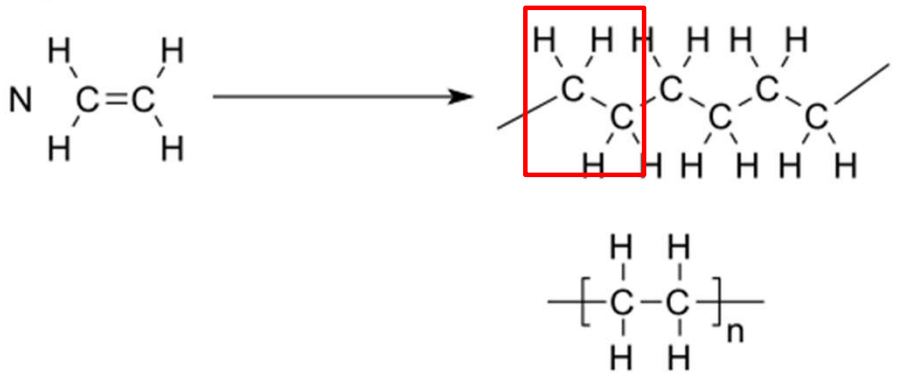
Classification of Polymers

Polymer *is a long-chain molecule that is composed of a large number of repeating units of identical structure.*

"All polymers are macromolecules but all macromolecules are not necessary polymers"





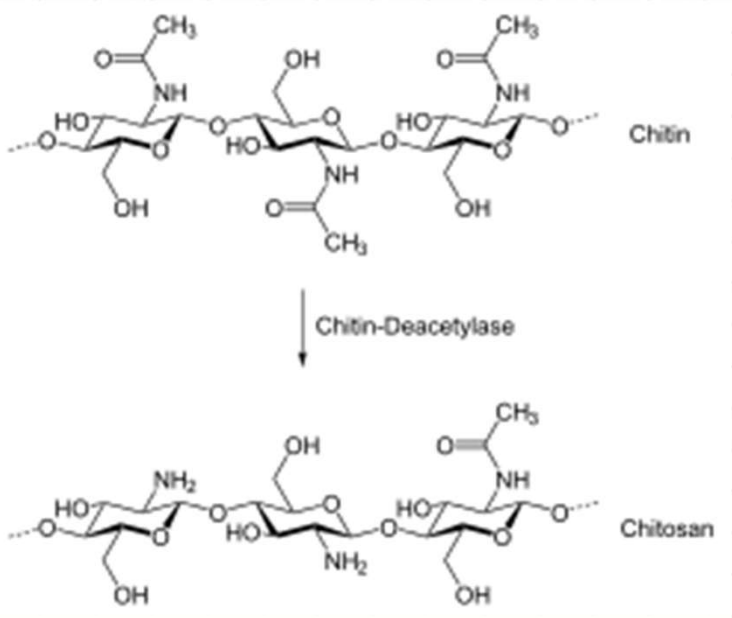
Polymers are numerous in number with different behaviors and can be classified in various ways.

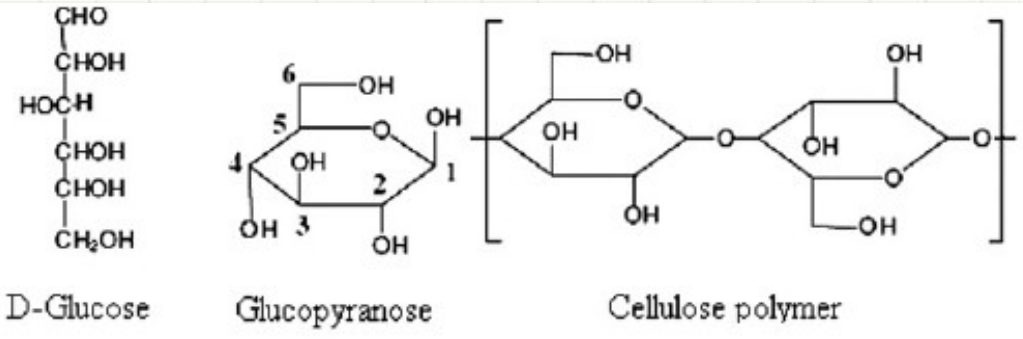
Classification of Polymers

Classification of Polymers Based on Origin

- **Natural polymers** are obtained from nature, e.g., plant origin, animal origin etc. Biologically degradable polymers are also present, called biopolymers.

  Examples; *Proteins (which are found in humans and animals alike), Cellulose and Starch (which are found in plants) or Rubber (which we harvest from the latex of a tropical plant).*





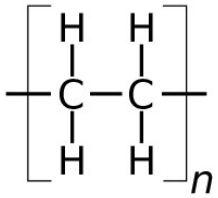
Classification of Polymers

Classification of Polymers Based on Origin

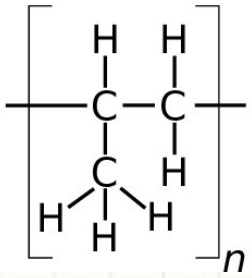
- **Synthetic polymers** have been prepared by humans in laboratories and are currently produced industrially.

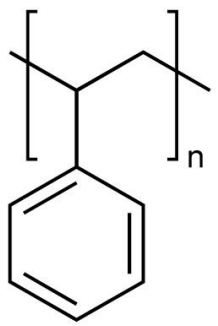
  Example; *Polyethylene (a mass-produced plastic which we use in packaging) or Nylon Fibers (commonly used in our clothes, fishing nets etc.)*

Polyethylene



Polypropylene



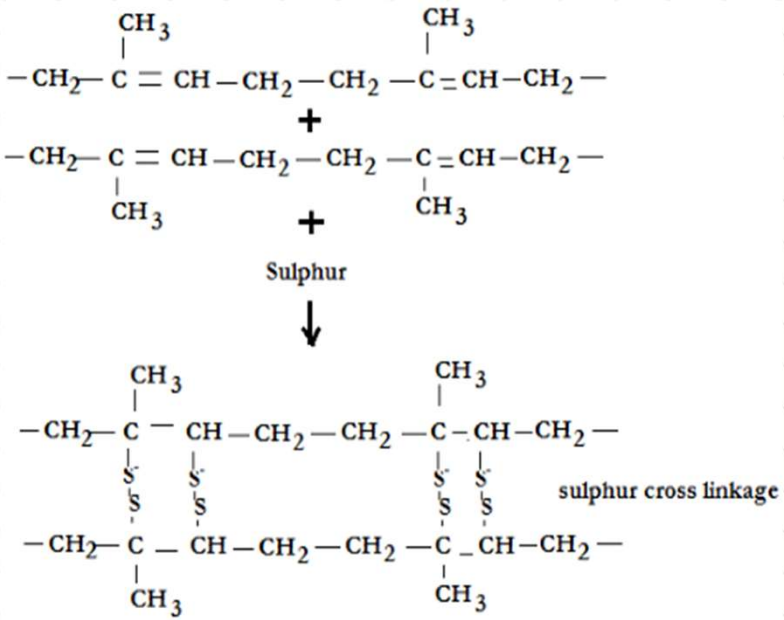


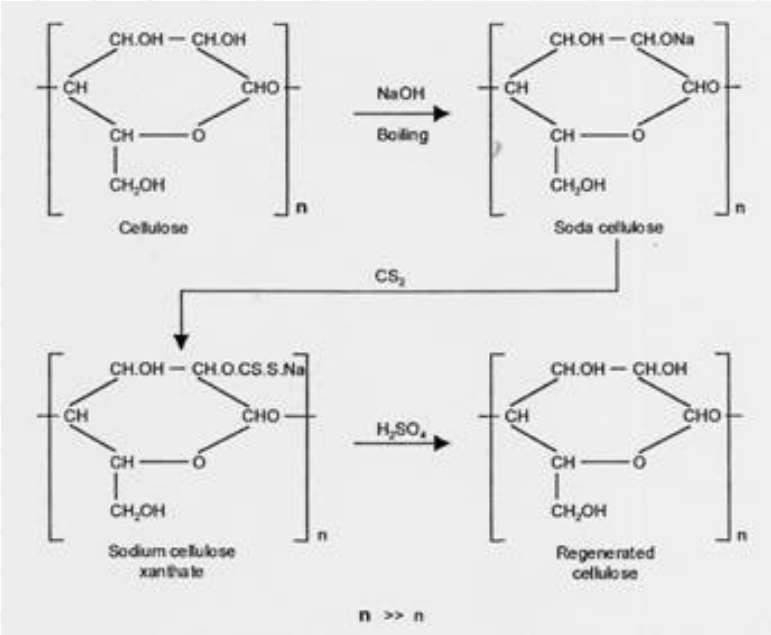
Classification of Polymers

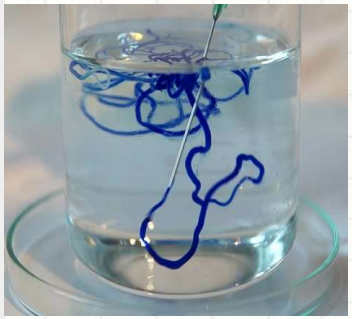
Classification of Polymers Based on Origin

- **Semi-synthetic polymers** are polymers obtained by making modification in natural polymers artificially in a lab.

  Example; *Vulcanized Rubber (Sulphur is used in cross bonding the polymer chains found in natural rubber) Cellulose acetate (rayon) etc.*







Classification of Polymers

Classification of Polymers Based on Structure

- **Linear Polymers** are similar in structure to a long straight chain which identical links connected to each other.

  These polymers have high melting points and are of higher density.

  Example: High density polyethylene (HDPE).

- **Branched Chain Polymers** are made of branching of linear chains of monomers.

  They have low melting points and low densities.

  Example: Low-density polyethene (LDPE) used in plastic bags etc.

- **Cross-linked Polymers/Network Polymers** are formed by bi-functional and tri-functional monomers with a strong covalent bond between the various linear polymer chains.

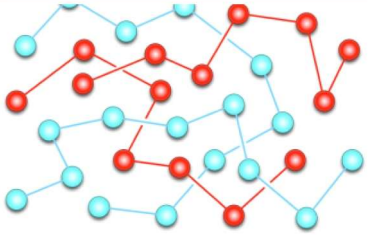
  These polymers are brittle and hard.

  Example: Bakelite (phenol-formaldehyde resins)

Classification of Polymers

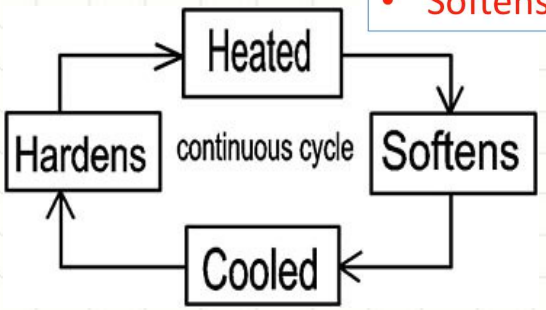
Classification of Polymers Based on Thermal Response

Thermosoftening (thermoplastic)

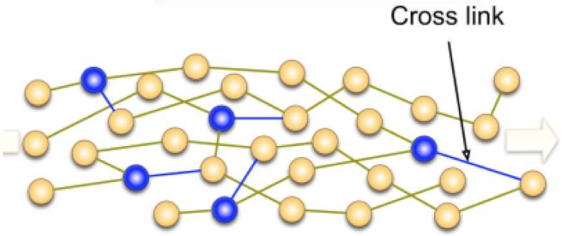


- Tangled polymer chains
- No cross-links between chains
- Weak forces of attraction between chains
- Softens when heated

Example
- Polystyrene,
- polyethylene,
- polypropylene

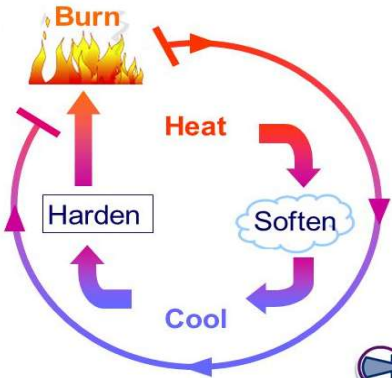


Thermosetting (thermoset)



- Polymer chains held together by **strong covalent cross-link bonding** that does not break on heating.
- Remains hard when heated

Example
- Fiberglas,
- melamine



Classification of Polymers

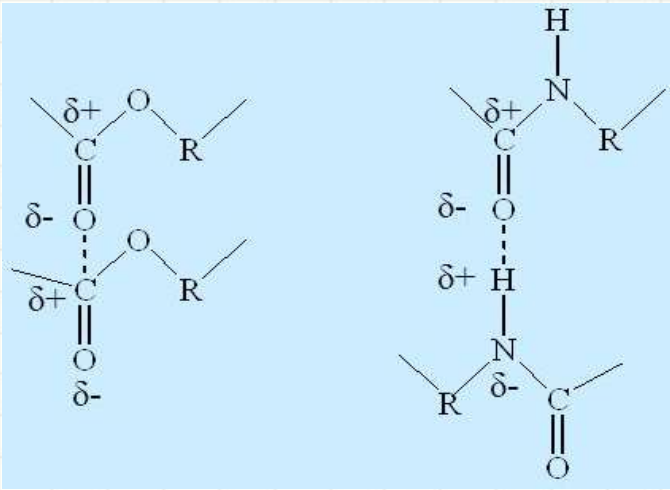
Classification of Polymers Based on Molecular Forces

- **Elastomers**;
  - *Polymer chains that are elastic and can be stretched like rubber.*
  - *They have weak intermolecular forces between the chains.*

  Example – Vulcanized rubber

- **Fibers**;
  - *They have strong intermolecular forces – either hydrogen bonds or dipole-dipole interactions between their chains.*
  - *These chains have a high tensile strength and less elasticity, and high melting points.*

  Example; polyester, Nylon etc.

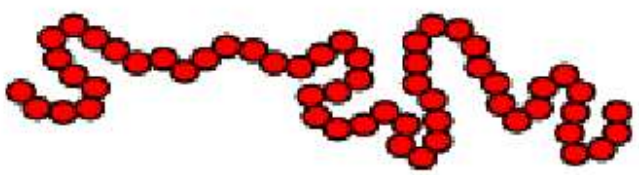


Classification of Polymers

Classification of Polymers Based on The Type of Monomer Involved in The Structure

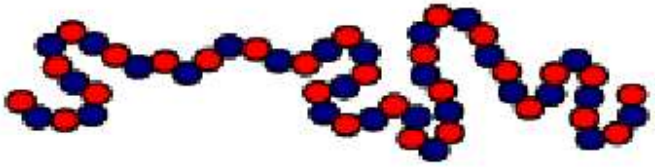
Homopolymer

Linear

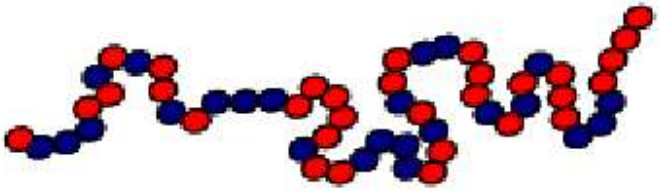


Copolymer

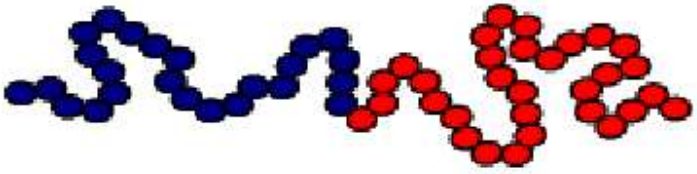
Alternating

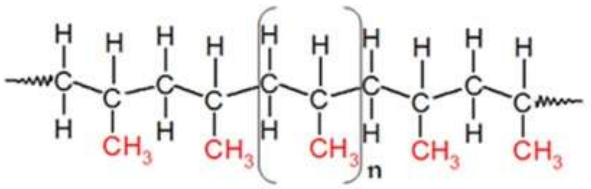


Random or statistical

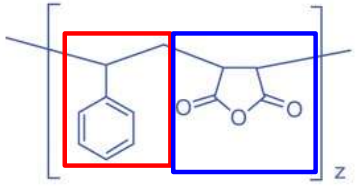


Block

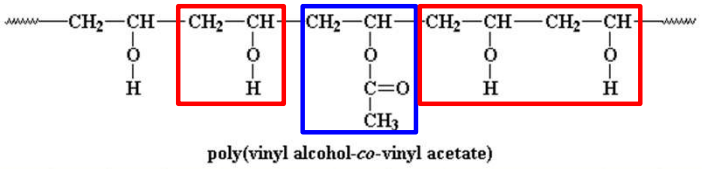




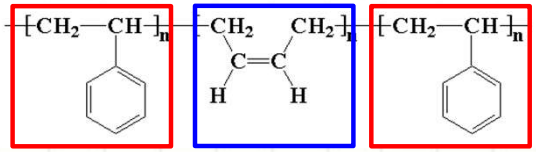
Polypropylene (PP)



Poly(styrene/maleic anhydride)



poly(vinyl alcohol-*co*-vinyl acetate)

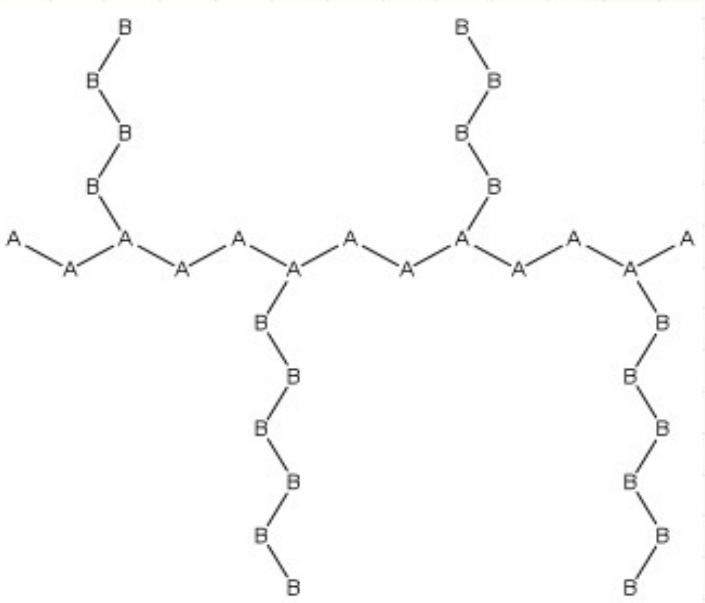


Poly(styrene-butadiene-styrene)

Classification of Polymers

Classification of Polymers Based on The Type of Monomer Involved in The Structure

- In **Graft or grafted copolymers**, the composition of the main chain is a preformed macromolecule and is compositionally or configurationally different from the side chains or branches with repeat units.



- They are often used as thermoplastics elastomers, compatibilizers or emulsifiers for the preparation of stable blends or alloys.
- They are more thermostable than their homopolymer counterparts.

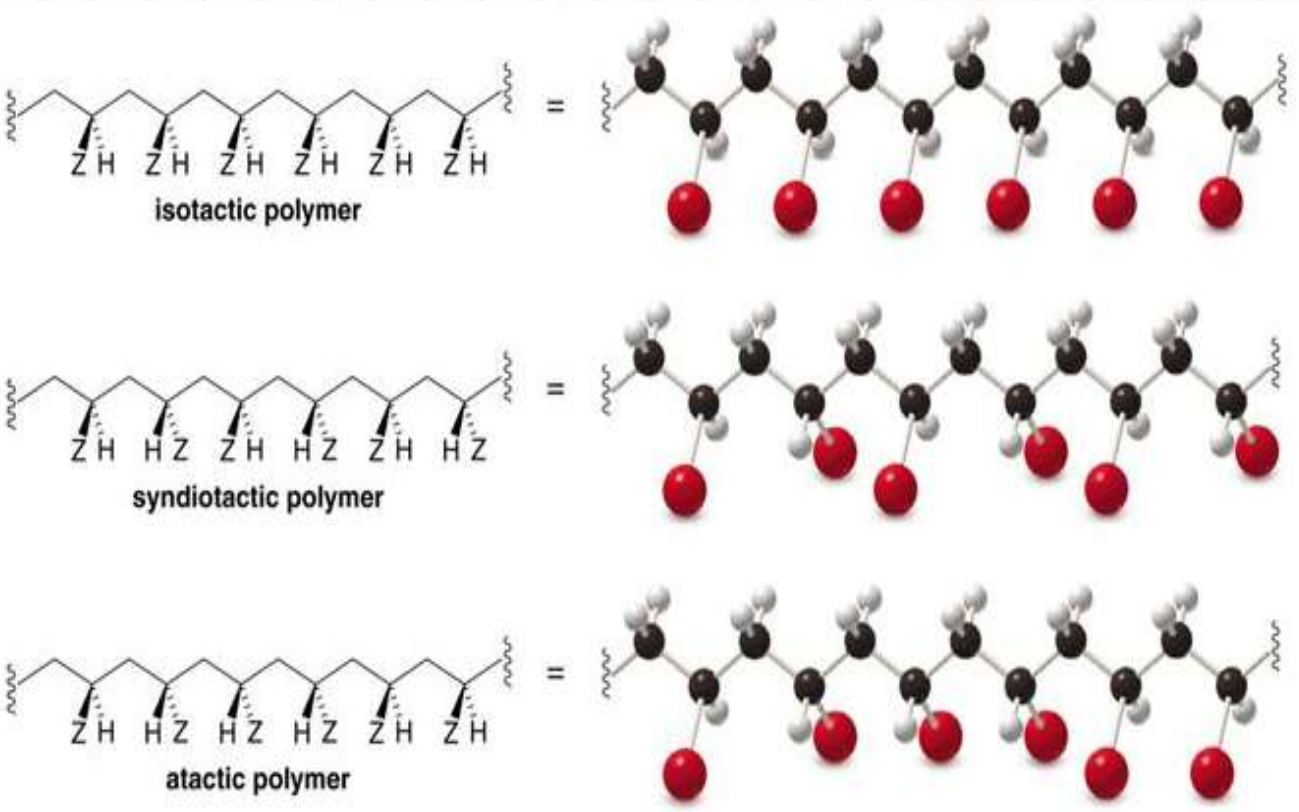
Classification of Polymers

Tacticity ($(CH_2=CHZ)$)

- **Isotactic polymers**, all Z groups on the same side of the carbon chain.
- Crystalline polymers

- **Syndiotactic polymers**, all Z groups alternating from one side of the carbon chain to the other.
- Crystalline polymers

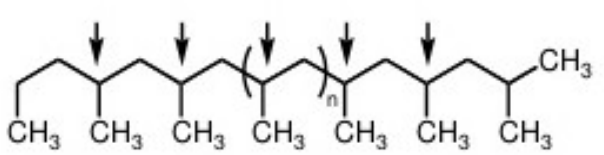
- **Atactic polymers**, all Z groups oriented randomly along the polymer chain.
- Amorphous polymers



