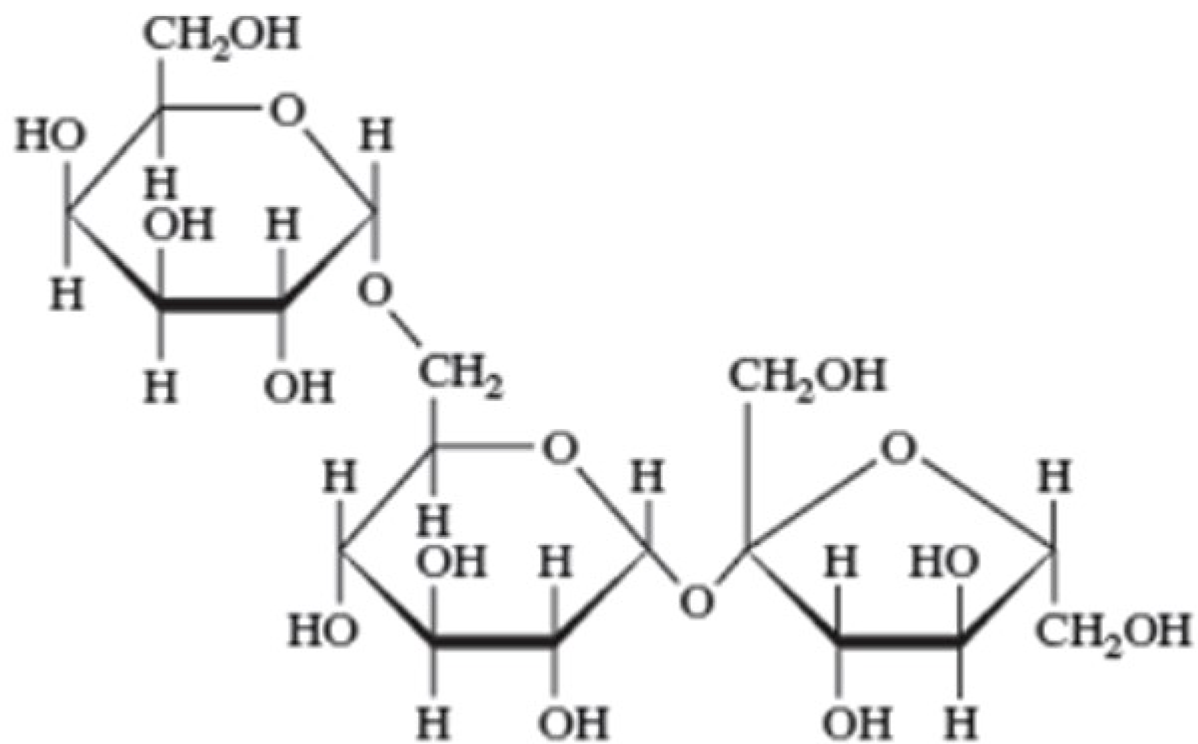
Chapter

POLYMER

Sinha Sir ,Kota

1. Find the monosaccharide present in each



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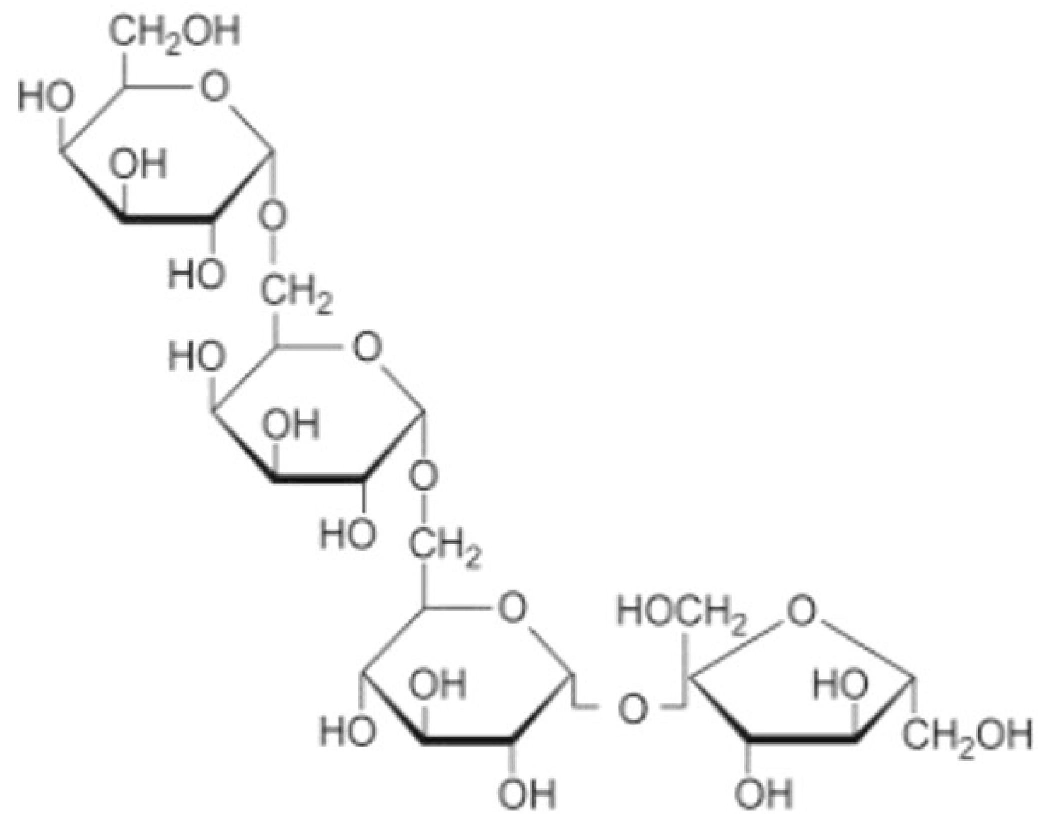