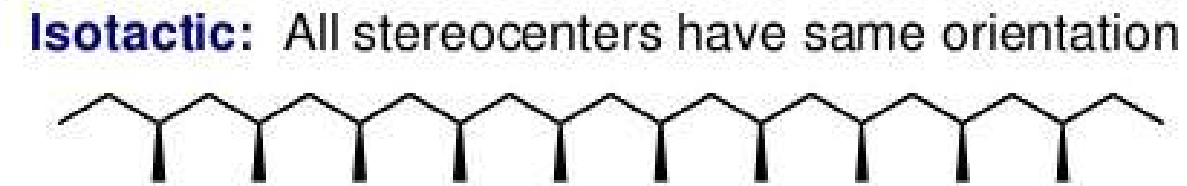
Classification of Polymers

Tacticity

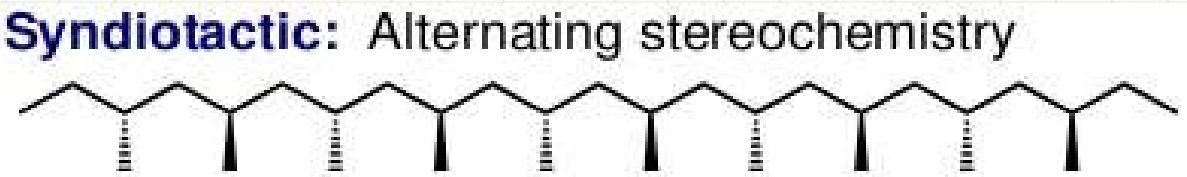
- **Polyolefins with side chains have stereocenters** :



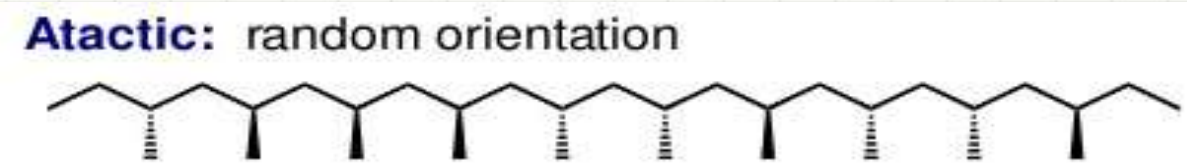
- **Isotactic polymers**, all Z groups on the same side of the carbon chain.
- Crystalline polymers



- **Syndiotactic polymers**, all Z groups alternating from one side of the carbon chain to the other.
- Crystalline polymers



- **Atactic polymers**, all Z groups oriented randomly along the polymer chain.
- Amorphous polymers



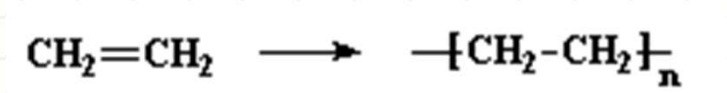
Classification of Polymers

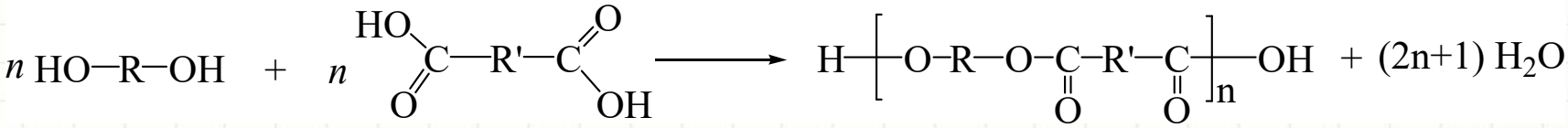
Classification of Polymers Based on Mode of Polymerization

General Methods for Preparation of Polymers

Addition Polymerization
(*Chain-growth Polymerization*)

Condensation Polymerization
(*Step-growth Polymerization*)





Mode of Polymerization; Addition Polymerization

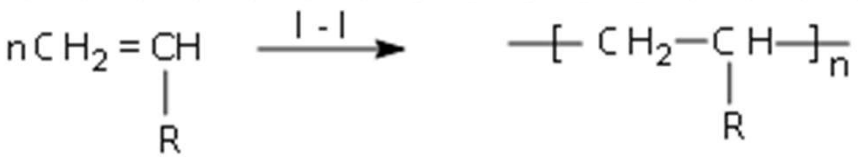
Addition polymerization *occurs by a chain reaction in which one carbon-carbon double bond adds to another.*

The polymerization process takes place in three distinct steps:

1. **Chain initiation;** *usually by means of* ***an initiator*** *that starts the polymerization process.*

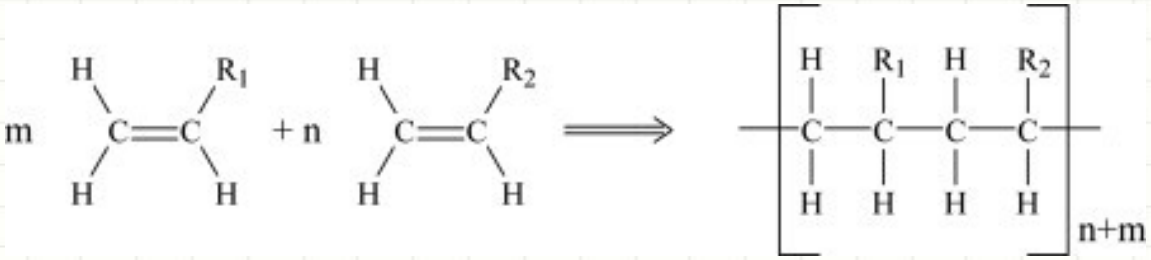
The reactive initiation molecule can be

- a radical (*free radical polymerization*),
- cation (*cationic polymerization*),
- anion (*anionic polymerization*), and/or
- organometallic complex (*coordination polymerization*).



Mode of Polymerization; Addition Polymerization

2. **Chain propagation;** *a monomer adds onto the chain and each new monomer unit creates an active site for the next attachment.*

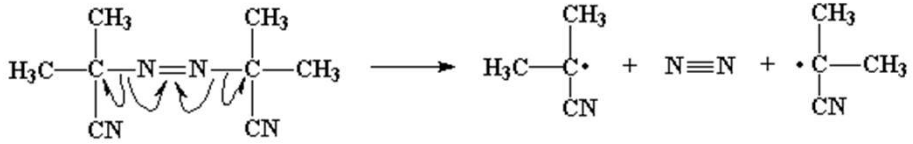


3. **Chain termination;** *the radical, cation, or anion is "neutralized" stopping the chain propagation.*

Mode of Polymerization; Addition Polymerization

Free Radica Polymerization

Thermal initiators



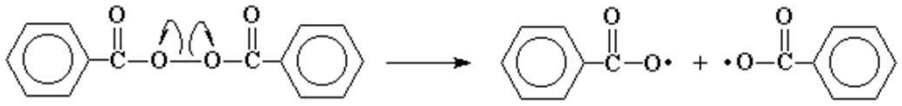
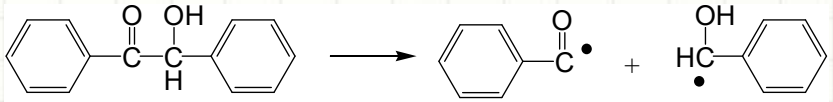
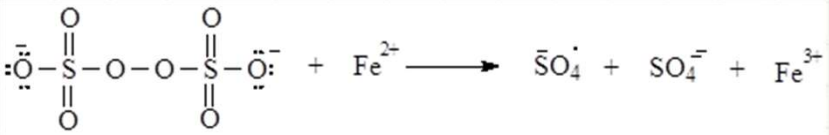


Photo initiators



2-Hydroxy-1,2-diphenyl-ethanone

Redox initiators

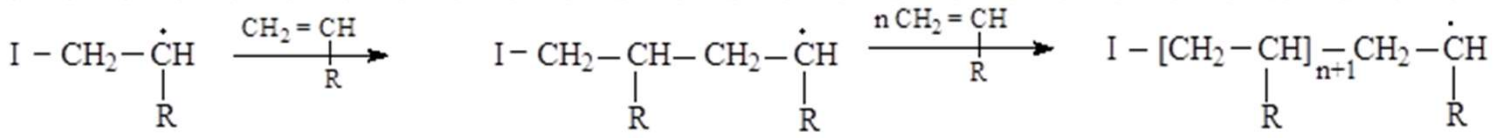


Mode of Polymerization; Addition Polymerization

Free Radica Polymerization

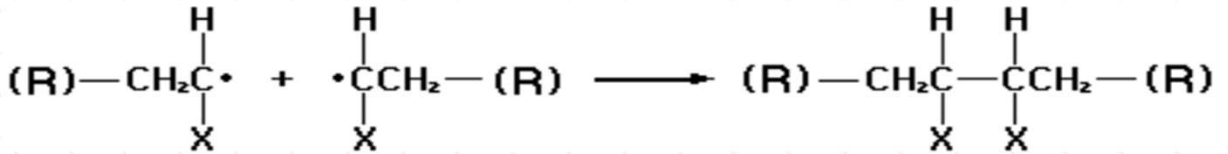
1. Chain initiation

2. Chain propagation

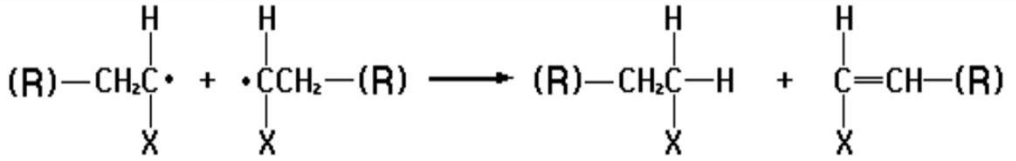


3. Chain termination;

Combination or coupling



Disproportionation

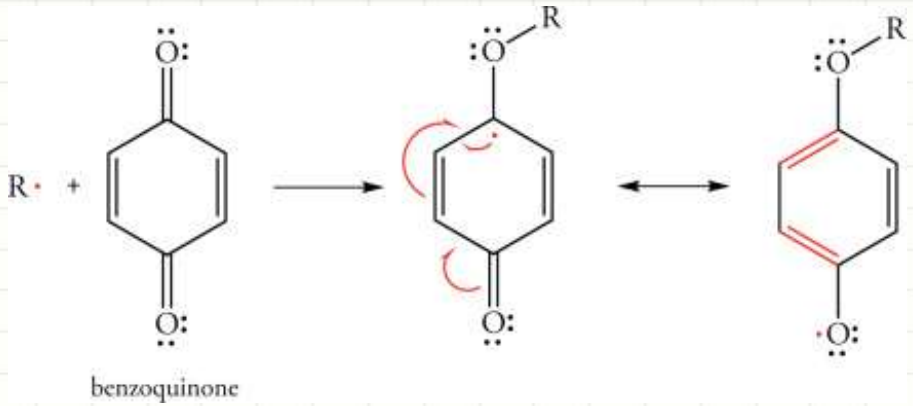


Mode of Polymerization; Addition Polymerization

Free Radica Polymerization

Inhibitors react with the radical site of a growing polymer chain to give a less reactive radical.

Benzoquinone is a typical inhibitor used in free radical polymerization reactions.



Mode of Polymerization; Addition Polymerization

Controlled Radical Polymerization (CRP)

- Few problems with **conventional radical polymerizations**, including
  - Free monomer levels
  - uniformity of the polymer chain.
- **Controlled radical polymerization** to
  - minimize monomer content
  - produce very uniform molecules.
- The control comes by a **variety of techniques (*reversible-deactivation radical polymerization (RDRP)*)** including the use of so-called
  - Stable free radical mediated polymerization (SFRP),
  - Atom transfer radical polymerization (ATRP)
  - Reversible addition-fragmentation chain transfer (RAFT) polymerization.

Mode of Polymerization; Addition Polymerization

Controlled Radical Polymerization (CRP)

A controlled radical polymerization process has some general features:

1. Polymerization rate (Rp) with respect to the monomer concentration ([M]) increases linearly with time (first order kinetics behavior).

   In this state, the concentration of the active species ([P*]) remains constant.

2. **Degree of polymerization and molecular weight** can be pre-determined, since the initiation is fast and termination and transfer can be almost ignored.

3. **The molecular weight distribution is narrow**, because the initiation rate is comparable to propagation rate, termination can be neglected and the exchange between species with different reactivity is faster than propagation

4. The majority of chains remain active for long time, until almost all monomer is consumed. If monomer is added, polymerization can restart again (**suitable for block copolymer synthesis**).

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

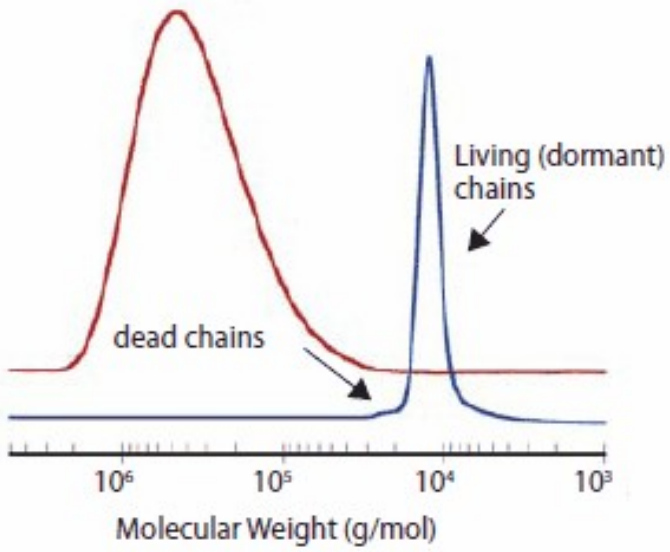
History

- **RAFT process** was first reported in the early 1970s.
- However, the technique was irreversible, so *the transfer reagents could not be used to control radical polymerization at this time*.
- It was used to help synthesize end-functionalized polymers.
- Scientists began to realize the potential of RAFT in controlled radical polymerization in the 1980s.
- Macromonomers were known as reversible chain transfer agents during this time, but had limited applications on controlled radical polymerization.
- In 1995, a key step in the "degenerate" reversible chain transfer step for chain equilibration was brought to attention.
- **RAFT polymerization** is mainly carried out by *thiocarbonylthio chain transfer agents*.
- It was first reported by Rizzardo et al. in 1998.

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

- **RAFT** offers the benefit of being able to readily synthesize polymers with
  - predetermined molecular weight and
  - narrow molecular weight distributions
- **RAFT** can be used in all modes of free radical polymerization: solution, emulsion and suspension polymerizations.
- **Components of RAFT**
  - Monomer
  - Initiator
  - Chain transfer agent (CTA) (RAFT agent)

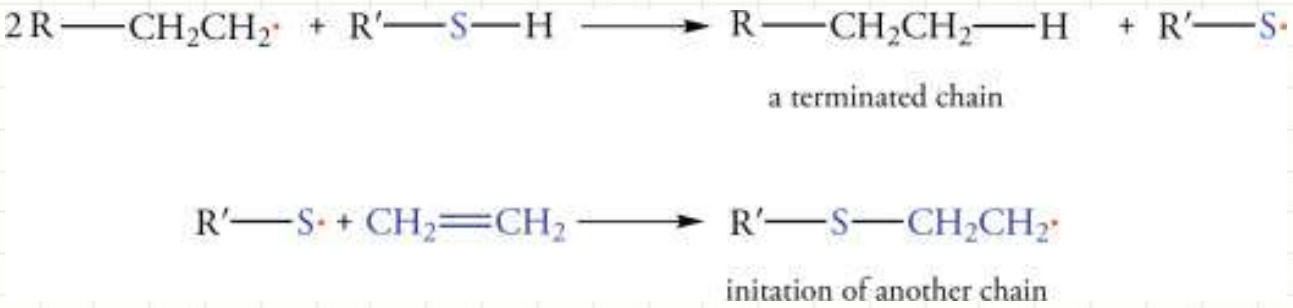


- Implementing the **RAFT** technique can be as simple as introducing a suitable **chain transfer agent (CTA) (RAFT agent)**, into a conventional free radical polymerization reaction.

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

- **CTA** control the chain length of a polymer by *interrupting the growth of one chain and then initiating the formation of another chain*.

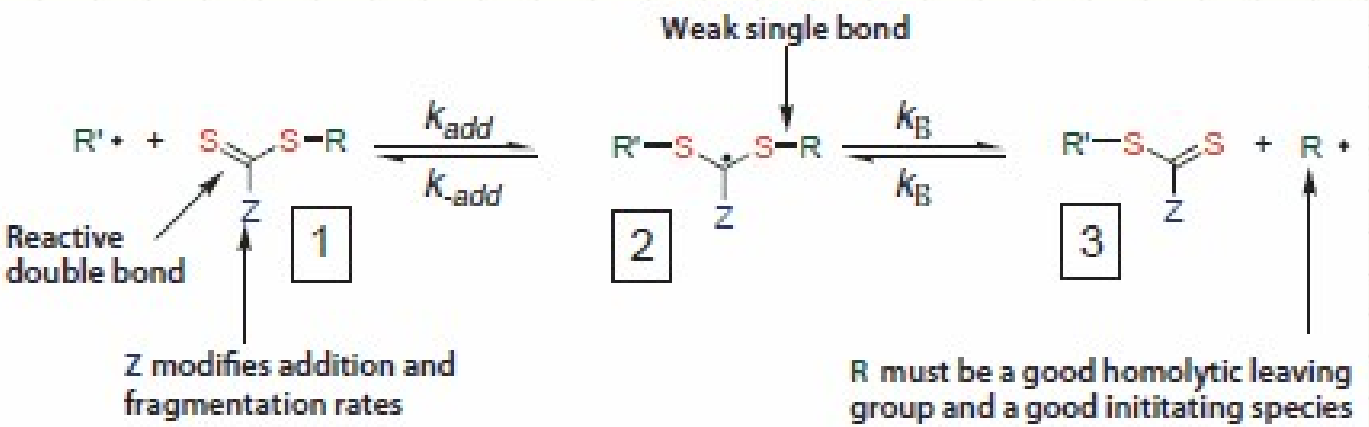


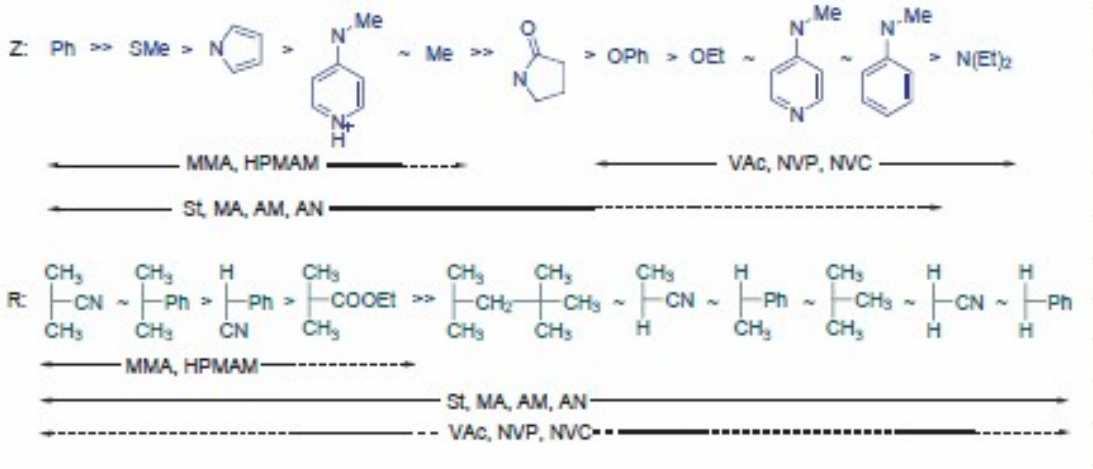
- **CTA** must be reactive enough to transfer a hydrogen atom, but the resulting radical must be reactive enough to add to a double bond.
- The polymerization continues, and monomer continues to be consumed.
- However, the average molecular weight of the product is smaller because more chains are formed by the chain-transfer process.