,Kota

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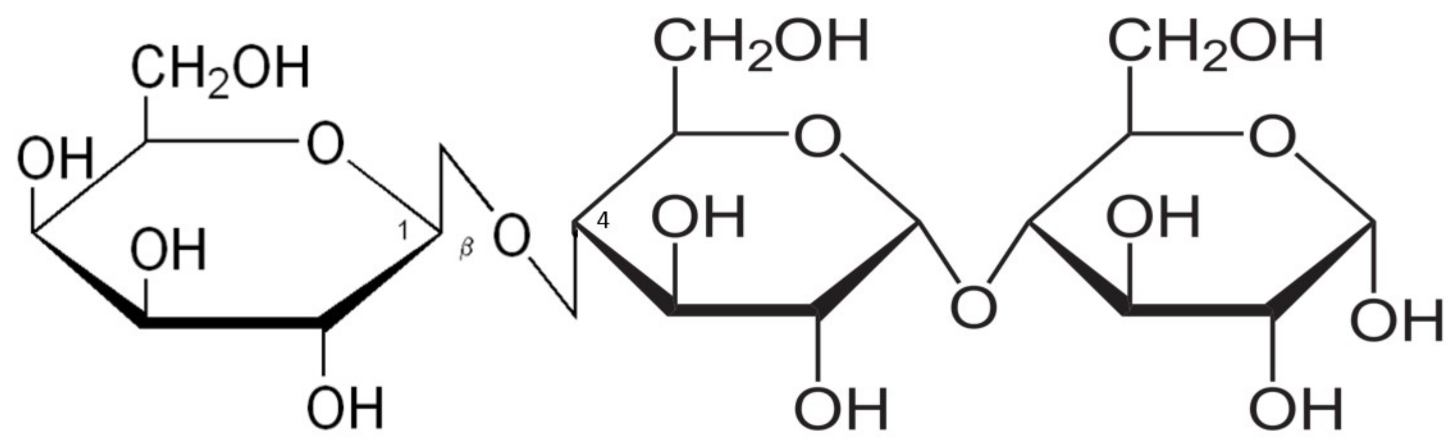
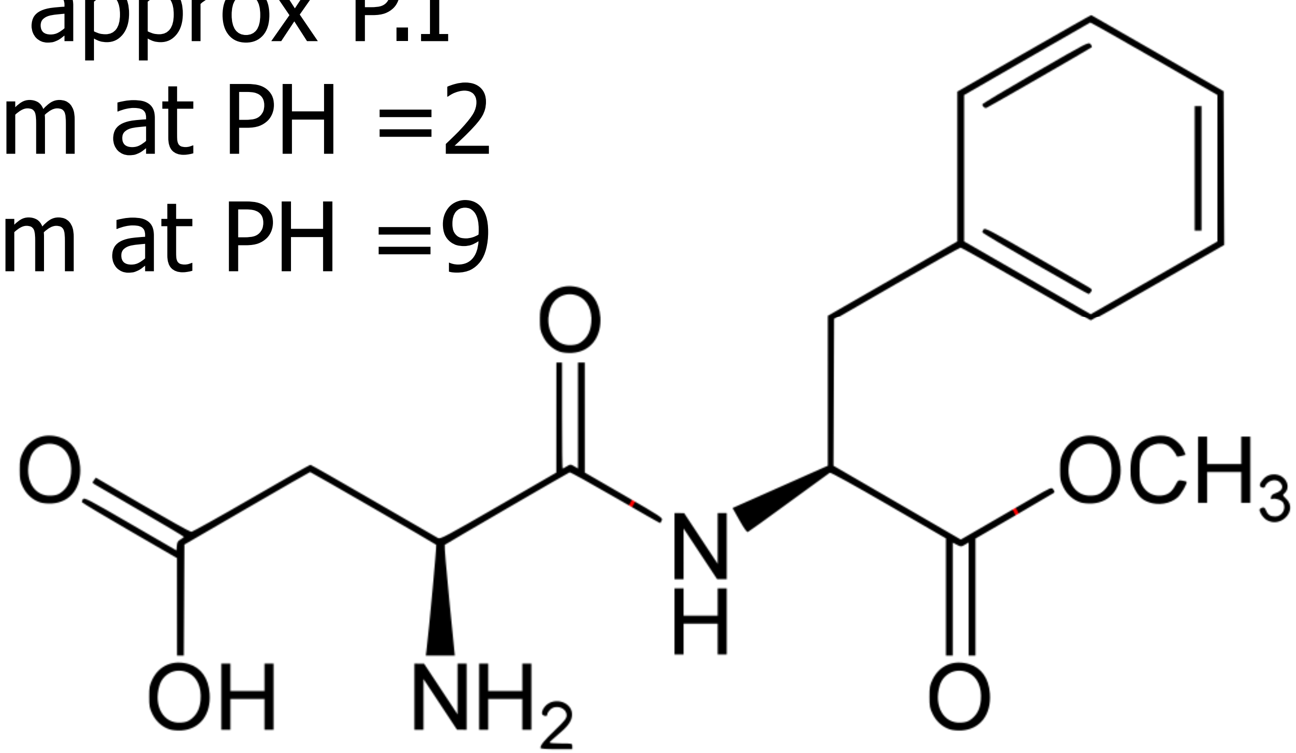


ɔta

1. Name the A.A present