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

- **CTA**, is a di- or tri-thiocarbonylthio compound





Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

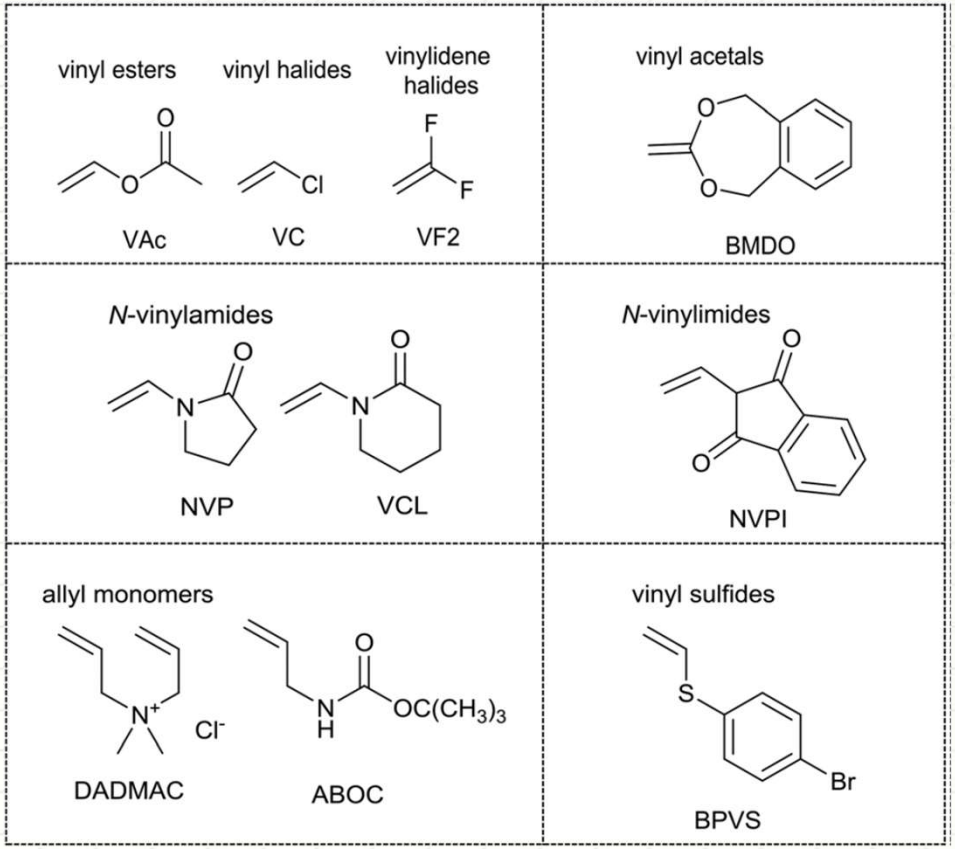
○ Monomers in RAFT polymerization

➢ **The 'less activated' monomers or LAMs** are *those where the double bond is adjacent to one or more oxygen, nitrogen, halogen or sulfur lone pairs*

e.g., vinyl acetate (VAc), N-vinylpyrrolidone (NVP), N-vinylcaprolactam (VCL), 5,6-benzo-2-methylene-1,3-dioxepane (BMDO), vinyl chloride (VC), vinylidene fluoride (VF2), (4-bromophenyl)(vinyl)sulfane (BPVS)

or saturated carbon

e.g., diallyldimethylammonium chloride (DADMAC), BOCprotected allylamine (ABOC))



Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

- **Monomers in RAFT polymerization**

➢ **The 'more-activated' monomers or MAMs** *are those where the double bond is conjugated to an aromatic ring*

e.g., the styrenes and vinyl aromatics: styrene (St) and substituted styrenes, 4-vinylpyridine (4VP), acenaphthalene (AcN)

a double bond

e.g., the dienes: butadiene (Bd), isoprene (Ip), chloroprene (Cp)

a carbonyl group

e.g., methacrylic acid (MAA), methyl methacrylate (MMA), acrylic acid (AA), methyl acrylate (MA), acrylamide (Am)] or a nitrile [e.g., acrylonitrile (AN)

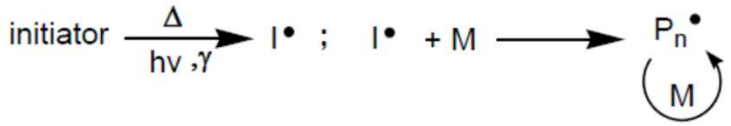
Maleic anhydride (MAH) and maleimides e.g., *N*-phenylmaleimide (NPMI)

Mode of Polymerization; Controlled Radical Polymerization (CRP)

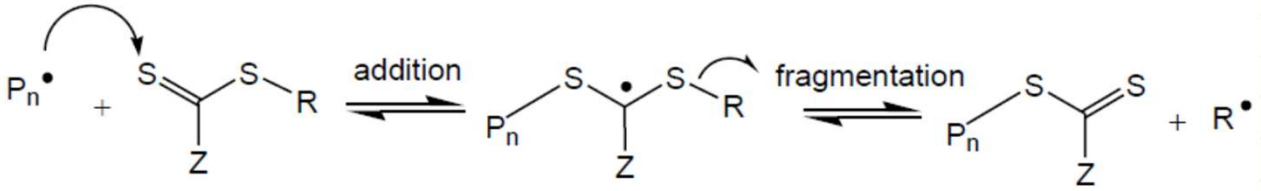
Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

- **Mechanism**

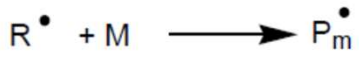
Radical generation



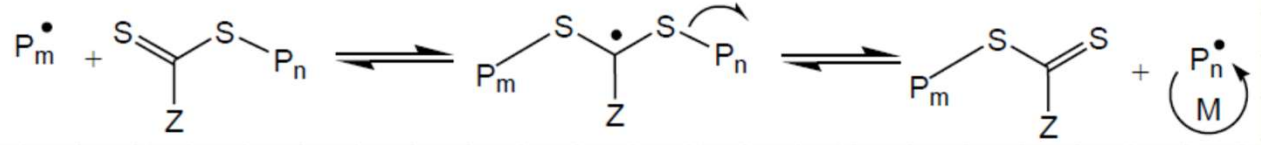
CTA activation/Addition/Fragmentation



Reinitiation



RAFT equilibrium



Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

Initiation:

- *The reaction is started by a free-radical source which may be a decomposing radical initiator such as AIBN.*
- *The initiator decomposes to form two fragments ($I^{\bullet}$) which react with a single monomer molecule to yield a propagating (i.e. growing) polymeric radical of length 1, denoted $P_1^{\bullet}$.*

Propagation:

- *Propagating radical chains of length n in their active (radical) form, $P_n^{\bullet}$, add to monomer, M, to form longer propagating radicals, $P_{n+1}^{\bullet}$.*

RAFT pre-equilibrium:

- *A polymeric radical with n monomer units (P_n) reacts with the RAFT agent to form a RAFT adduct radical.*
- *This may undergo a fragmentation reaction in either direction to yield either the starting species or a radical ($R^{\bullet}$) and a polymeric RAFT agent ($S=C(Z)S-P_n$).*
- *This is a reversible step in which the intermediate RAFT adduct radical is capable of losing either the R group ($R^{\bullet}$) or the polymeric species ($P_n^{\bullet}$).*

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

Re-initiation:

- *The leaving group radical ($R^{\bullet}$) then reacts with another monomer species, starting another active polymer chain.*

Main RAFT equilibrium:

- *This is the most important part in the RAFT process, in which, by a process of rapid interchange, the present radicals (and hence opportunities for polymer chain growth) are "shared" among all species that have not yet undergone termination ($P_n^{\bullet}$ and $S=C(Z)S-P_n$).*
- *Ideally the radicals are shared equally, causing chains to have equal opportunities for growth and a narrow PDI.*

Termination:

- *Chains in their active form react via a process known as*
  - *bi-radical termination to form chains that cannot react further, known as dead polymer.*
  - *Ideally, the RAFT adduct radical is sufficiently hindered such that it does not undergo termination reactions.*

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Reversible Addition-fragmentation Chain Transfer (RAFT) Polymerization

Applications:

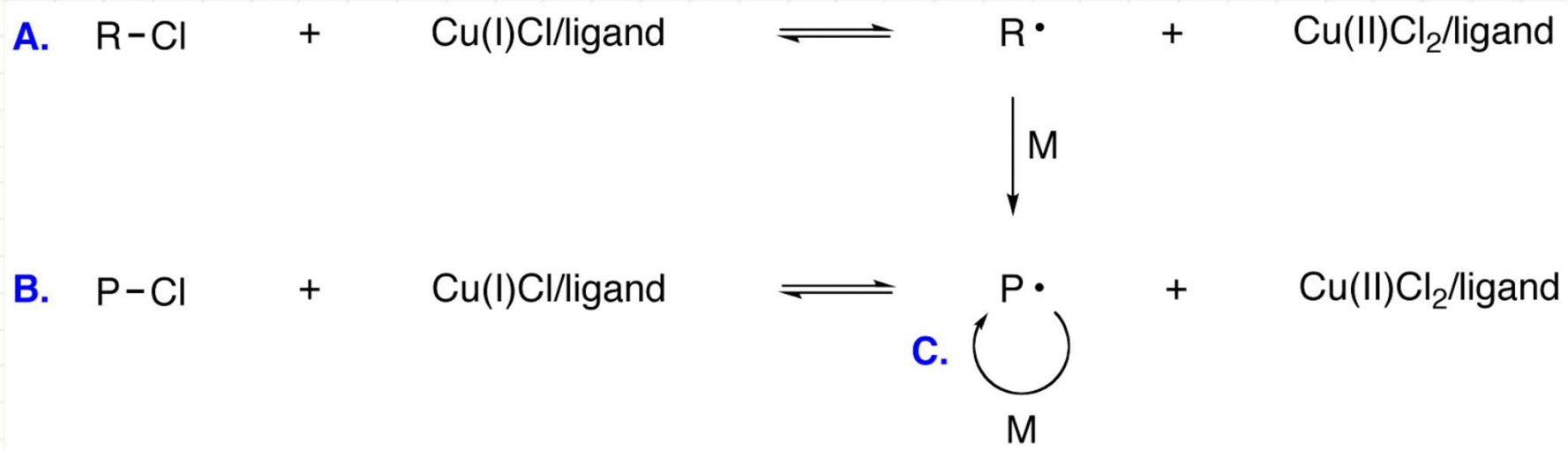
- **RAFT polymerization** has been used to synthesize a wide range of polymers with controlled molecular weight and low polydispersities (between 1.05 and 1.4 for many monomers).
- **RAFT polymerization** is known for its compatibility with a wide range of monomers as compared to other controlled radical polymerizations including styrenes, acrylates, acrylamides, and many vinyl monomers.
- **RAFT process** allows the synthesis of polymers with specific macromolecular architectures such as block, gradient, statistical, comb, brush, star, hyperbranched, and network copolymers.

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

- **ATRP** is a means of forming a carbon-carbon bond **with a transition metal catalyst**.
- **ATRP** (or transition metal-mediated living radical polymerization) was independently discovered by Mitsuo Sawamoto and by Krzysztof Matyjaszewski in 1995.
- **General ATRP reaction**.

  A. Initiation. B. Equilibrium with dormant species. C. Propagation



Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

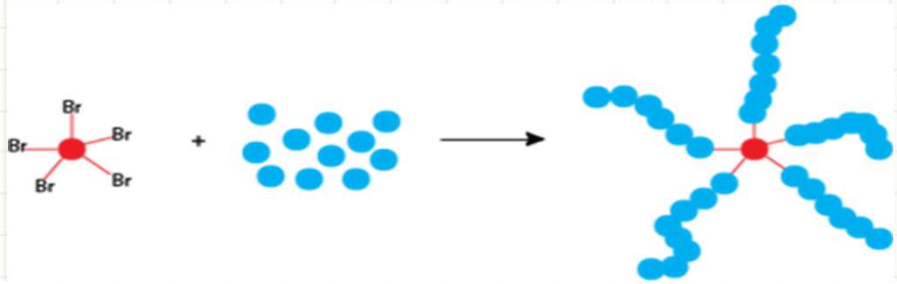
- **Components of normal ATRP**

Monomer

- Monomers are molecules with substituents that can stabilize the propagating radicals; for example, styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile.

Initiator

- Initiators are alkyl halides such as alkyl bromides are more reactive than alkyl chlorides.
- The shape or structure of the initiator influences polymer architecture.
  - For example; initiators with multiple alkyl halide groups on a single core can lead to a star-like polymer shape



Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

- **Components of normal ATRP**

  Catalyst

  - The catalyst is the most important component of ATRP because it determines the equilibrium constant between the active and dormant species.
  - **There are several requirements for the metal catalyst:**
    - There needs to be two accessible oxidation states that are differentiated by one electron.
    - The metal center needs to have reasonable affinity for halogens.
    - The coordination sphere of the metal needs to be expandable when it is oxidized as to accommodate the halogen.
    - The transition metal catalyst should not lead to significant side reactions, such as irreversible coupling with the propagating radicals and catalytic radical termination

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

- **Components of normal ATRP**

  Ligand

  - As copper halides are primarily used as the catalyst, amine based ligands are most commonly chosen.
  - However, a too active catalyst can lead to a loss of control and increase the polydispersity of the resulting polymer.

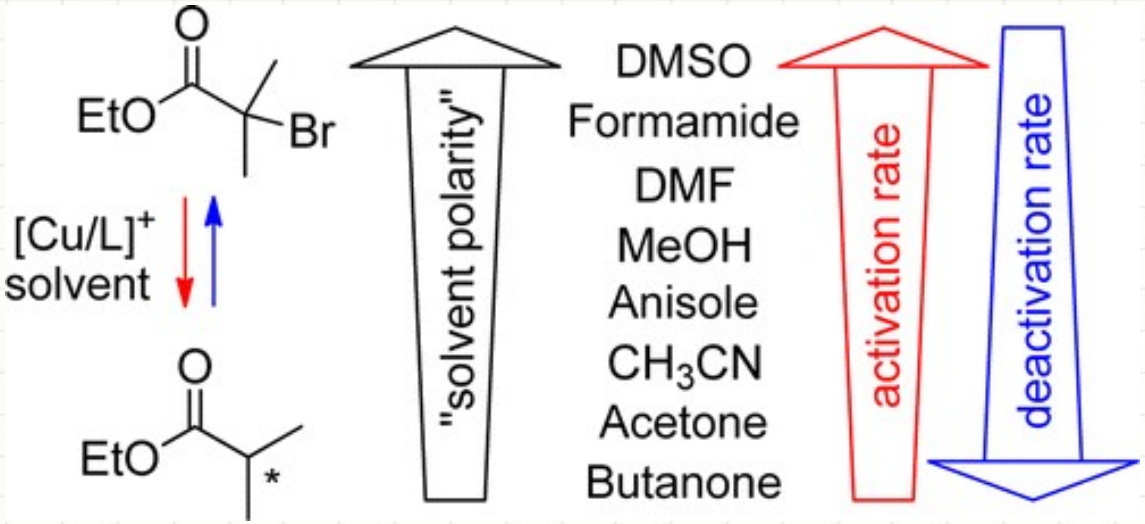
Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

- **Components of normal ATRP**

  Solvents

  - Toluene, 1,4-dioxane, xylene, anisole, DMF, DMSO, water, methanol, acetonitrile, or even the monomer itself (described as a bulk polymerization) are commonly used.



Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

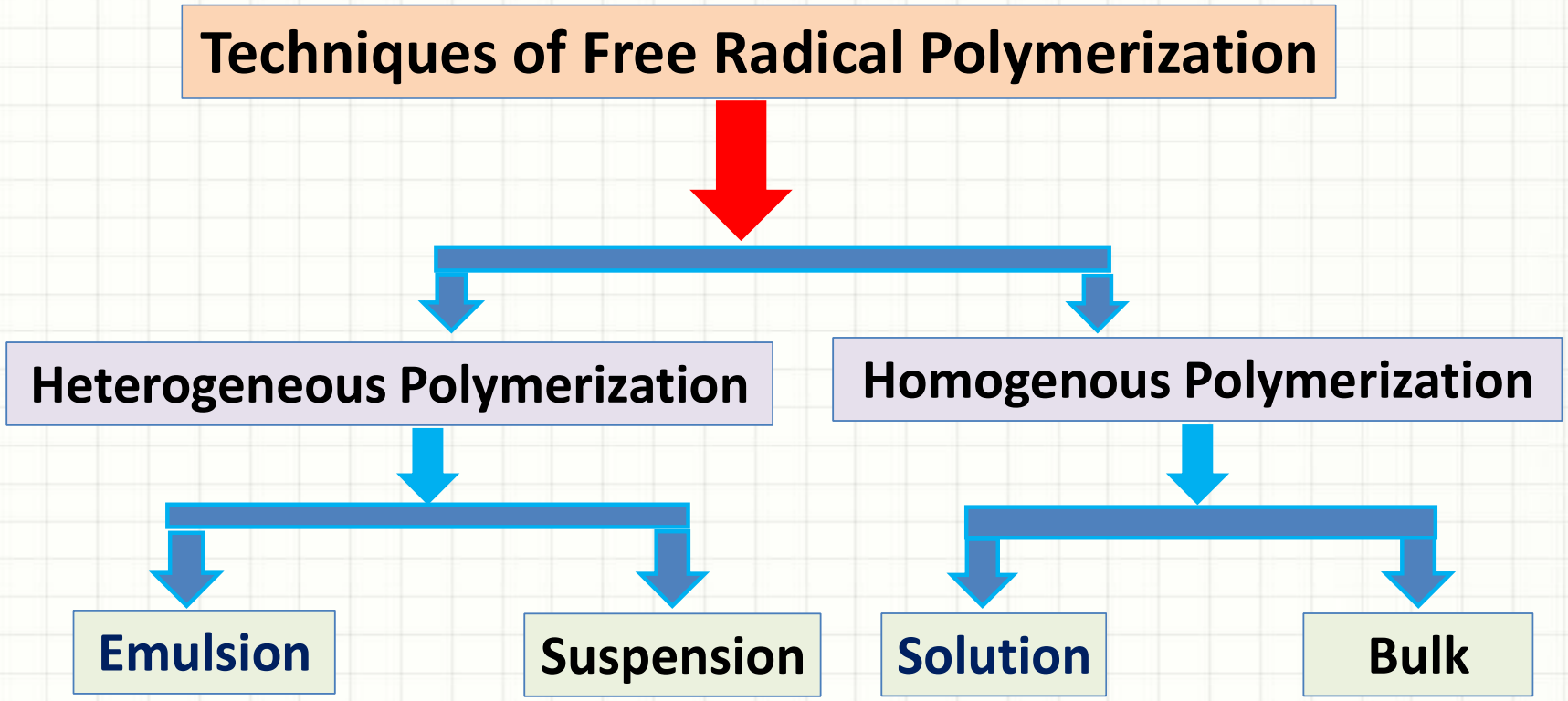
- **Advantages**
  - **ATRP** enables the polymerization of a wide variety of monomers with different chemical functionalities, proving to be more tolerant of these functionalities than ionic polymerizations.
  - It provides increased control of molecular weight, molecular architecture and polymer composition while maintaining a low polydispersity (1.05-1.2).
  - The halogen remaining at the end of the polymer chain after polymerization allows for facile post-polymerization chain-end modification into different reactive functional groups.

Mode of Polymerization; Controlled Radical Polymerization (CRP)

Atom Transfer Radical Polymerization (ATRP)

- **Disadvantages**
  - The high concentrations of catalyst required for the reaction.
  - The removal of the copper from the polymer after polymerization is often tedious and expensive, limiting ATRP's use in the commercial sector.
  - ATRP is also a traditionally air-sensitive reaction normally requiring freeze-pump thaw cycles.
  - The difficulty of conducting ATRP in aqueous media.

Mode of Polymerization; Addition Polymerization

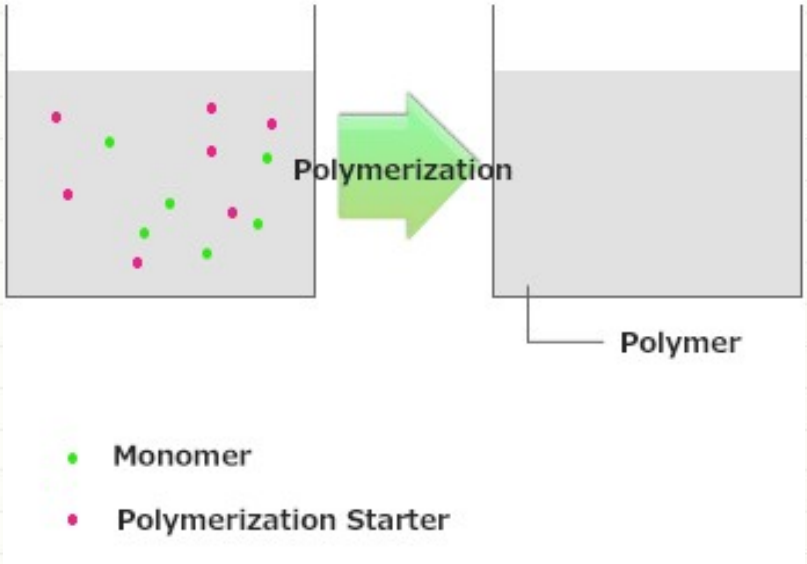


Mode of Polymerization; Addition Polymerization

Techniques of Free Radical Polymerization

Bulk Polymerization (Mass Polymerization)

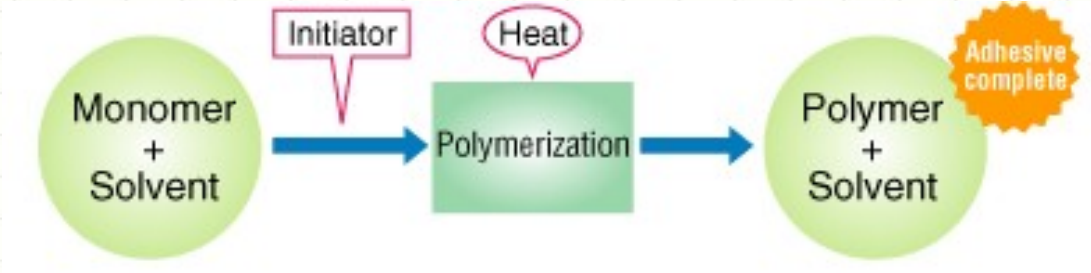
- Polymerization of a monomer in the absence of any medium other than a catalyst or accelerator.
- Monomers are usually liquids
- **Common Problems**
  - Heat transfer
  - Increase in viscosity
- **Commercial uses**
  - Low Mw polymers for adhesives, plasticizers and lubricant additives.



Mode of Polymerization; Addition Polymerization

Techniques of Free Radical Polymerization

Solution Polymerization



- Polymerization process where the monomers and the initiators are dissolved in a solvent.
- Heat transfer is very efficient
- Mw may be severely limited by chain transfer reaction (caused by the solvent molecule or its impurities).
- **Common problems**

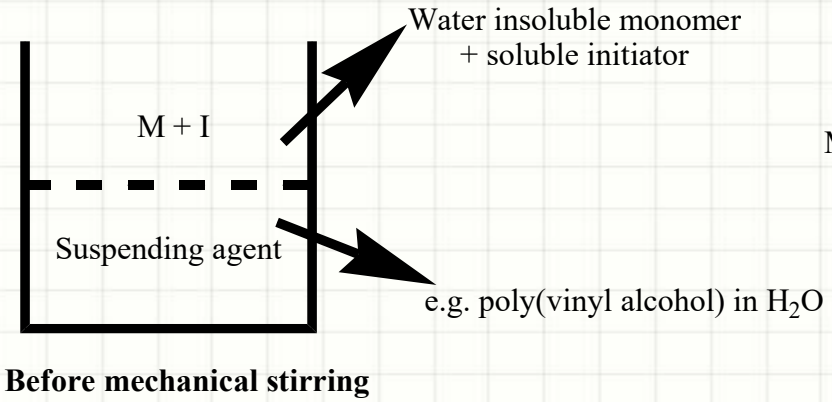
- Solvent residues; difficult to remove completely
- Environmental concerns; organic solvent waste.

Mode of Polymerization; Addition Polymerization

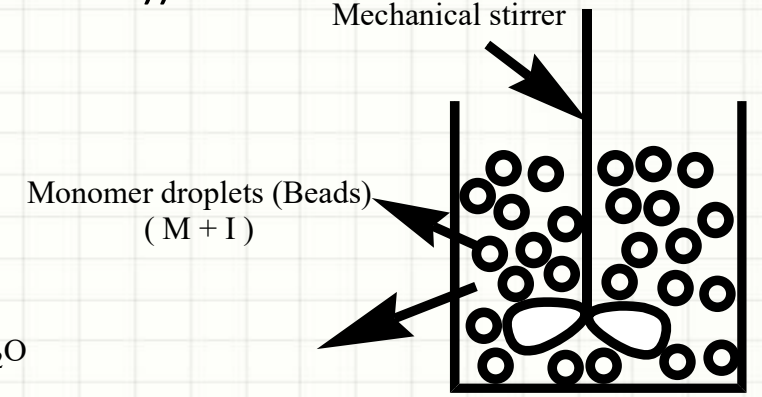
Techniques of Free Radical Polymerization

Suspension Polymerization

- Polymerization process where monomer / mixture of monomers dispersed by mechanical agitation in liquid phase like water.
- Initiators used are monomer soluble.
- Polymer is produced in heterogeneous medium.
- The size of monomer droplets is 50-200 μm in diameter.
- Mostly used in PVC processes (poly(vinyl chloride)).



Before mechanical stirring



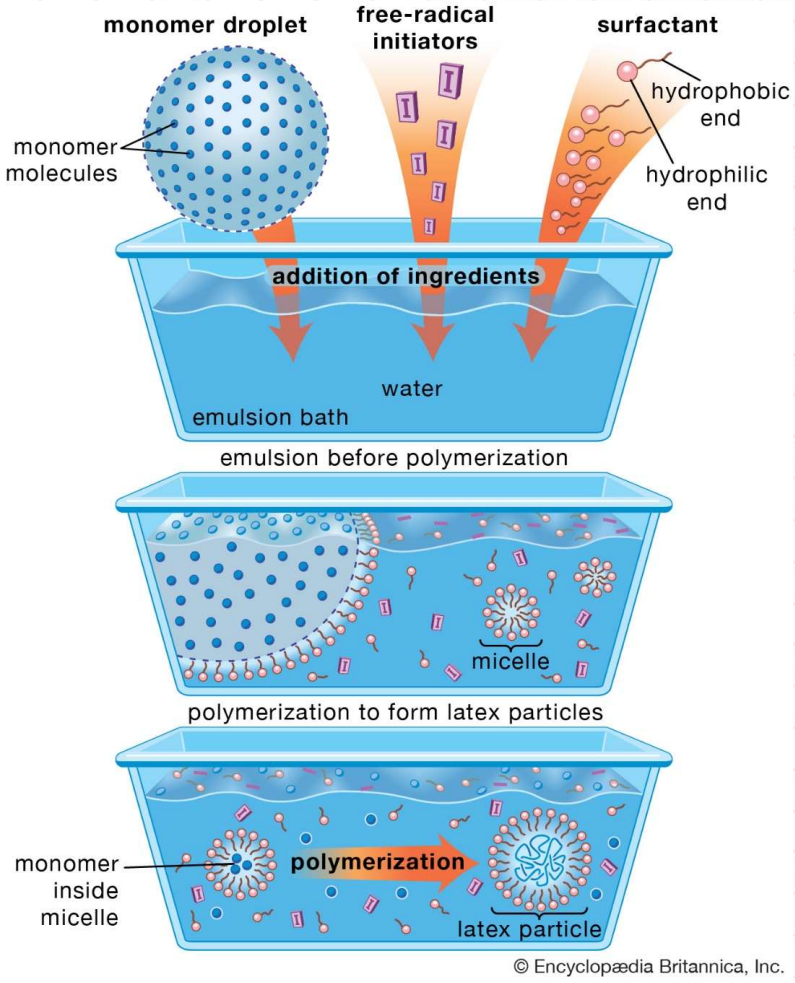
After mechanical stirring

Mode of Polymerization; Addition Polymerization

Techniques of Free Radical Polymerization

Emulsion Polymerization

- Ingredients:
  - Water-insoluble monomer
  - Water-soluble initiator
  - Dispersing medium (water)
  - Surfactant (as PVA)
- Some examples of products are:
  - Paints
  - paper & paperboard
  - Textiles
  - packaging and adhesives

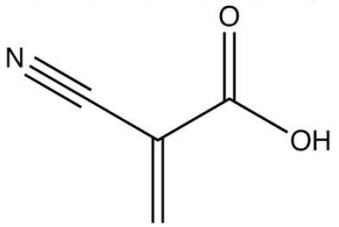


Mode of Polymerization; Addition Polymerization

Anionic Polymerization

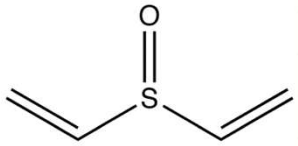
Monomer characteristics

- The substituents on the double bond must be able to stabilize a negative charge. through delocalization.
- **Polar monomers (***acrylonitrile, cyanoacrylate, propylene oxide, vinyl ketone, acrolein, vinyl sulfone, vinyl sulfoxide, vinyl silane and isocyanate***)**, using controlled conditions and **low temperatures**, can undergo anionic polymerization.
- **At higher temperatures** they do not produce living stable, because their polar substituents can undergo side reactions with both initiators and propagating chain centers.



cyanoacrylate

acrolein

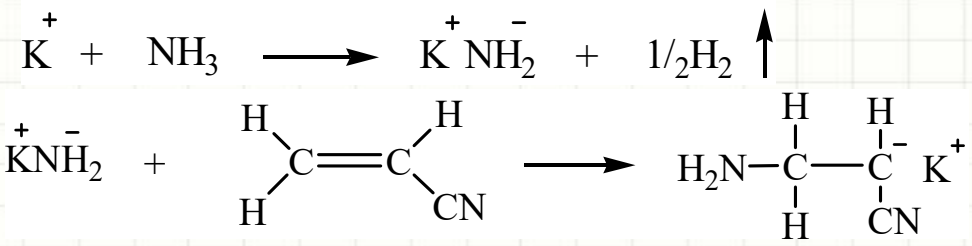


vinyl sulfoxide

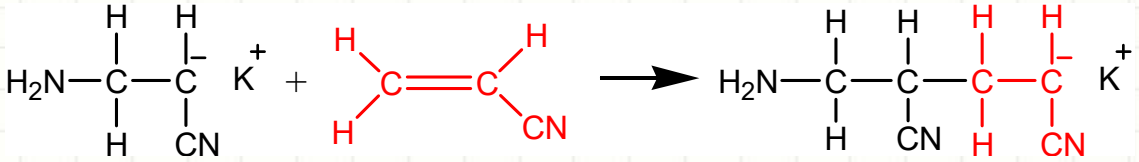
Mode of Polymerization; Addition Polymerization

Anionic Polymerization

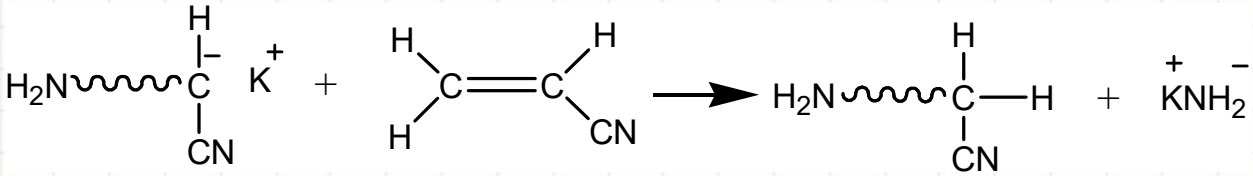
1. Chain initiation



2. Chain propagation



3. Chain termination;



Anionic addition polymerizations have no formal termination pathways because proton transfer from solvent or other positive species does not occur.

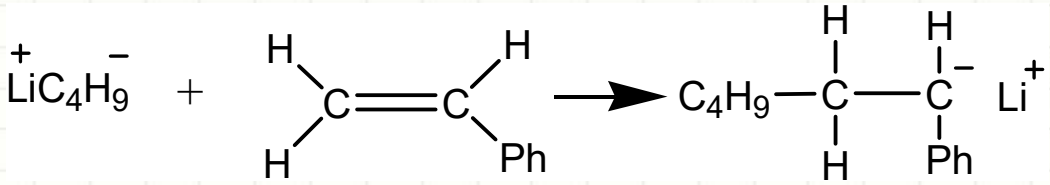
Mode of Polymerization; Addition Polymerization

Anionic Polymerization

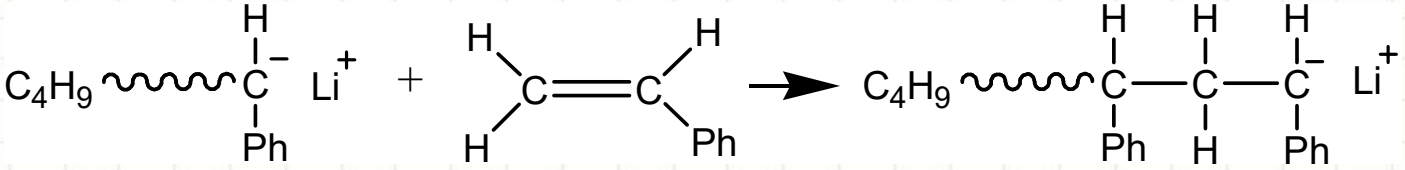
Living Polymer

- Living polymerization was demonstrated by Szwarc and co workers in 1956.
- In the absence of impurities, the carbanion would still be active and capable of adding another monomer.
- The chains will remain active indefinitely unless there is inadvertent or deliberate termination or chain transfer.

1. Chain initiation



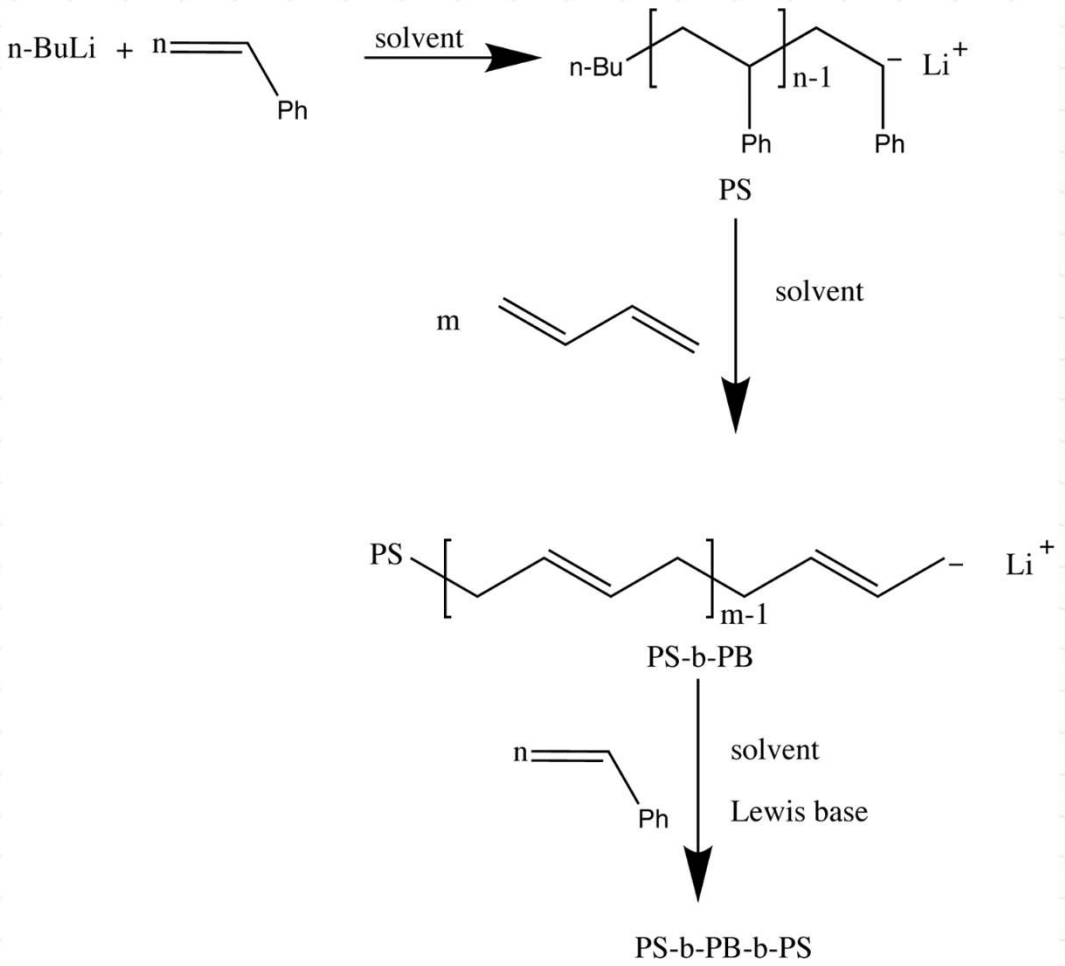
2. Chain propagation



Mode of Polymerization; Addition Polymerization

Anionic Polymerization

Block copolymers

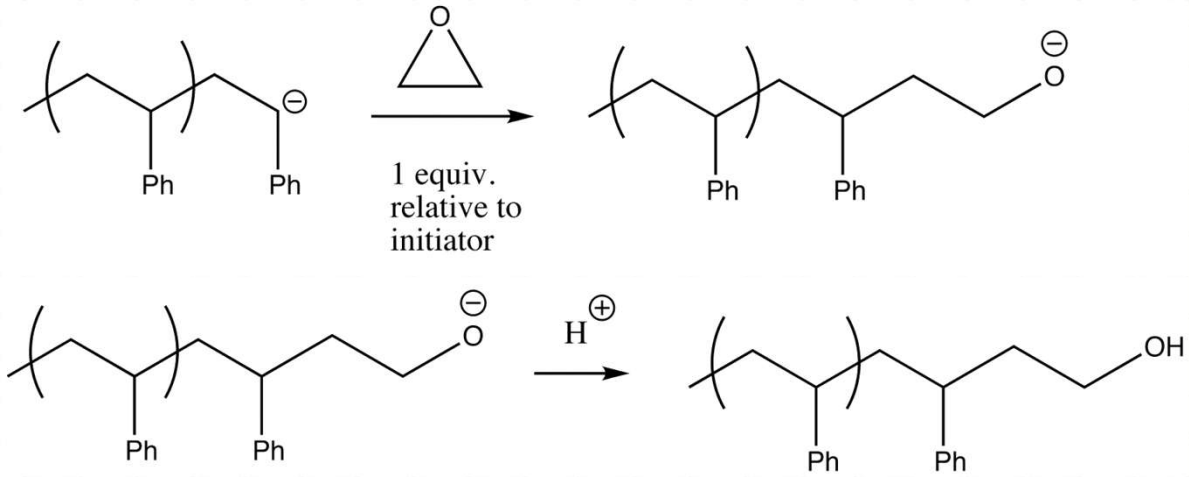


Mode of Polymerization; Addition Polymerization

Anionic Polymerization

End-group functionalization

- Living anionic polymerization can also be used to incorporate functional groups.
- These end-groups are usually added post-polymerization.
- End-groups that have been used in the functionalization of α-haloalkanes include hydroxide, -NH_2, -OH, -SH, -CHO,-$COCH_3$, -COOH, and epoxides.

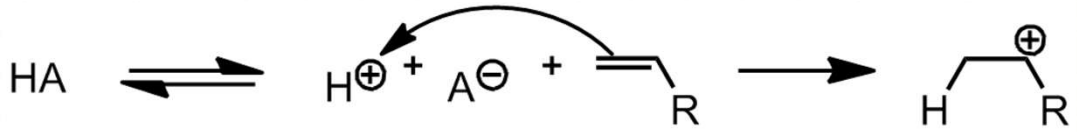


Mode of Polymerization; Addition Polymerization

Cationic Polymerization

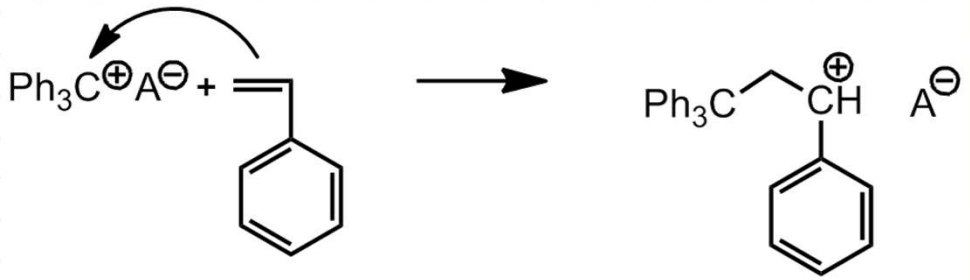
Initiation

- **Classical protonic acids (phosphoric, sulfuric, fluro-, and triflic acids)**



  - The counter ion (A−) produced must be weakly nucleophilic so as to prevent early termination due to combination with the protonated olefin.
  - Only low molecular weight polymers are formed with these initiators.

- **Carbenium ion salts**

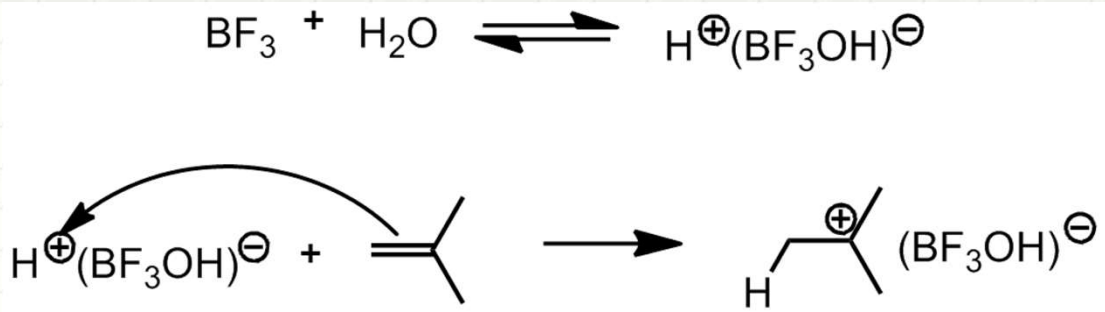


Mode of Polymerization; Addition Polymerization

Cationic Polymerization

Initiation

- **Lewis acids/Friedel-Crafts catalysts ($SnCl_4$, $AlCl_3$, BF_3, and $TiCl_4$)**

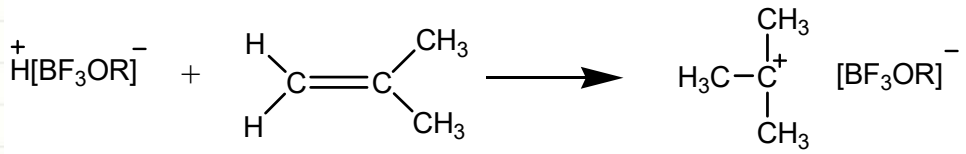


- The reaction occurs much faster with a suitable cation source (e.g. water, alcohols, ester or an anhydride.
- Lewis acid is referred to as a coinitiator while the cation source is the initiator.
- The counter ion produced by the initiator-coinitiator complex is less nucleophilic than that of the Brønsted acid A^- counter ion.

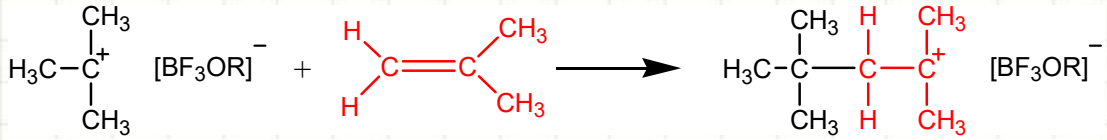
Mode of Polymerization; Addition Polymerization

Cationic Polymerization

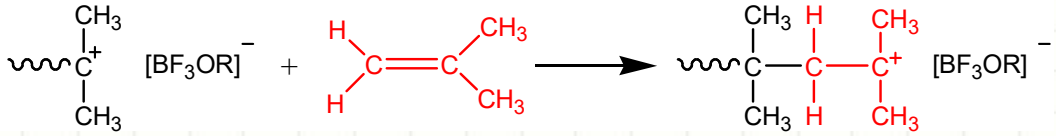
1. Chain initiation



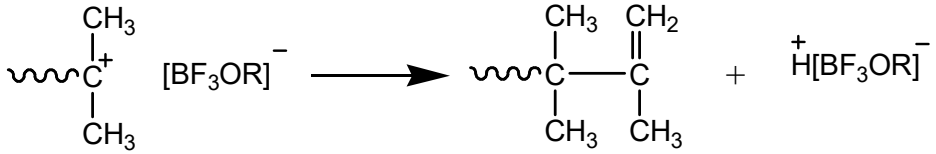
2. Chain propagation



And subsquently:



3. Chain termination;



Mode of Polymerization; Addition Polymerization

Cationic Polymerization

Effect of temperature

- Low reaction temperatures, are preferred for producing longer chains.
- As the temperature is raised, the energy barrier for the termination reaction is overcome, causing shorter chains to be produced during the polymerization process.

Effect of solvent and counterion

- The size of the counter ion is also a factor.
  - A smaller counter ion, with a higher charge density, will have stronger electrostatic interactions with the carbenium ion than will a larger counter ion which has a lower charge density.
- A smaller counter ion is more easily solvated by a polar solvent than a counter ion with low charge density.
- The propagation rate increased with increased solvating capability of the solvent.

Mode of Polymerization; Addition Polymerization

Polyethylene (PE)

- Based on the structure of the molecule of the polyethylene, There are three main types of polyethylene:
  - **High density polyethylene (HDPE),**

    HDPE is a more linear molecule where there are very few side chains caused by branching, and these side chains are usually very short compared to LDPE.
  - **Low density polyethylene (LDPE),**

    Branches are relatively long and intertwine and link with other polyethylene molecules
  - **Linear low density polyethylene (LLDPE)**

    LLDPE as the name suggests is a more linear, low density polyethylene molecule. It still has a large number of side branches, however these branches are shorter.
- Due to the differences in structure,
  - HDPE is stronger and has a higher melting point than LDPE,
  - with LLDPE generally between the two.

Mode of Polymerization; Addition Polymerization

Polyethylene (PE)

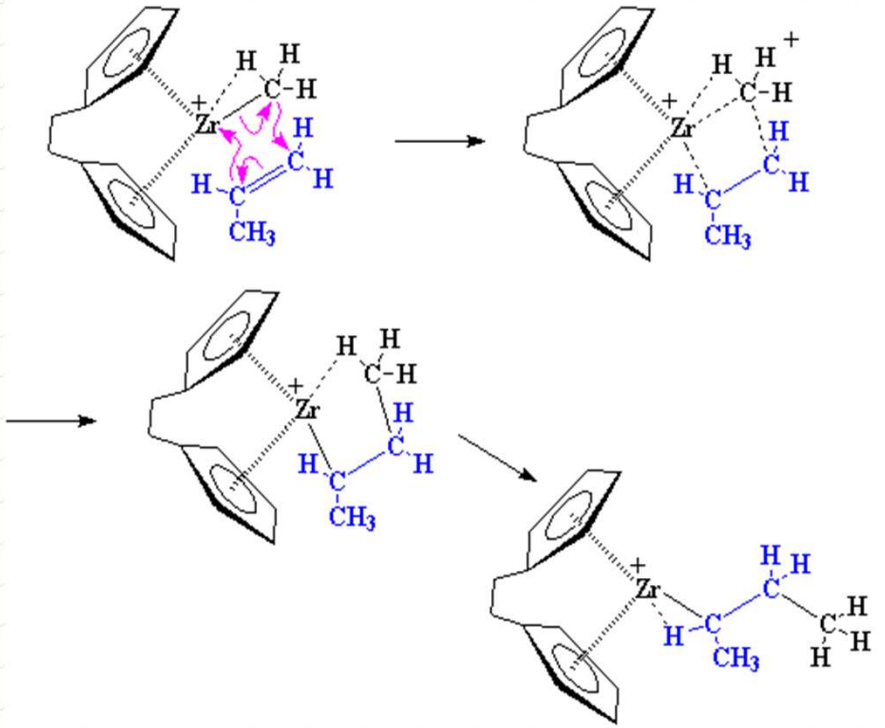
There are 3 main polymerization reactions used to make polyethylene:

- **Free radical polymerization**, this type of polymerization is used to make the highly branched LDPE at high pressures (1000 to 3000 atm), and 150-300ºC.
- **Ziegler-Natta polymerization**, is used to make HDPE and LLDPE; uses transition metal catalysts at temperatures of around 70 to 150ºC and pressures less than 10 atm.
- **Metallocene catalyst polymerization**, metallocene molecules (metal ions sandwiched between two carbon-based rings), as the catalyst.
  - They are very good at allowing the manufacturer to control the exact structure of the polyethylene.
  - They are commonly used to increase the strength of LDPE and HDPE,
  - They are also able to make Ultra High Density Polyethylene (UHDPE) that is very strong.