2. Calculate approx P.I
3. Major form at PH =2
4. Major form at PH =9

Aspartane



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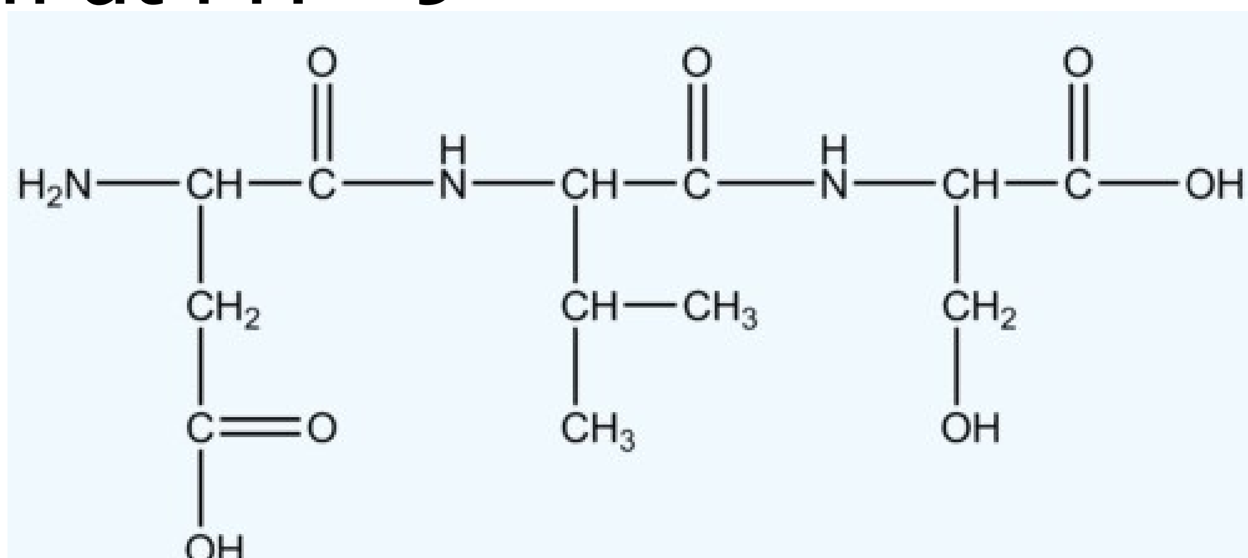