Mode of Polymerization; Addition Polymerization

Polypropylene (PP)

- **Polypropylene** has very similar mechanical and chemical properties to it's PE cousin.
- Structurally PP forms a large amount of crystals, making it stronger than polyethylene.
- The different structure also gives PP a higher melting point, around 160ºC.
- It is also relatively chemically inert and resistant to chemical attack from most solvents, bases and acids. Like PE, PP also has high electrical resistance, making it a good insulator



Polypropylene is manufactured by metallocene catalysis

Mode of Polymerization; Addition Polymerization

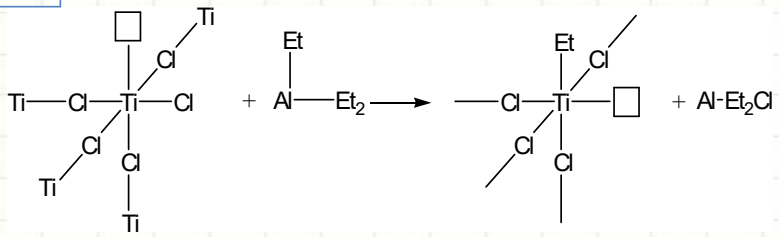
Polypropylene (PP)

$$TiCl_4 + AlEt_3 \longrightarrow TiCl_3Et + AlEt_2Cl$$

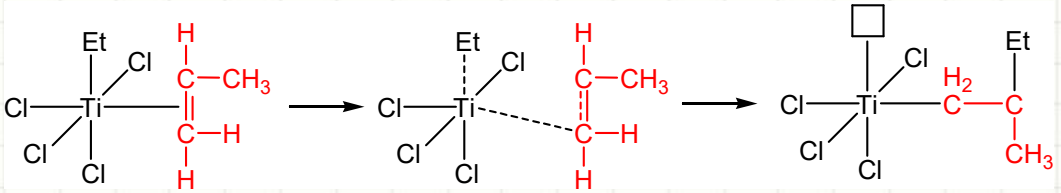
$$2\ TiCl_3Et \longrightarrow 2\ TiCl_3\downarrow + C_2H_4 + C_2H_6\ (\text{or } C_4H_{10})$$

$$TiCl_3Et + TiCl_4 \longrightarrow 2\ TiCl_3\downarrow + EtCl$$

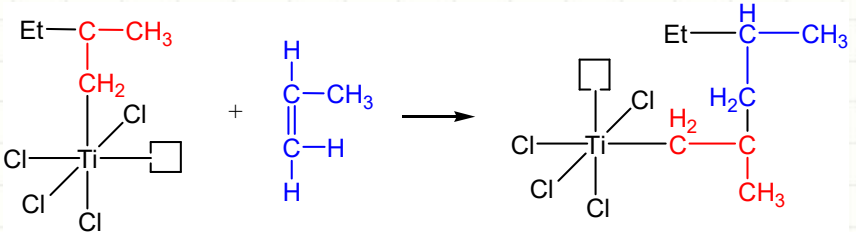
Alkylation of Ti^{3+} with a vacant orbital



Initiation Step;

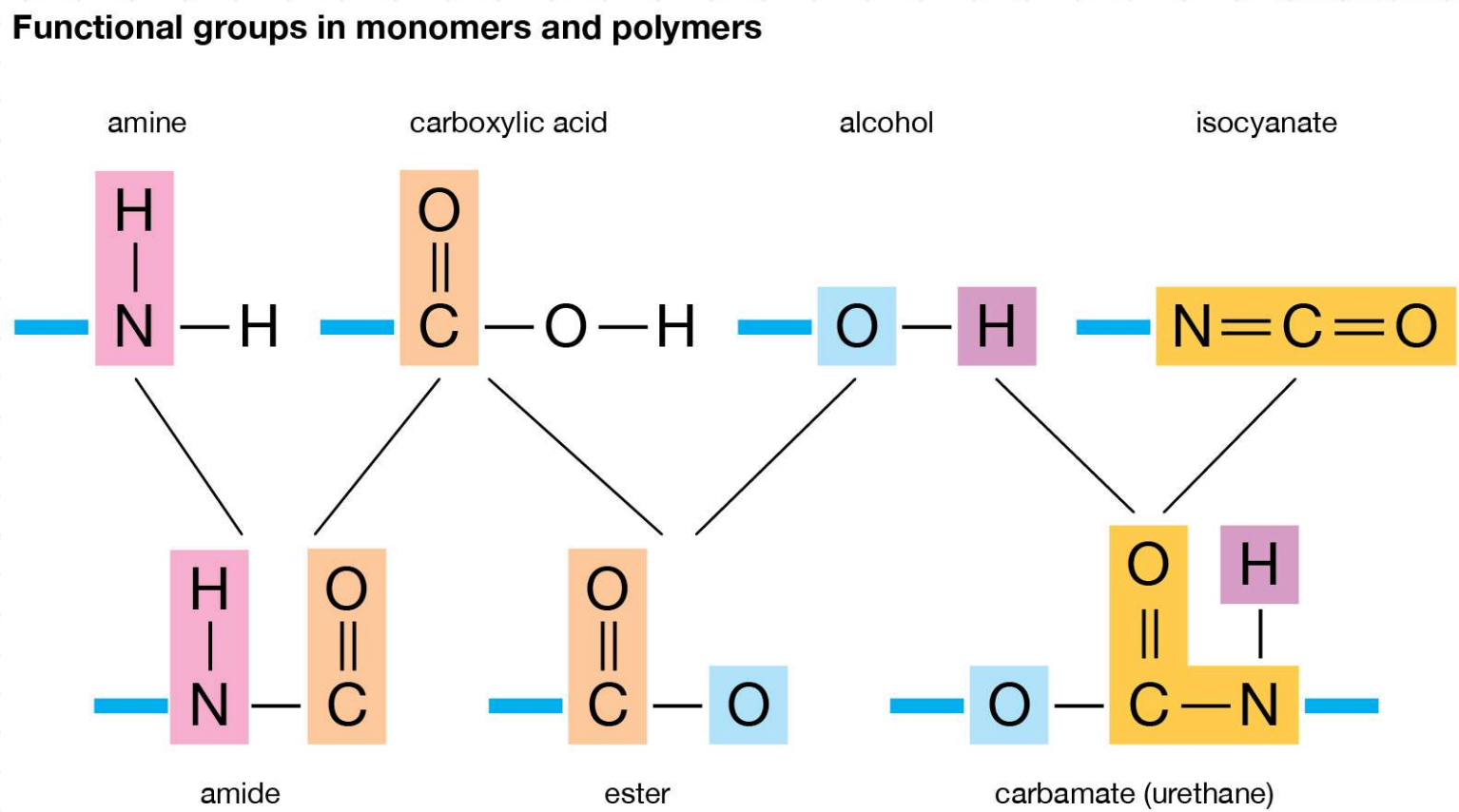


Propagation Step;



Mode of Polymerization; Condensation Polymerization

- **Condensation polymers** *are made from monomers with two functional groups which can be the same or different.*

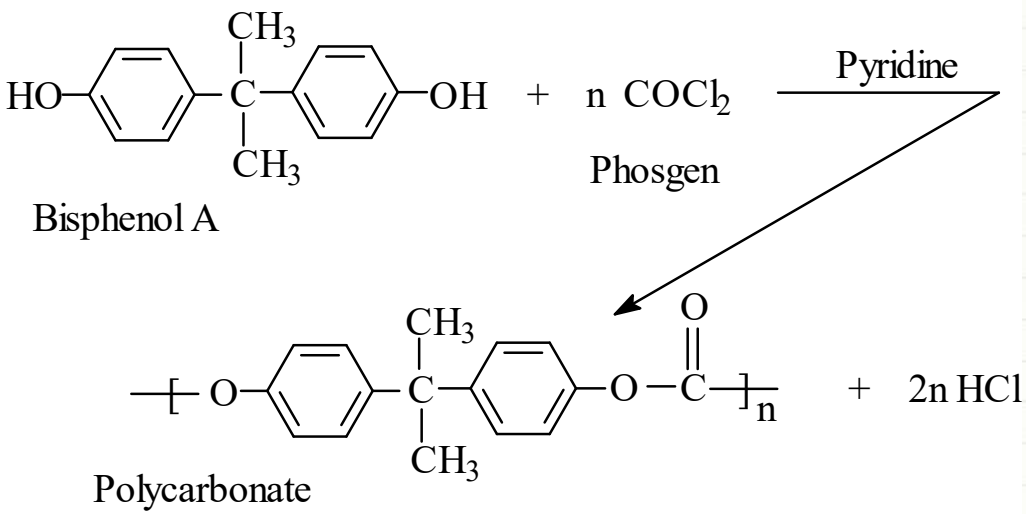


Mode of Polymerization; Condensation Polymerization

Polycarbonate (Pc)

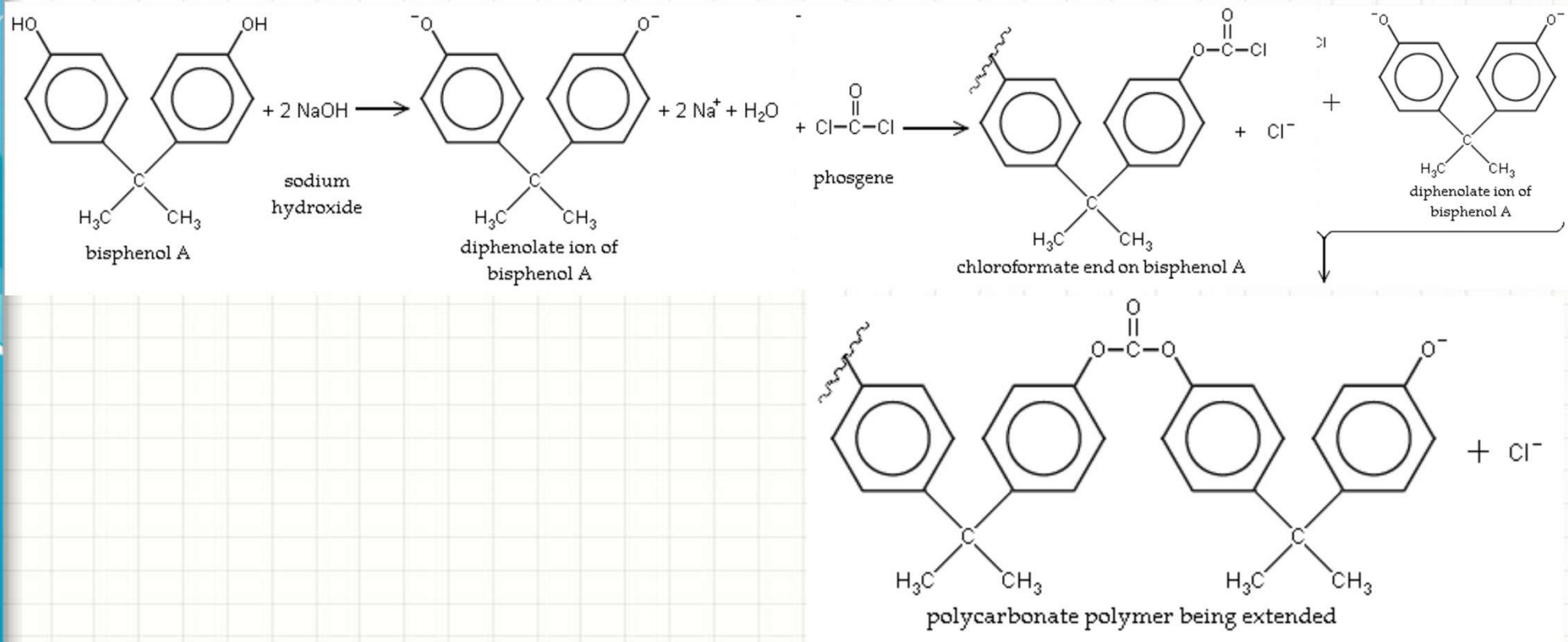
- **Polycarbonate (PC),** was first developed in 1953 by Bayer in Germany, and General Electric in the US independently. Its most popular trade name is LEXAN®
- **PC** is one of the high performance heterochain polymeric materials that comprise the family of "engineering thermoplastics"
- **PC** is a good material choice in industry not only due to its characteristics, but also because its processing is environmentally friendly, and it can be recycled

- The Bisphenol A group also contributes to PC's inability to crystallize.
- This amorphous structure gives the polymer its particular transparency.



Mode of Polymerization; Condensation Polymerization

Polycarbonate



Mode of Polymerization; Condensation Polymerization

Polycarbonate

Physical Properties of PC

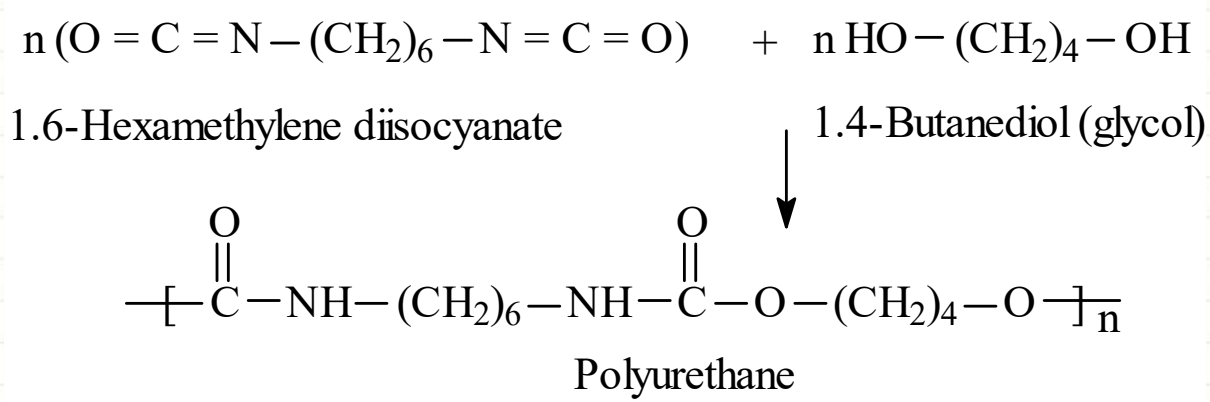
- It maintains good mechanical properties between -40° F and 280° F.
- High strength that makes it resistant to impact and fracture.
- It can be easily colored, it's non-toxic, and can be absolutely transparent.
- PC also features high electrical and heat resistance.
- It is biologically inert.
- Readily recyclable and cost effective.

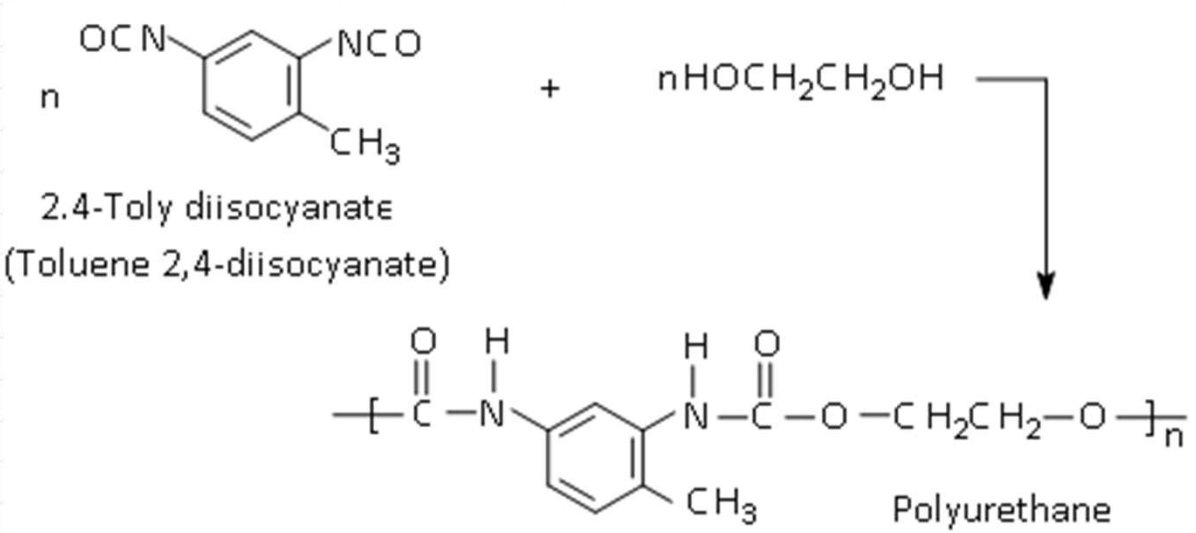
PC Blends

- **PC** can be blended to enhance its properties:
- **PC/ABS** blends exhibit high ductility and impact strength at temperatures below those of pure PC
- **PC** tends to scratch easily, **Silicone-polycarbonate copolymers** can yield a hard thermoplastic that doesn't get scratched.

Mode of Polymerization; Condensation Polymerization

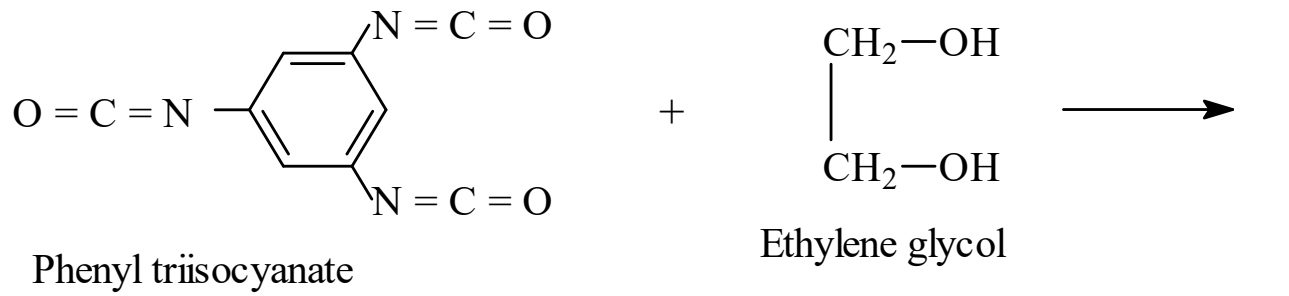
Polyurethane





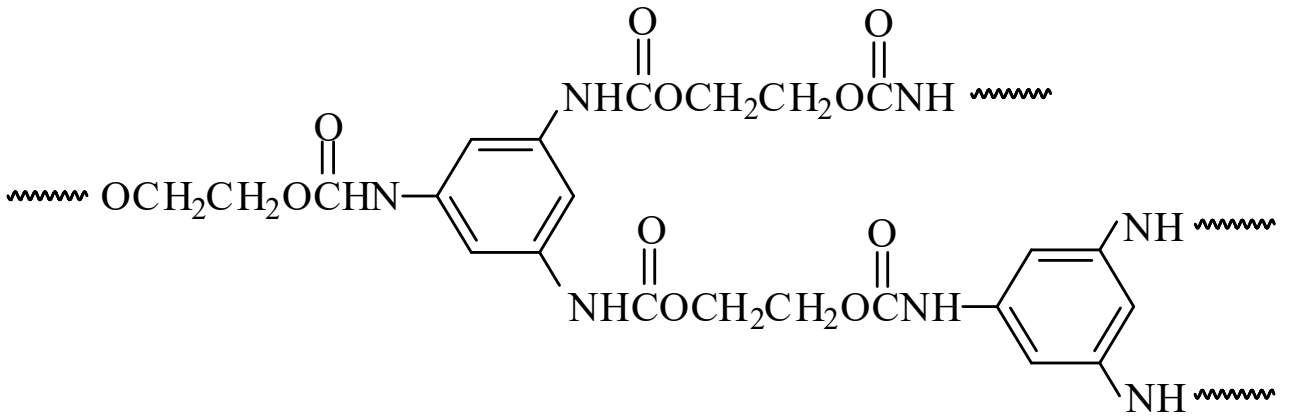
Mode of Polymerization; Condensation Polymerization

Polyurethane



Phenyl triisocyanate

Ethylene glycol



Cross-linked polyurethane

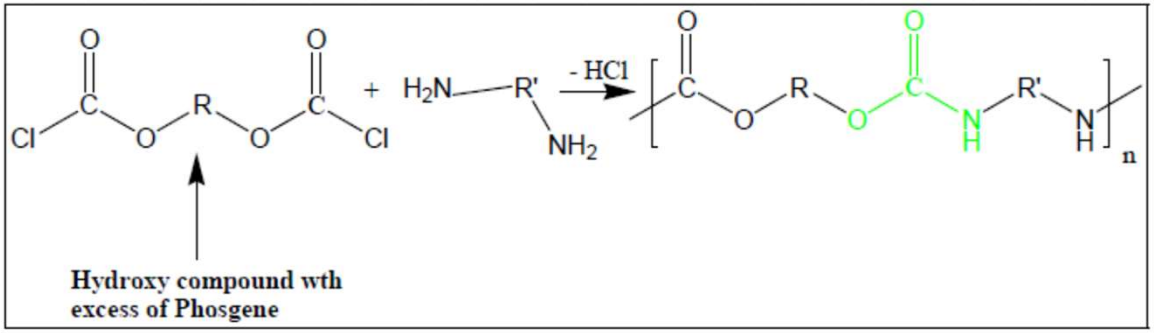
Mode of Polymerization; Condensation Polymerization

Polyurethane

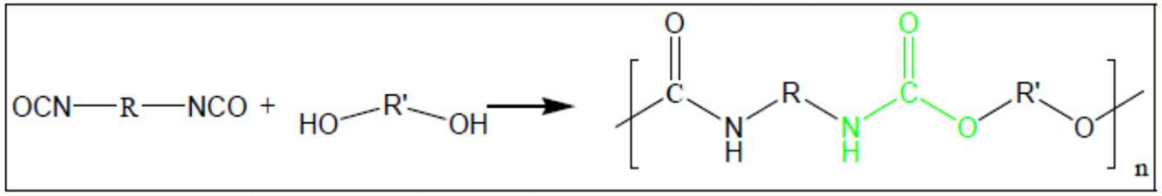
Chemistry of PU

- **PU** are carbonic acid derivatives.
- **PU** are formed by

(i) the condensation polymerization reaction of **bischloroformates with diamine**:



(ii) addition polymerization reaction of diisocyanates with di or polyfunctional hydroxy compounds (industrial point of view since in this method no by-product is formed).