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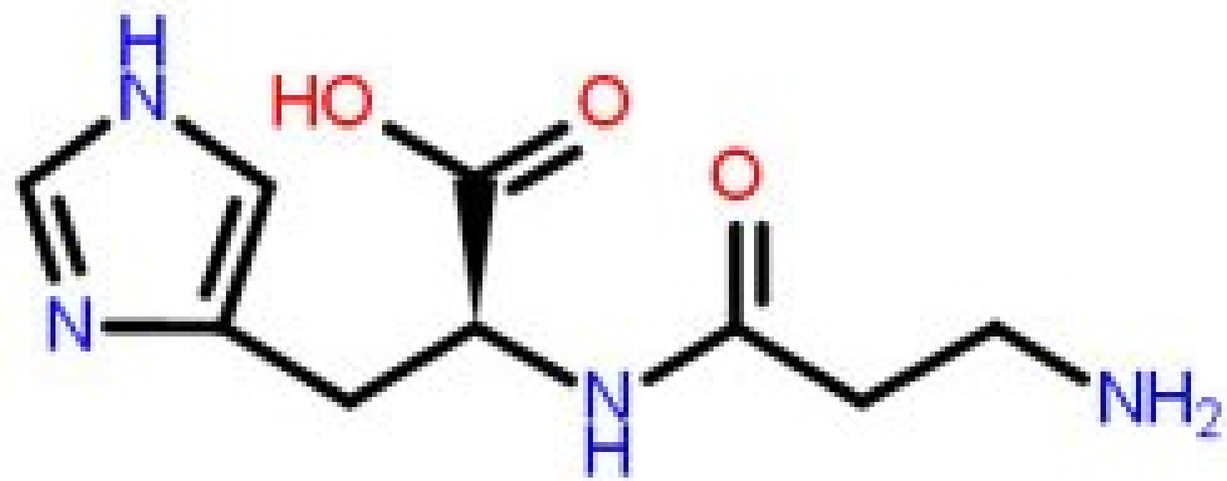