Mode of Polymerization; Condensation Polymerization

Polyurethane

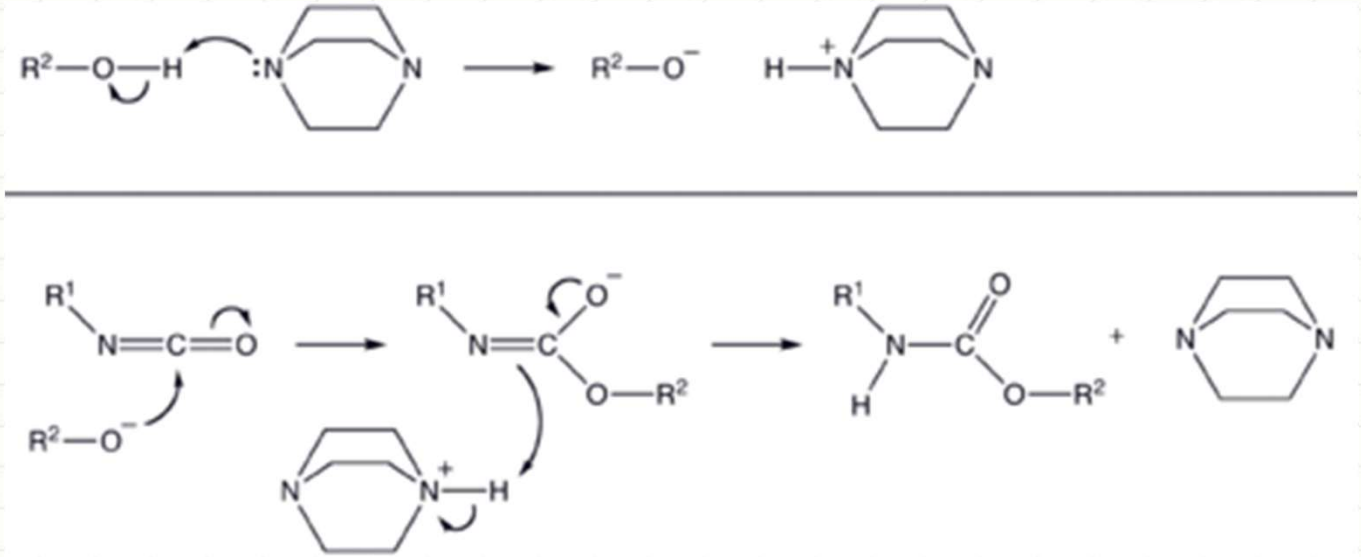
Additives

- Some additives (*catalysts, chain extenders, crosslinkers, fillers, moisture scavengers, colorants*) may also be required during PU production, to
  - control the reaction,
  - modify the reaction conditions, and
  - finish or modify the final product.

Mode of Polymerization; Condensation Polymerization

Polyurethane

- **Catalysts** [aliphatic and aromatic amines (e.g., diaminobicyclooctane DABCO), organometallic compounds (e.g.,dibutyltin diacetate), alkali metal salts of carboxylic acids and phenols (calcium, magnesium, strontium, barium, salts of hexanoic acid) are added to *promote the reaction to occur at enhanced reaction rates, at lower temperatures*.



Mode of Polymerization; Condensation Polymerization

Polyurethane

- **Chain extenders**; difunctional low molecular weight diols (ethylene glycol, 1,4-butanediol, 1,6-hexanediol).
- Since isocyanates are too sensitive to moisture or water even in traces, **moisture scavengers**, which react more readily with water than an isocyanate,
- **Blowing agents** are used to produce PU foams with cellular structures by foaming process (e.g., hydrocarbons, CO_2, hydrazine).

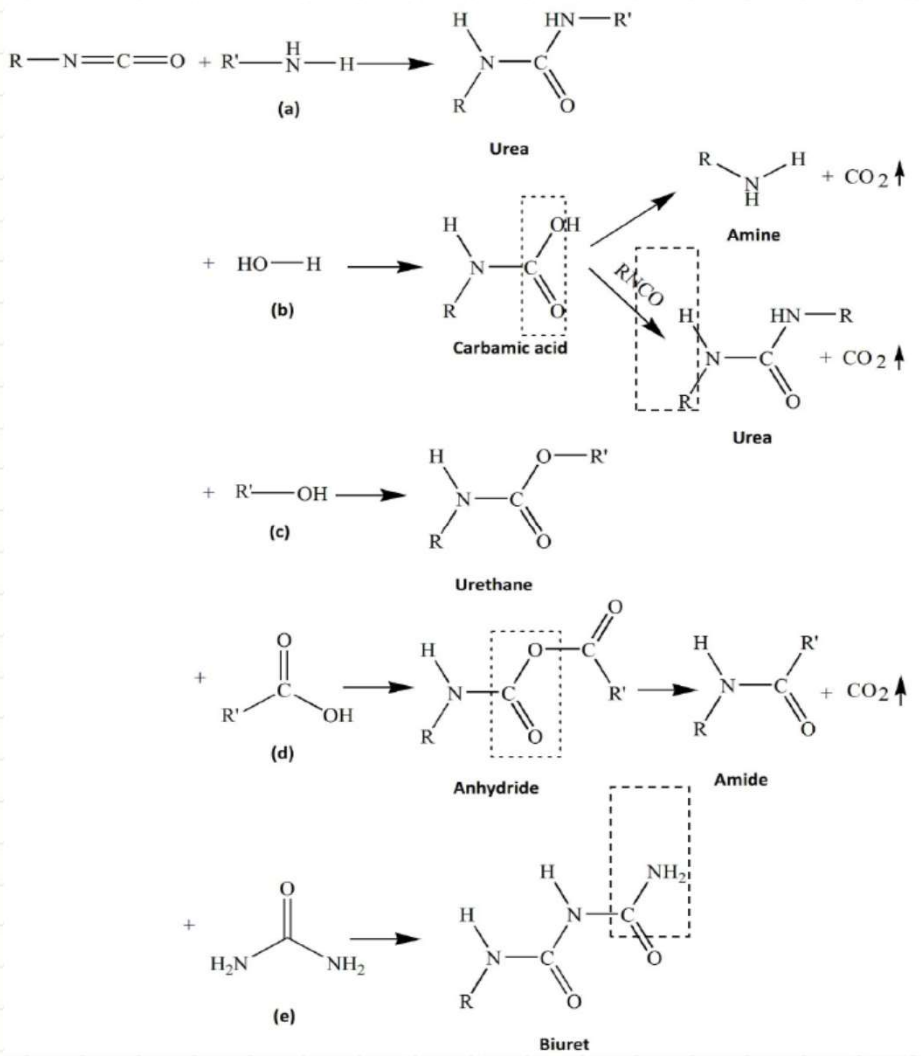
Mode of Polymerization; Condensation Polymerization

Polyurethane

Isocyanate reaction

- **Generally, the isocyanate reactions are divided into two classes,**

  (a) addition (primary and secondary) reaction with compound containing active hydrogen.

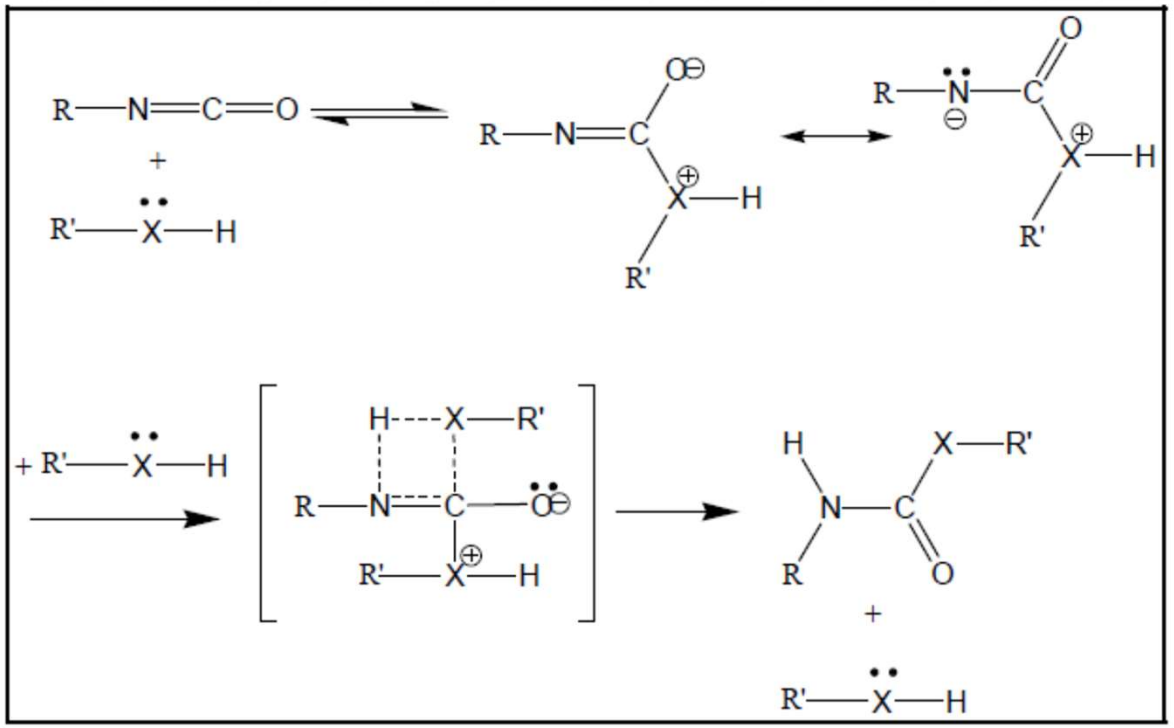


Mode of Polymerization; Condensation Polymerization

Polyurethane

Mechanism

- The reaction of an isocyanate with active hydrogen compounds.
- The active compound itself acts catalytically in the reaction as follows



Mode of Polymerization; Condensation Polymerization

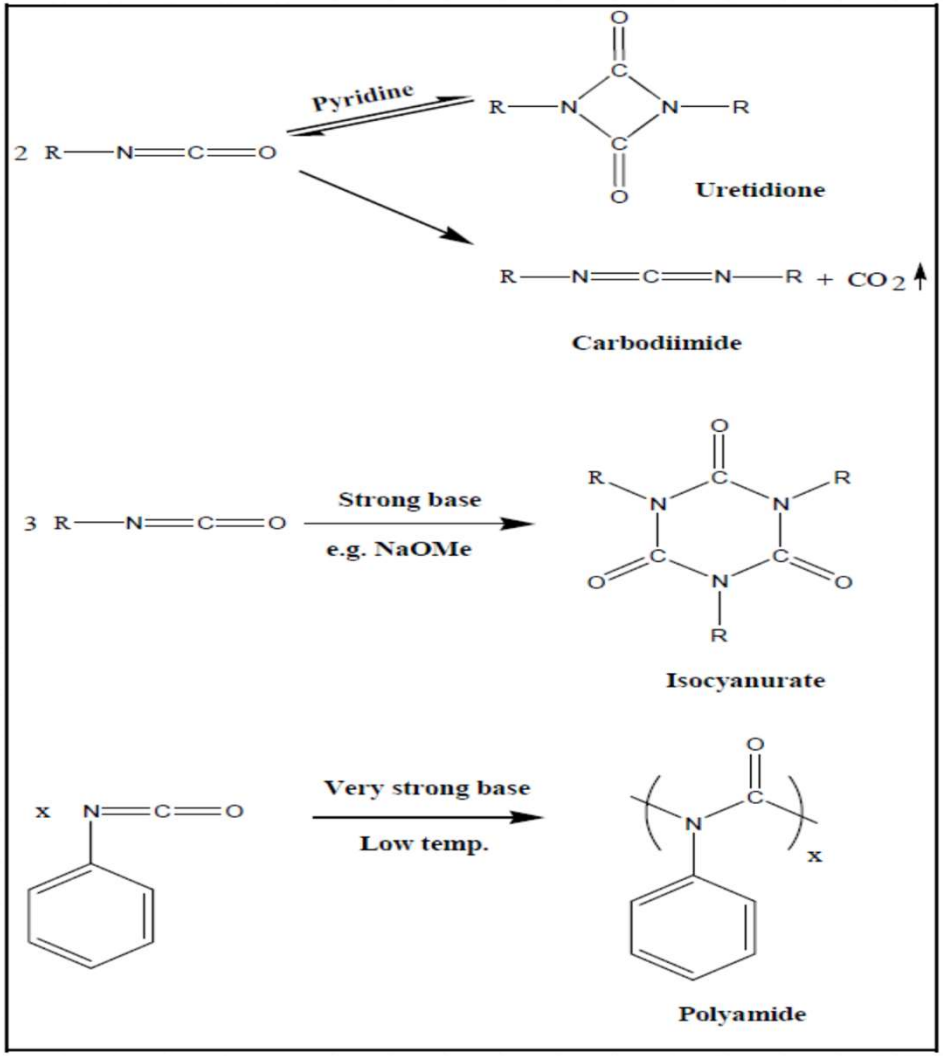
Polyurethane

Isocyanate reaction

- **Generally, the isocyanate reactions are divided into two classes,**

(b) self-addition reaction.

In some of the reactions, CO_2 is released which assists in the formation of **PU foams**.



Mode of Polymerization; Condensation Polymerization

Polyurethane

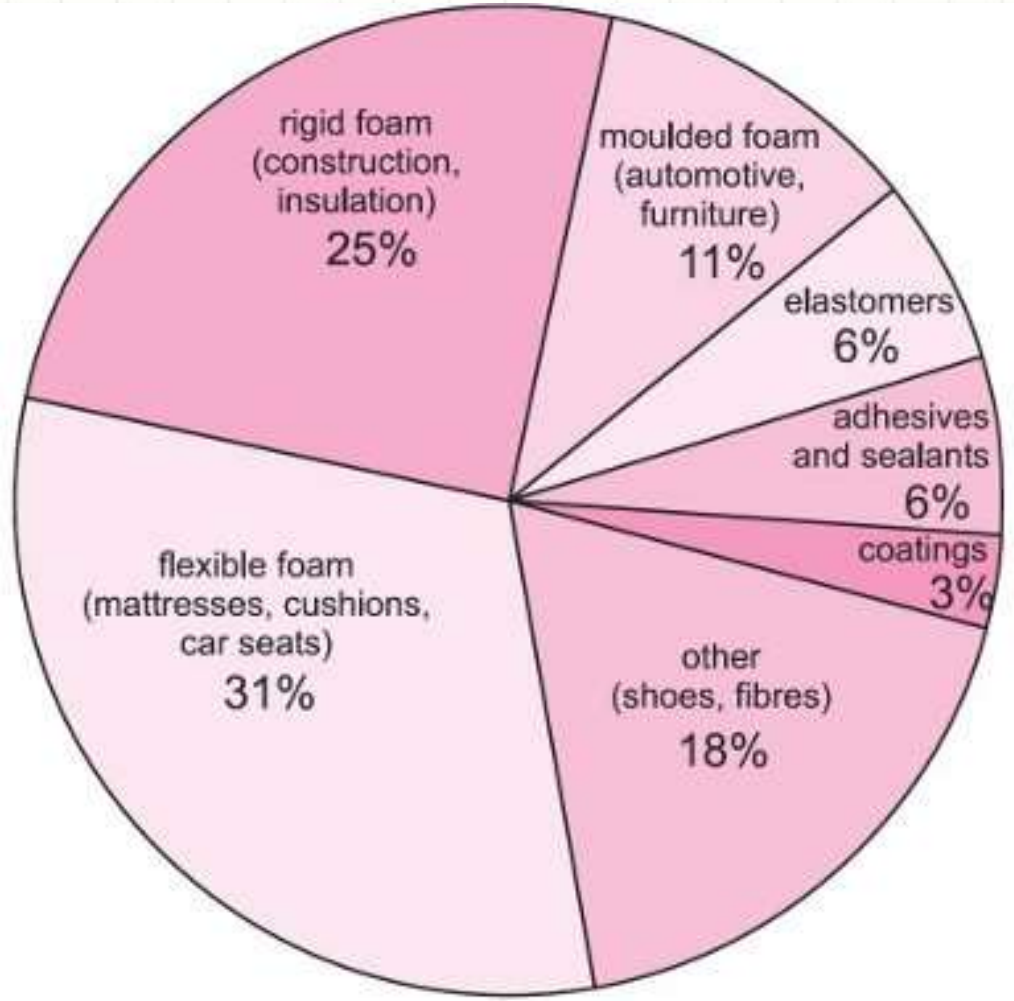
Hazards

- **PU** are chemically inert in their fully reacted form.
- The risks due to the volatility associated with *isocyanates*;
  - Asthmatic symptoms arise on human exposure even in smaller concentrations.
  - On exposure to flames, hazards of ignition are feared.
  - Isocyanates may also be sensitive on our skin.
  - Some isocyanates may also be anticipated as carcinogens.
- Thus, persons working with isocyanates must be equipped with proper protection devices such as gloves, masks, respirators, goggles, and others, as precautionary measures.

Mode of Polymerization; Condensation Polymerization

Polyurethane

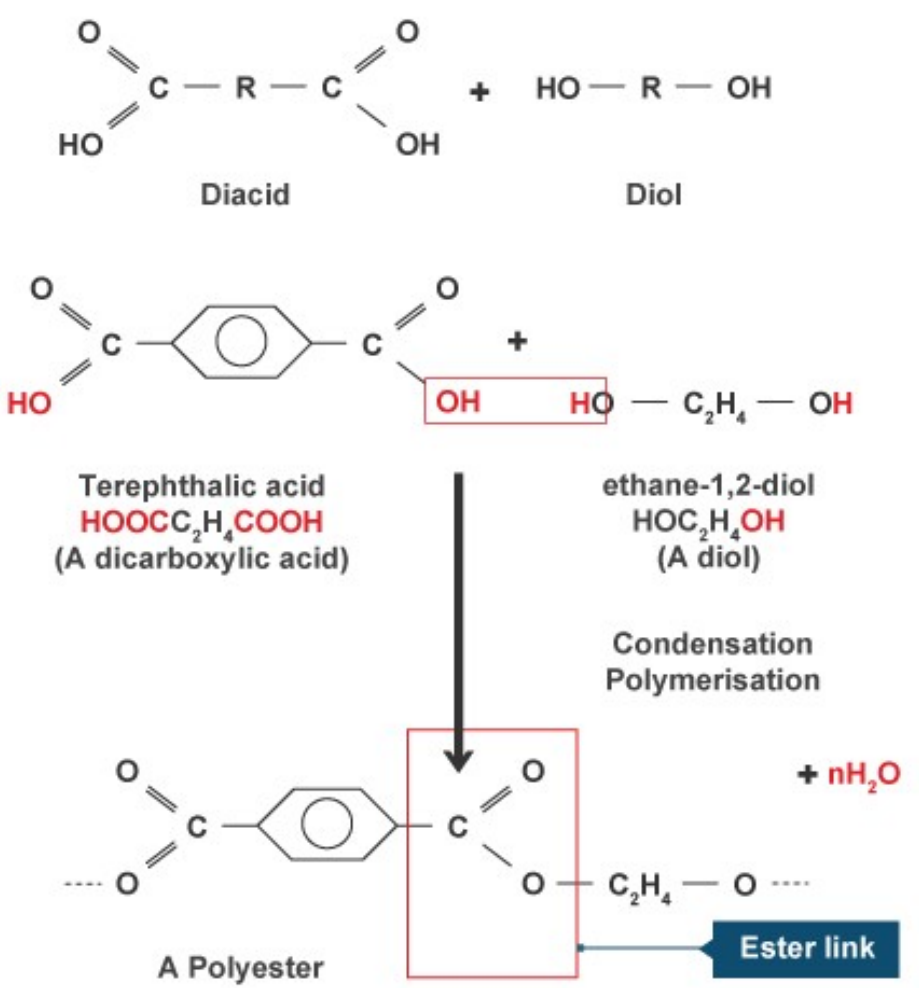
Uses of polyurethanes.



Mode of Polymerization; Condensation Polymerization

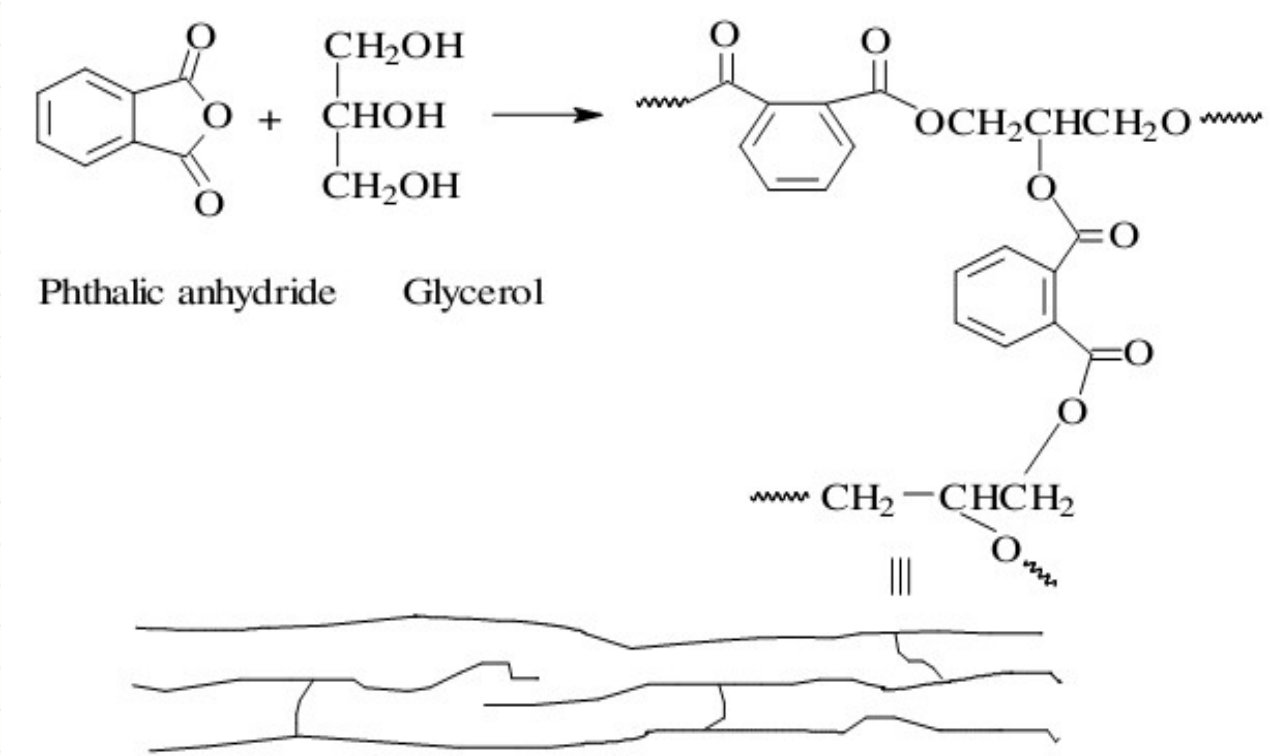
Polyester

- The relatively easy accessible raw materials: Purified terephthalic acid (PTA) or Dimethylterephthalate (DMT) and Mono-ethylene glycol (MEG).
- The wide variety of intermediate and final products made of polyester; PET & fibers.
- The recyclability.
- Increasing the aromatic parts of polyesters increases their glass transition temperature (T_g), melting temperature, thermal stability, chemical stability and solvent resistance.