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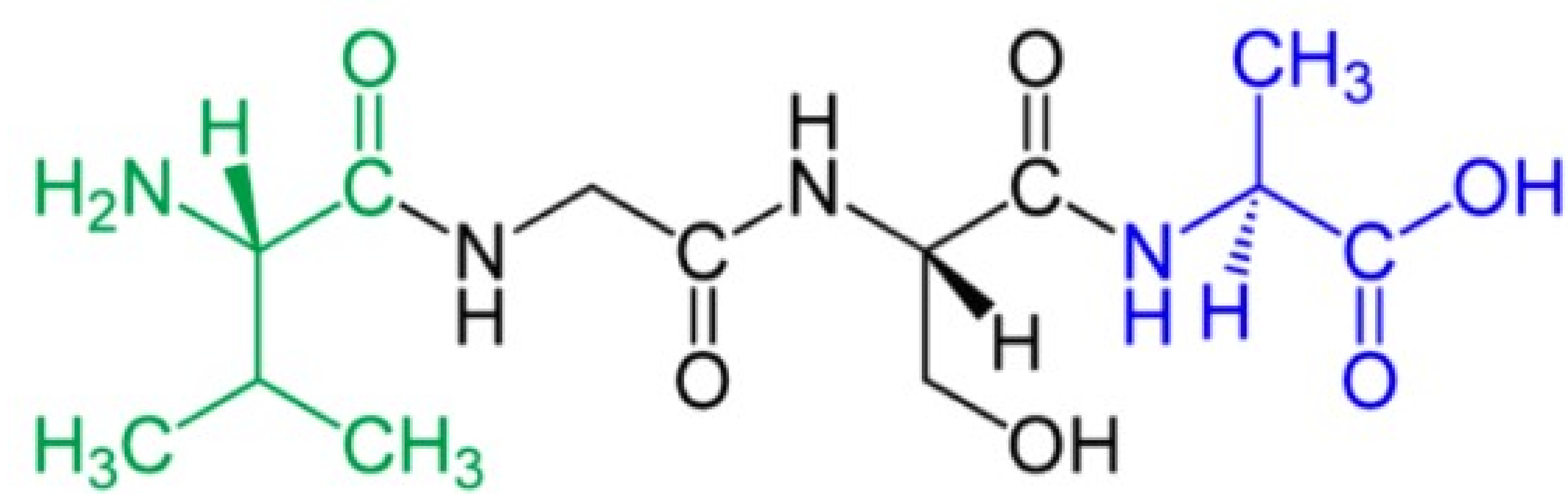

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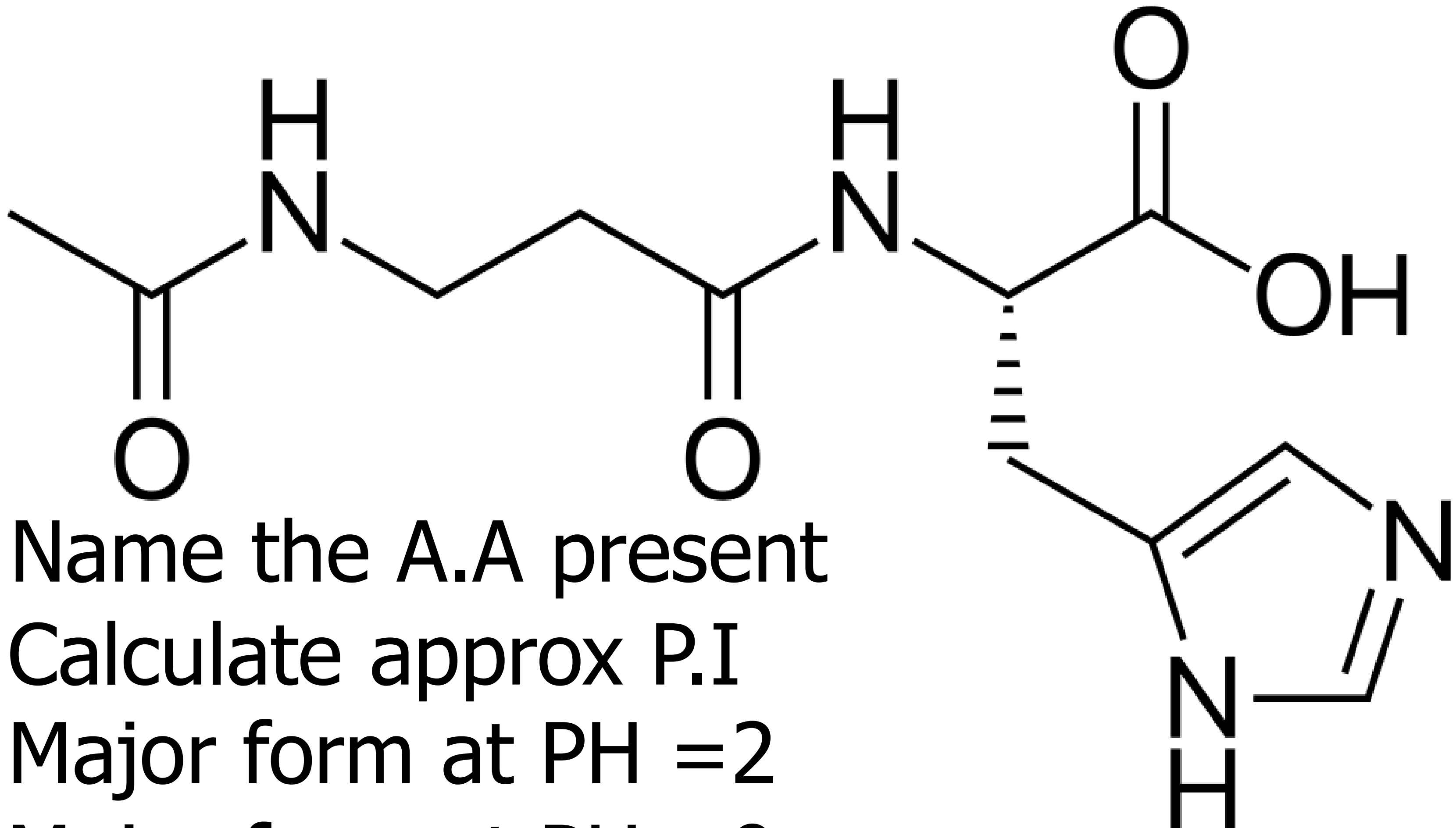