Mode of Polymerization; Condensation Polymerization

Polyester

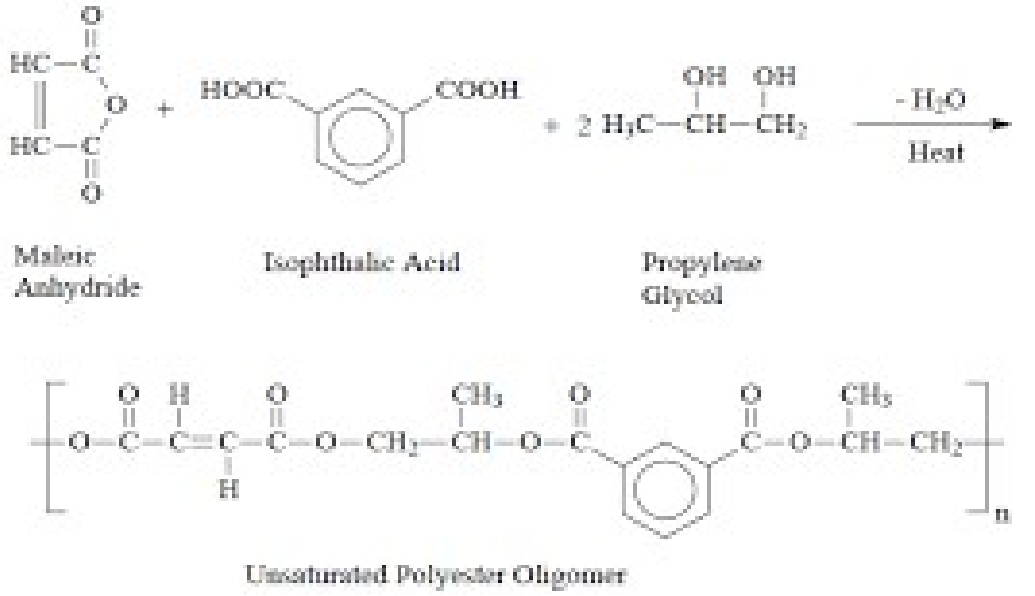


Crosslinked polyester

Mode of Polymerization; Condensation Polymerization

Polyester

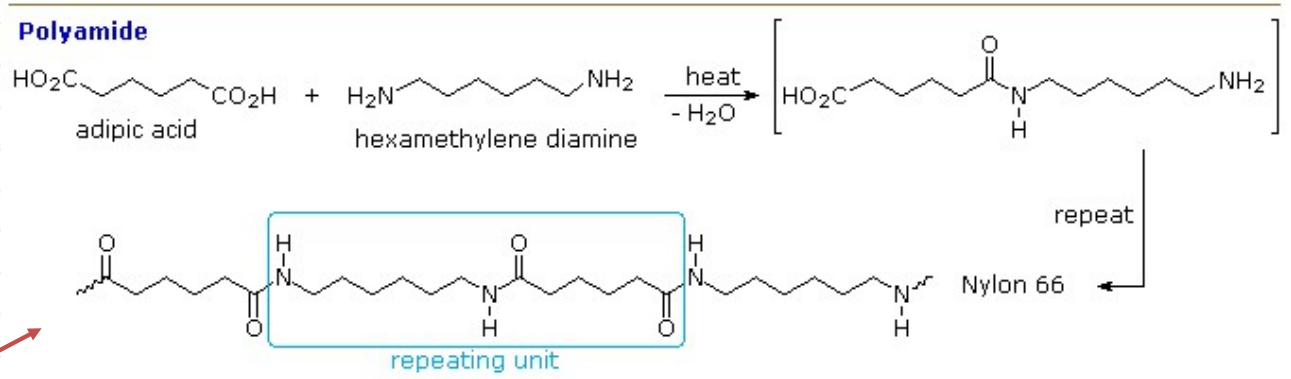
- **Unsaturated polyesters** (one or more diol with saturated and unsaturated dicarboxylic acids or anhydride) are thermosetting resins.
- The double bond of unsaturated polyesters reacts with a vinyl monomer, resulting in a 3-D cross-linked structure.



- **Saturated polyesters;**
  - They consist of low molecular weight liquids used as plasticizers, and
  - as reactants in forming urethane polymers, and linear, high molecular weight thermoplastics such as polyethylene terephthalate (dacron and Mylar).
  - Usual reactants for the saturated polyesters are a glycol and an acid or anhydride.

Mode of Polymerization; Condensation Polymerization

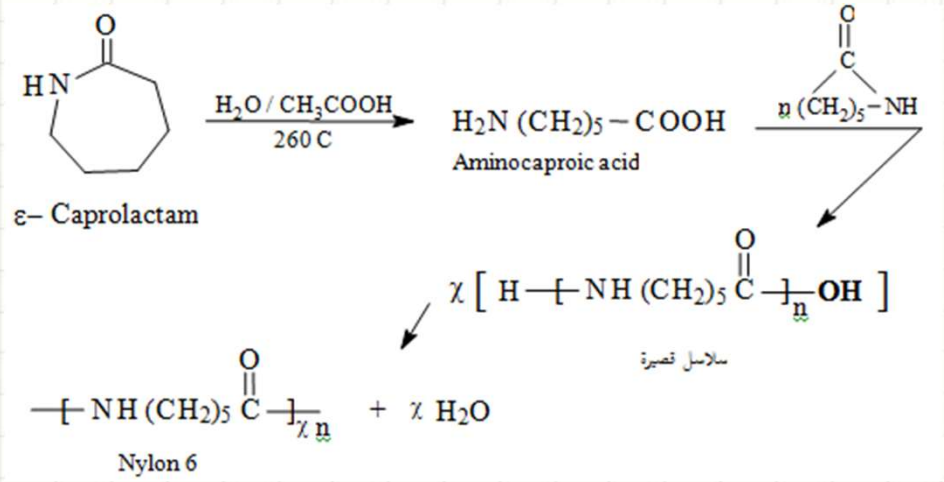
Polyamide



$$n\ H_2N(CH_2)_{10}COOH \longrightarrow \text{-}[\text{-}NH(CH_2)_{10}CO\text{-}]\text{-} + n\,H_2O$$

ω–Amino undecanoic acid — Nylon 11

The two most important polyamides



Mode of Polymerization; Condensation Polymerization

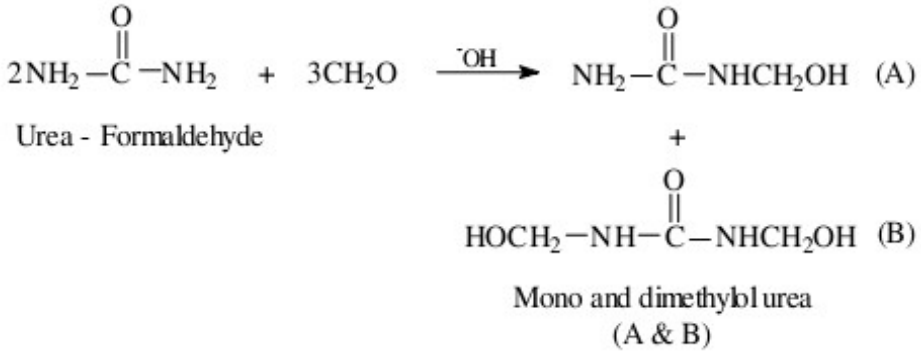
Polyamide

- The aliphatic polyamides (Nylon 6 and Nylon 6,6) are produced on a much larger scale than the fully aromatic polyamides (important class of engineering thermoplastics).
- They are amorphous or only moderately crystalline when injection molded.
- The degree of crystallinity can be much increased for fiber and film applications by orientation via mechanical stretching.
- They also have good resistance to oils, bases, fungi, and many solvents.
- The main limitation is the strong moisture sensitivity (water acts as a plasticizer) and the resulting changes in mechanical properties.
- Another important polyamide is Nylon 6,12.
  - It is less hydrophilic than Nylons 6,6 and 6 due to the larger number of methylene groups in the polymer backbone.
  - It has better moisture resistance.

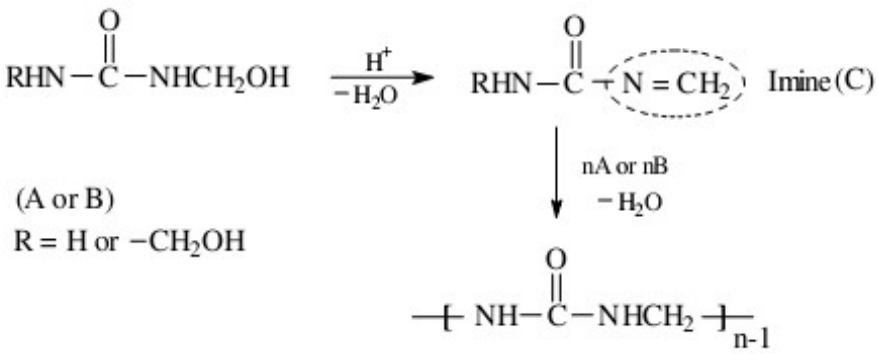
Mode of Polymerization; Condensation Polymerization

Urea-Formaldehyde Resins

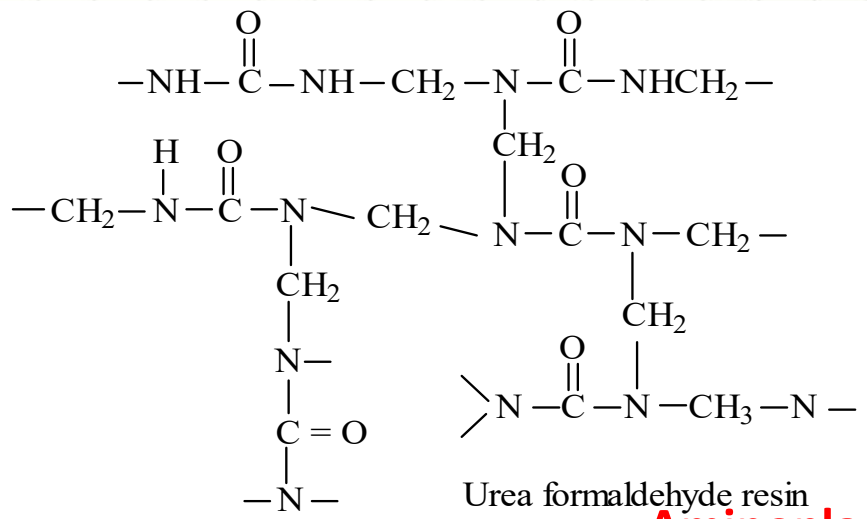
1) Formation of Methylol



2) In acid medium; Network Structure



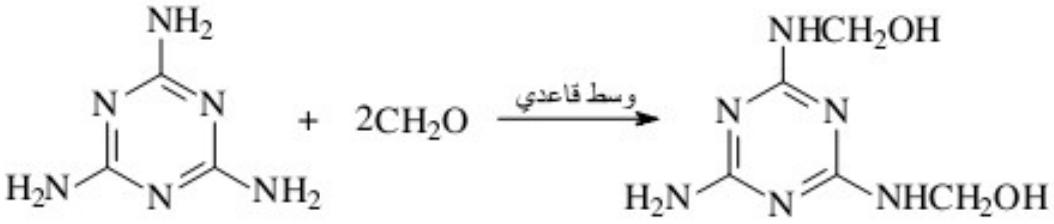
- The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of:
- *methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules.*



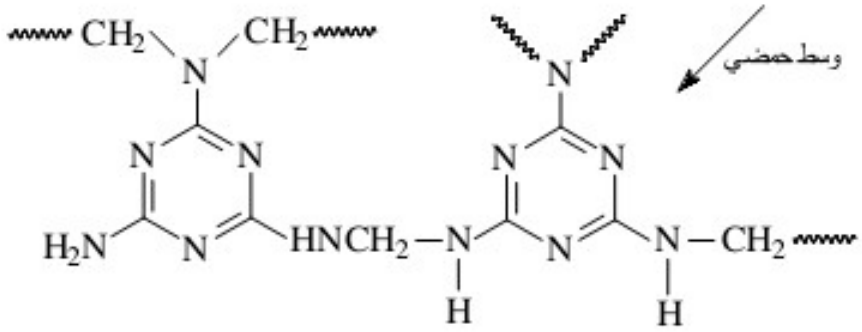
Aminoplast

Mode of Polymerization; Condensation Polymerization

Melamine-Formaldehyde Resins

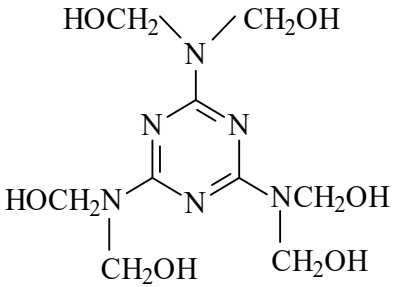


Dimethylol

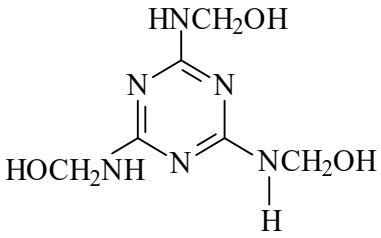


Melamine formaldehyde resin

Melanoplast



Hexamethylol



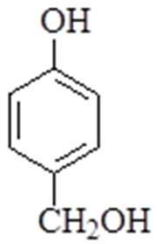
Trimethylol

Mode of Polymerization; Condensation Polymerization

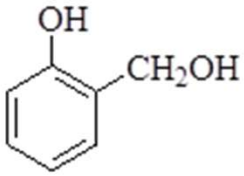
Phenol-Formaldehyde Resins (Bakelite)

Resol Resins

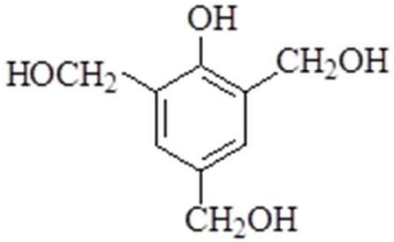
- A basic (alkaline) catalyst and, usually but not necessarily,
- A molar excess of formaldehyde (5:1) is used to make resol resins.
- The following two stages describe a simplified view of the reaction:
  - First, phenol reacts with methylene glycol to form methylol phenol:



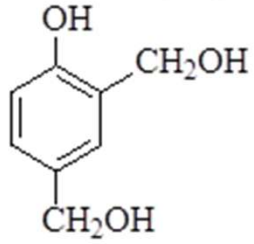
p-Methylol-Phenol



o-Methylol-Phenol



2.4.6- Tri-methylol-Phenol



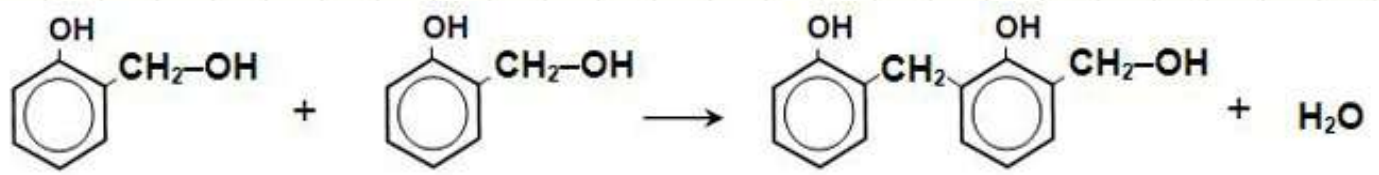
2.4- Tri-methylol-Phenol

Mode of Polymerization; Condensation Polymerization

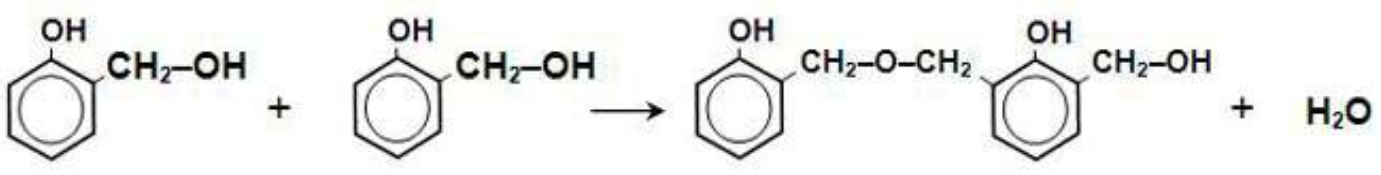
Phenol-Formaldehyde Resins (Bakelite)

Resol Resins

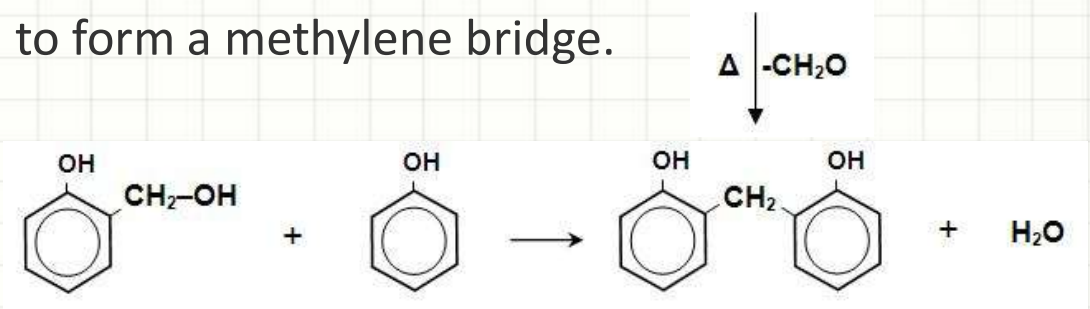
- Methylol phenol can react with itself to form a longer chain methylol phenolic:



- or form dibenzyl ether:



- or react with phenol to form a methylene bridge.

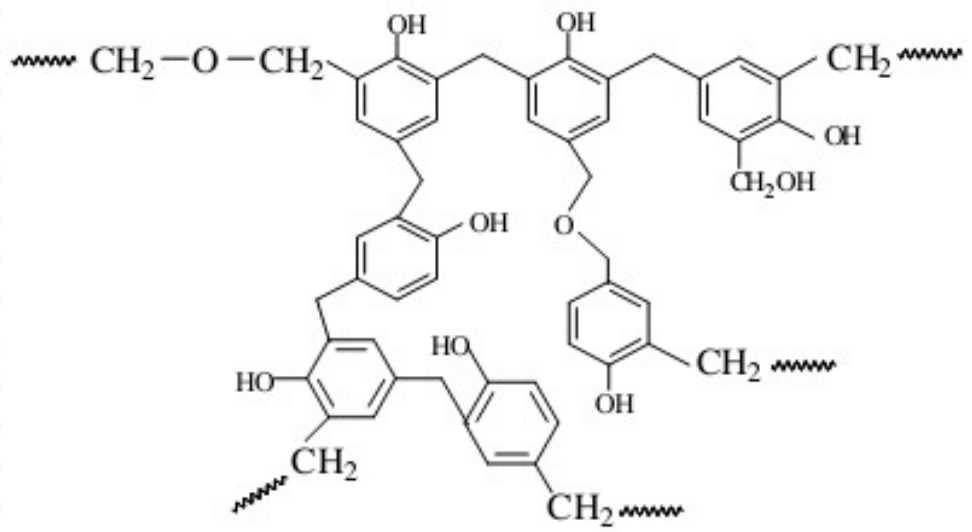


Mode of Polymerization; Condensation Polymerization

Phenol-Formaldehyde Resins (Bakelite)

Resol Resins

- When an excess of formaldehyde is used, a sufficient number of methylol and dibenzyl ether groups remain reactive to complete the polymerization.
- The resin cured without incorporation of a cure agent such as hexa.
- For this reason, the industry commonly refers to resol resins as "single-stage" or "one-step" type products.



Mode of Polymerization; Condensation Polymerization

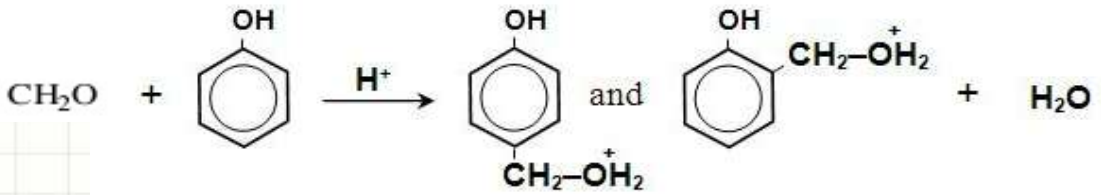
Phenol-Formaldehyde Resins (Bakelite)

Novolak Resins

- An acidic catalyst and a molar excess of phenol to formaldehyde (1.25:1) are conditions used to make novolac resins.

The following simplified chemistry illustrates the wide range of polymers possible.

- The initial reaction is between formaldehyde and phenol.

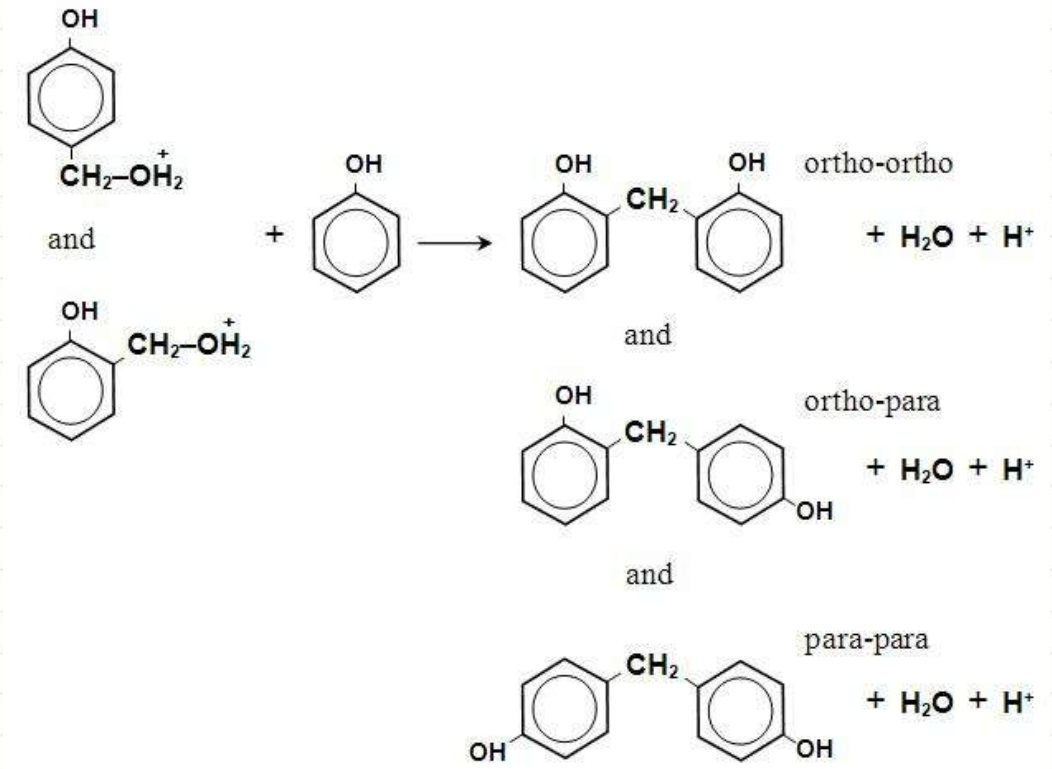


Mode of Polymerization; Condensation Polymerization

Phenol-Formaldehyde Resins (Bakelite)

Novolak Resins

- The reaction continues with additional phenol, and splitting off of water.