1. Name the A.A present
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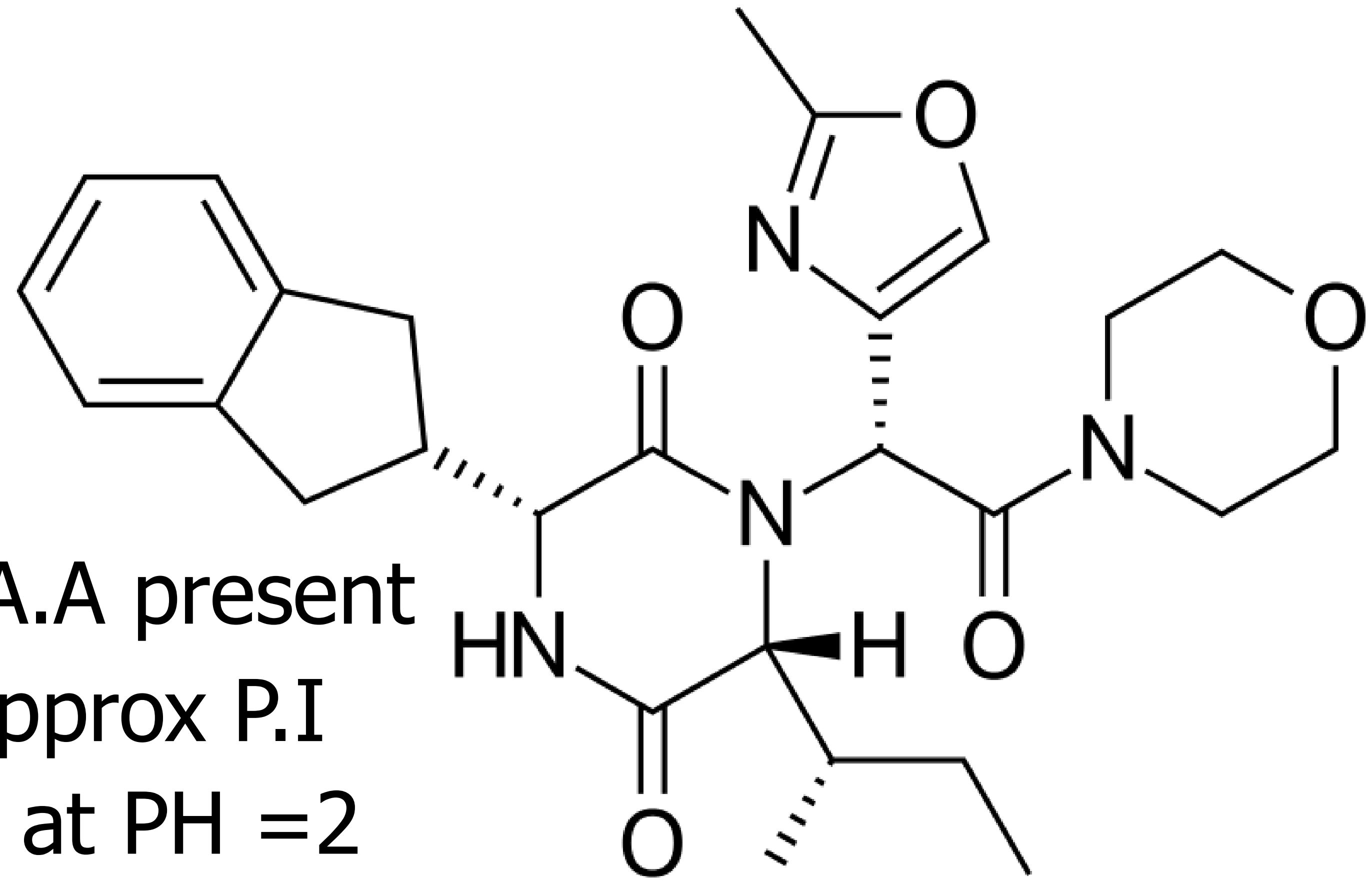
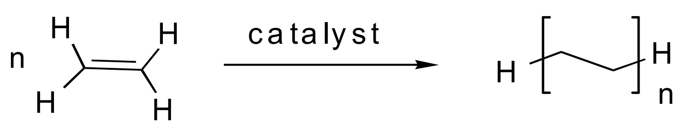


1. Name the A.A present
2. Calculate approx P.I
3. Major form at PH =2
4. Major form at PH =9

What are polymers?

Poly = many & meros = parts (Greek)

Macromolecules = large molecules



ethylene

polyethylene

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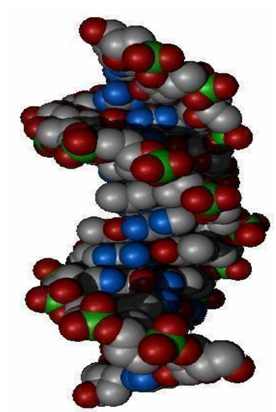
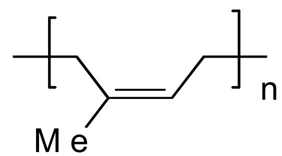
Origins: Two Families of Polymers

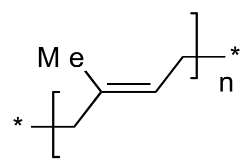
Biological Polymers



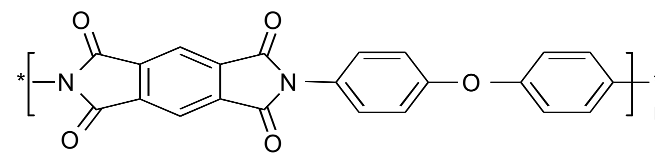
Synthetic



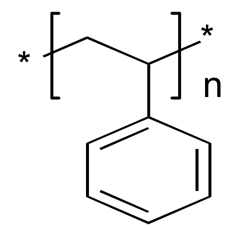
latex rubber



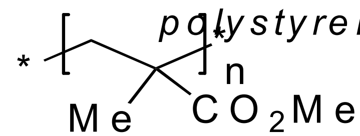
gutta percha



polyimide (PI)



polystyrene



polymethylmethacrylate (PMMA)