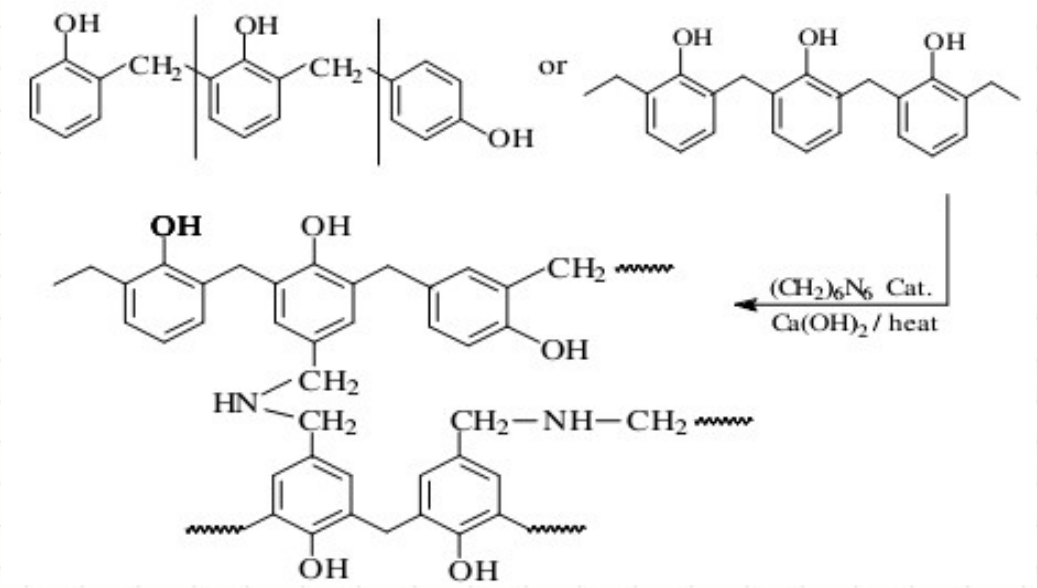


Mode of Polymerization; Condensation Polymerization

Phenol-Formaldehyde Resins (Bakelite)

Novolak Resins

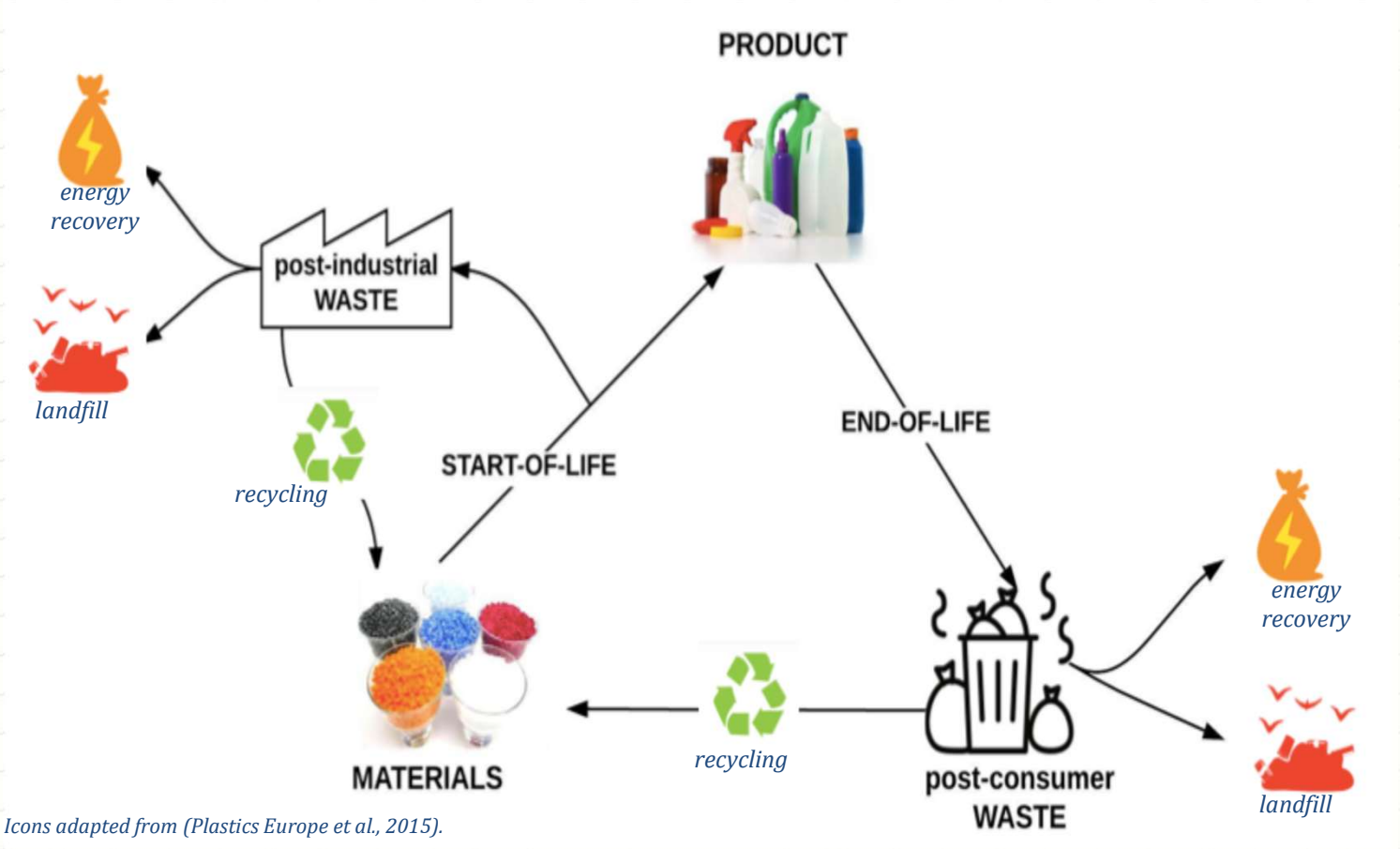
- The final novolac resin is unable to react further without the addition of a cross-linking agent (hexamethylenetetramine, also known as hexa, hexamine).



- Because an additional agent is required to complete the resin's cure,
- The industry commonly refers to novolac resins as "two-stage" or "two-step" products.

Mode of Polymerization; Solid Waste Produced in KSA

The Lifecycle of Polymer Materials



Icons adapted from (Plastics Europe et al., 2015).

Mode of Polymerization; Solid Waste Produced in KSA

Solid waste production in different cities of KSA

Region /City	Population (millions)	Amount of waste (x 10^3 tons per year)
Saudi Arabia	30.8	15,300
Major cities of KSA	14.12	8633
Riyadh	5.328	2871
Jeddah	3.456	1888
Makkah	1.675	915
Madina	1.180	645
Al-Taif	0.987	540
Dammam	0.903	1093
Al-Hassa	0.60	681

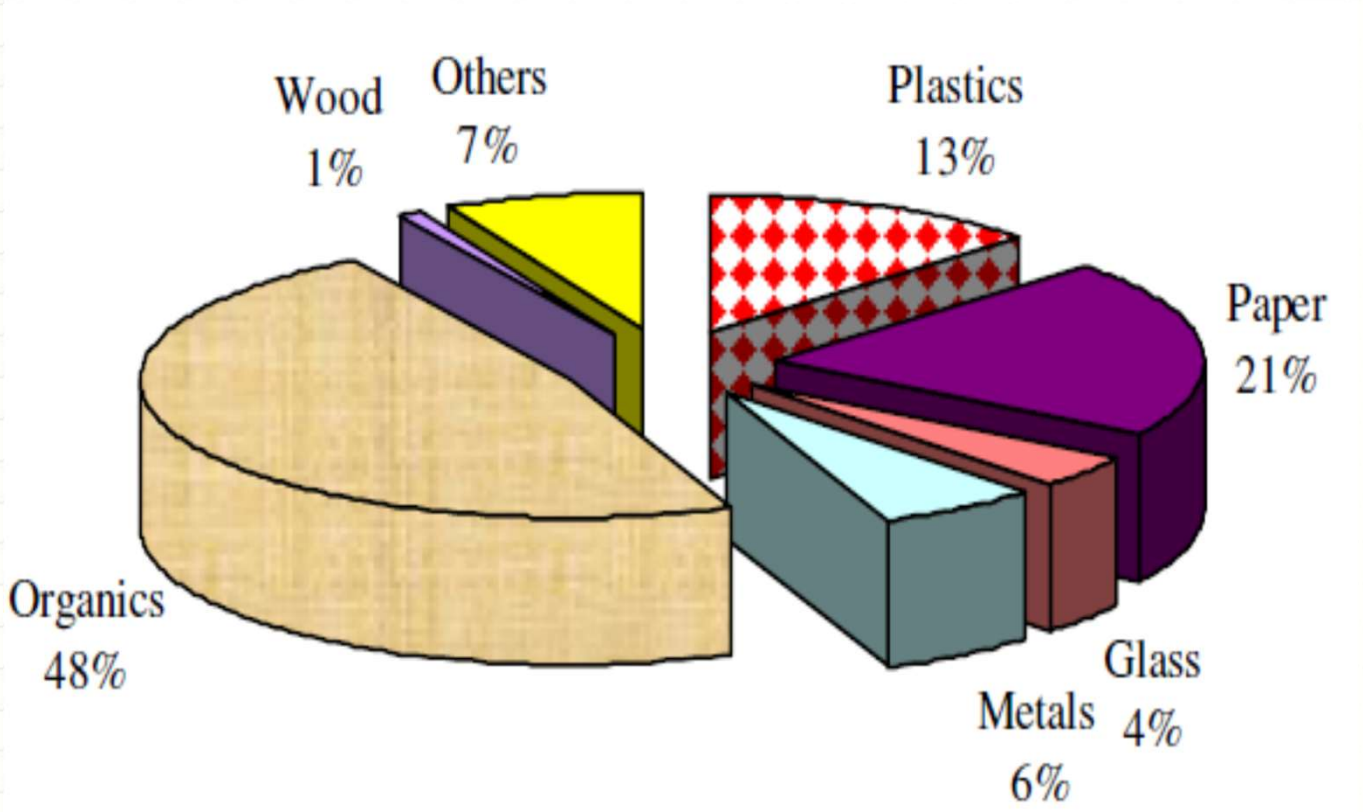
Mode of Polymerization; Solid Waste Produced in KSA

Composition of municipal solid waste produced in KSA

S #	Waste Categories	Fraction (%)	Components
1	Organic materials	65.5	Food waste and paper materials
	Food Waste	37.0	Food stuff, fruits and vegetable refuse, peel etc.
	Paper	28.5	Wasted Papers, cardboard, box board, bags, magazines, tissue papers, newspapers, toilet papers,
2	Plastics	5.2	Disposable glass, spoons, plates, wrapping films, wrapping film, bags, plastic bottles and polythene
3	Glass	4.6	Bottles, glassware, bulbs, ceramics etc.
4	Wood	8.0	All products comprised of wood
5	Textile	6.4	Cloths, dippers etc.
6	Metals/minerals	8.3	Cans, knives, wires bottles , aluminum cans, foils
7	Others	2.0	Leathers, rubber, fibers, rubber, yard waste, soils, tyres, appliances and electronics and appliances

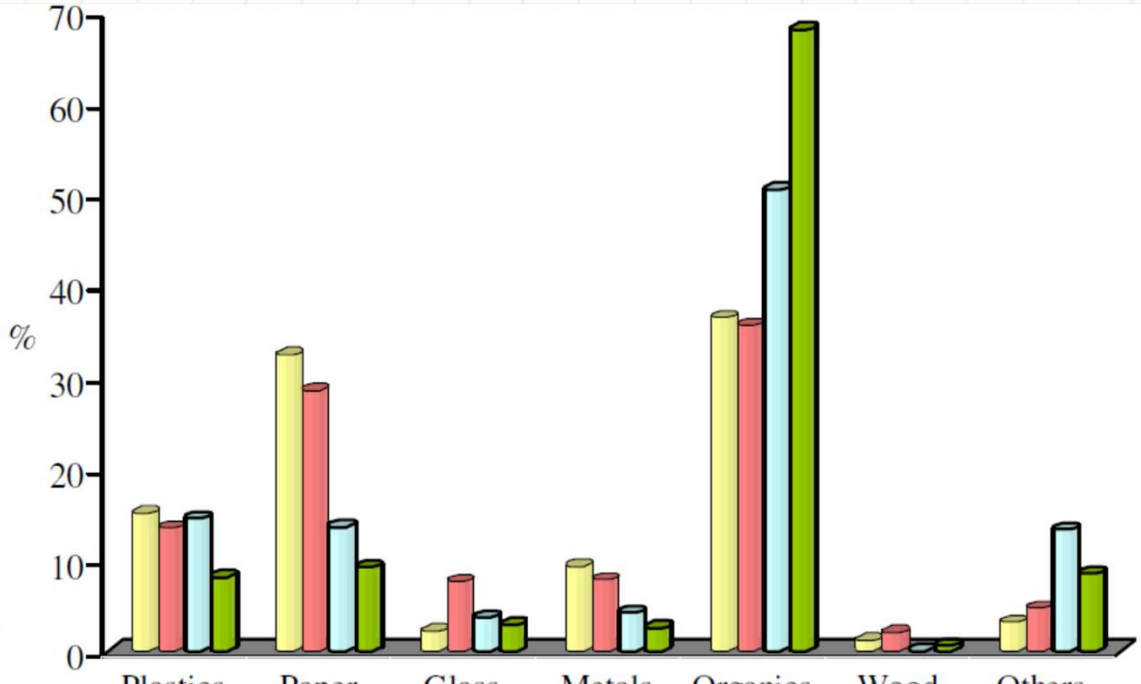
Mode of Polymerization; Solid Waste Produced in KSA

Abundances of household solid wastes in Jeddah city (average value of 400 samples



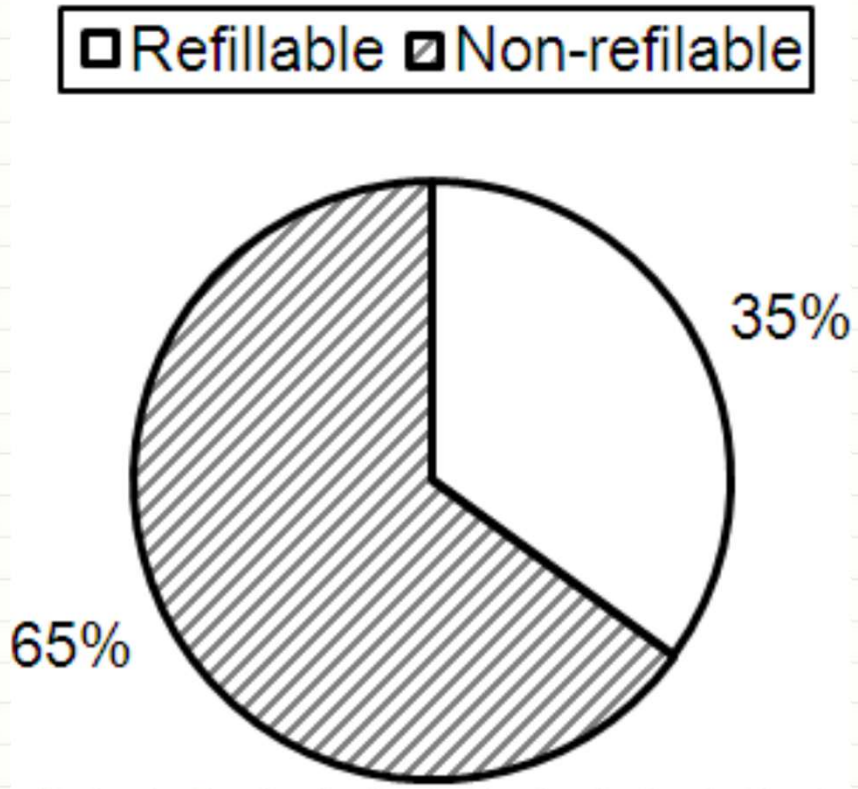
Mode of Polymerization; Solid Waste Produced in KSA

Because of differences in density population, life-style and economic level; Jeddah city was divided into four sampling zones:
N: north sampling zone;
CN: central north sampling zone;
CS: central south sampling zone;
S: south sampling zone

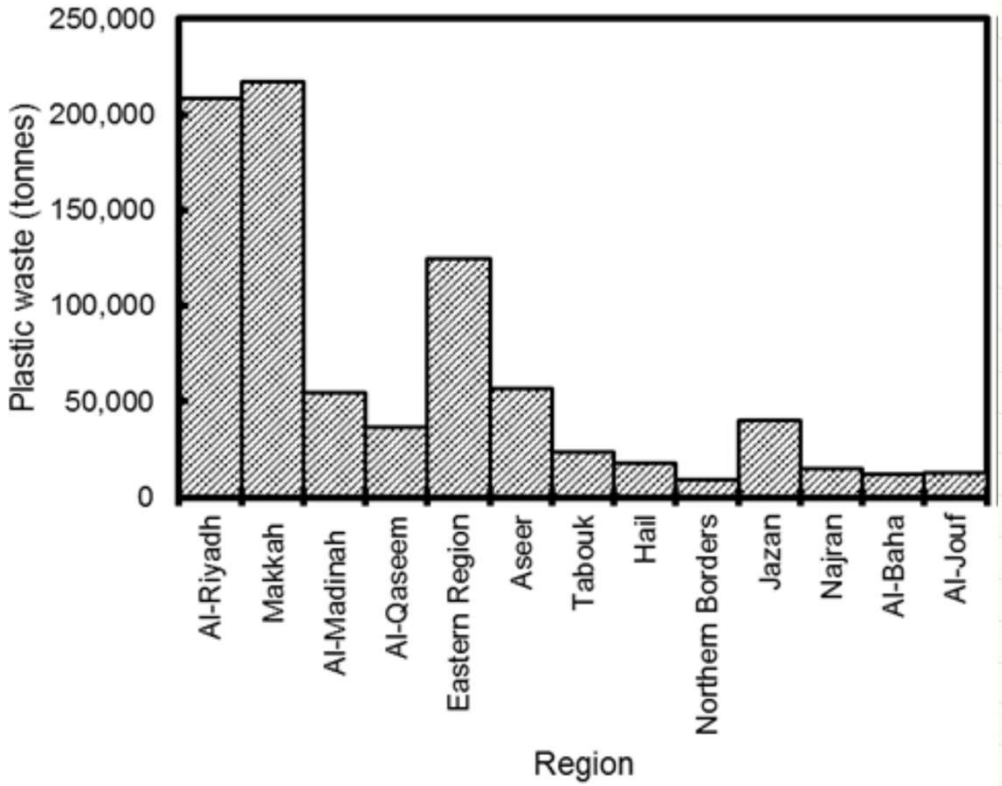


	Plastics	Paper	Glass	Metals	Organics	Wood	Others
N	15.1	32.5	2.2	9.3	36.5	1.2	3.2
CN	13.48	28.56	7.64	7.79	35.72	2.06	4.75
CS	14.57	13.62	3.73	4.22	50.56	0.02	13.28
S	8.09	9.19	2.91	2.56	68.08	0.61	8.56

Mode of Polymerization; Consumption of Bottled Waters in KSA



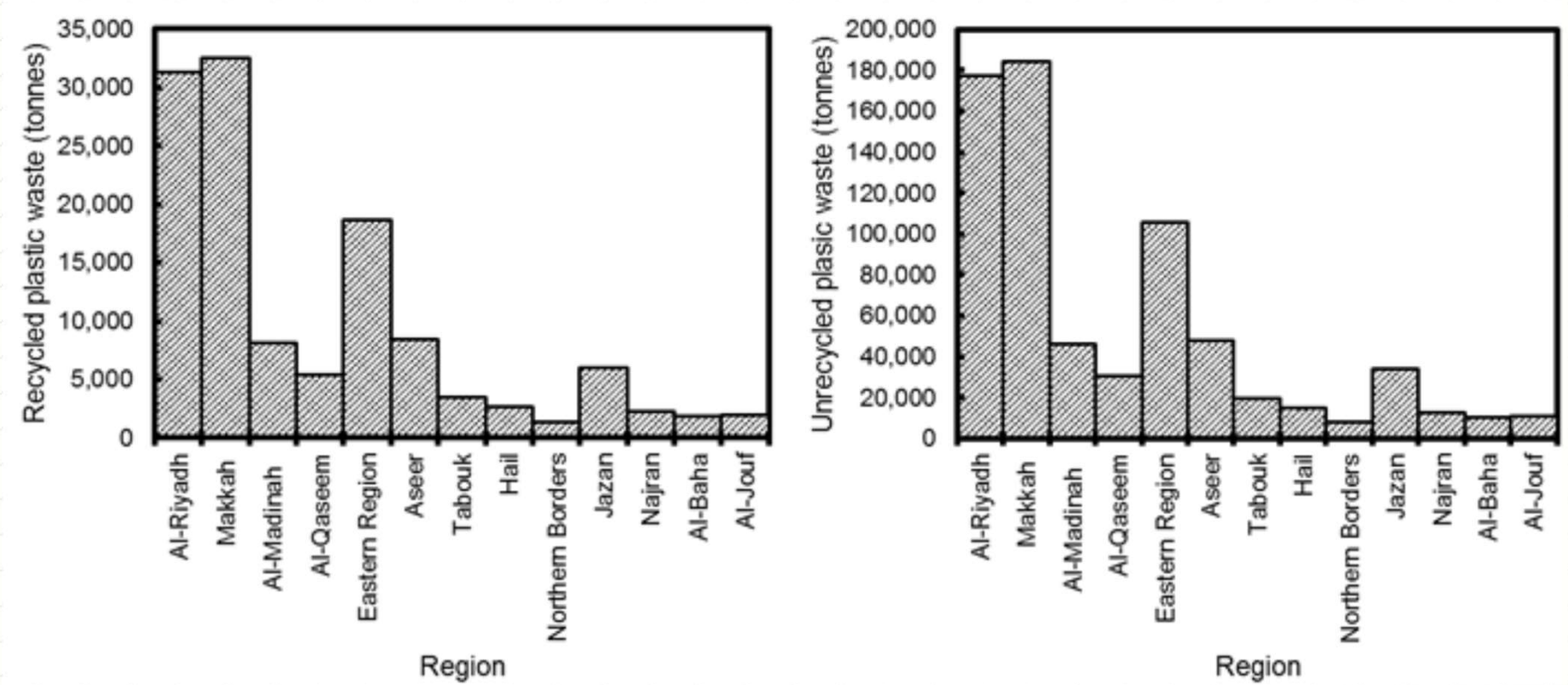
Percentage of plastic bottle consumption.



Region wise annually plastic bottle production in KSA.

Mode of Polymerization; Consumption of Bottled Waters in KSA

Region-wise recycled and unrecycled plastic waste production per year.



THANK YOU