Physical Behavior & Architecture

- Thermoplastics

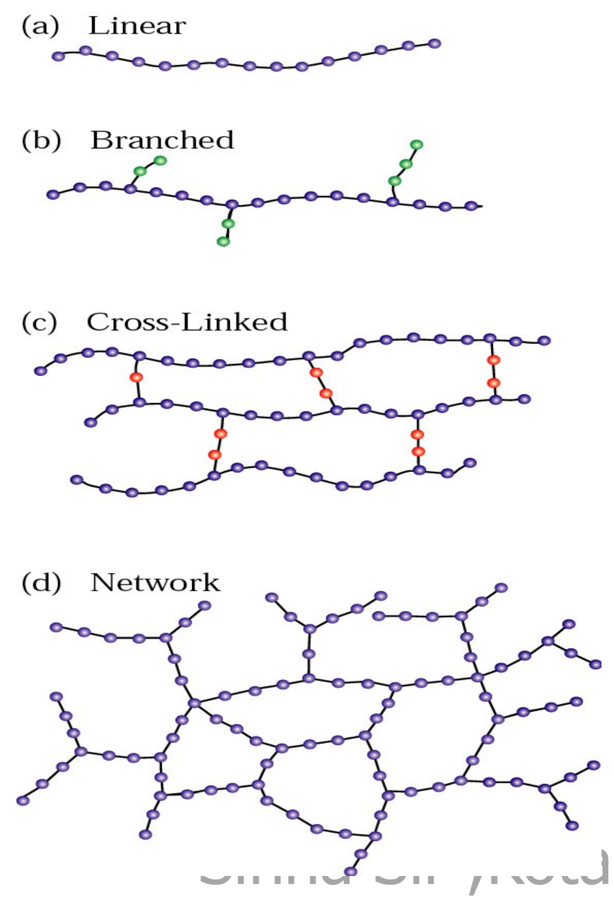
Polystyrene
Polyvinylchloride

- Elastomers

Synthetic rubbers
Poly-cis-isoprene

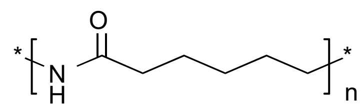
- Thermosets

Phenolic Resins
Melamines
epoxies

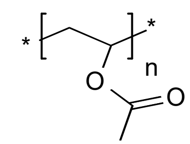


Applications/Function

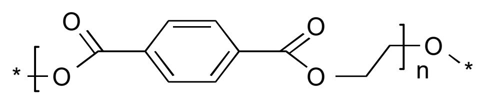
- Structural
- Coatings
- Fibers
- Adhesives



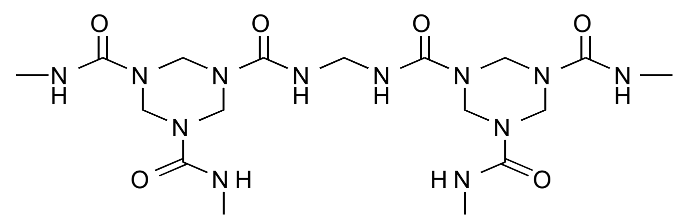
Nylon-6



Poly(vinyl acetate) or PVA



Poly(ethylene terephthalate) or PETE



Urea-Formaldehyde

Taxonomy by polymerization mechanism

Chain Growth Mechanism

- Free radical
- Anionic
- Cationic

Step growth

- Condensation

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Polymer Functionality

Vinyl Polymers

Polyethers

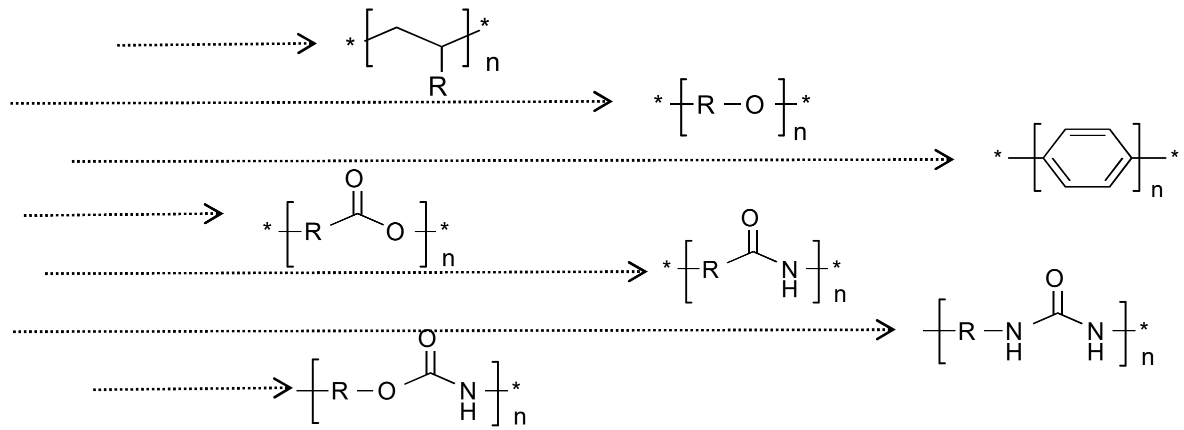
Polyarylenes

Polyesters

Polyamides

Polyureas

Polyurethanes



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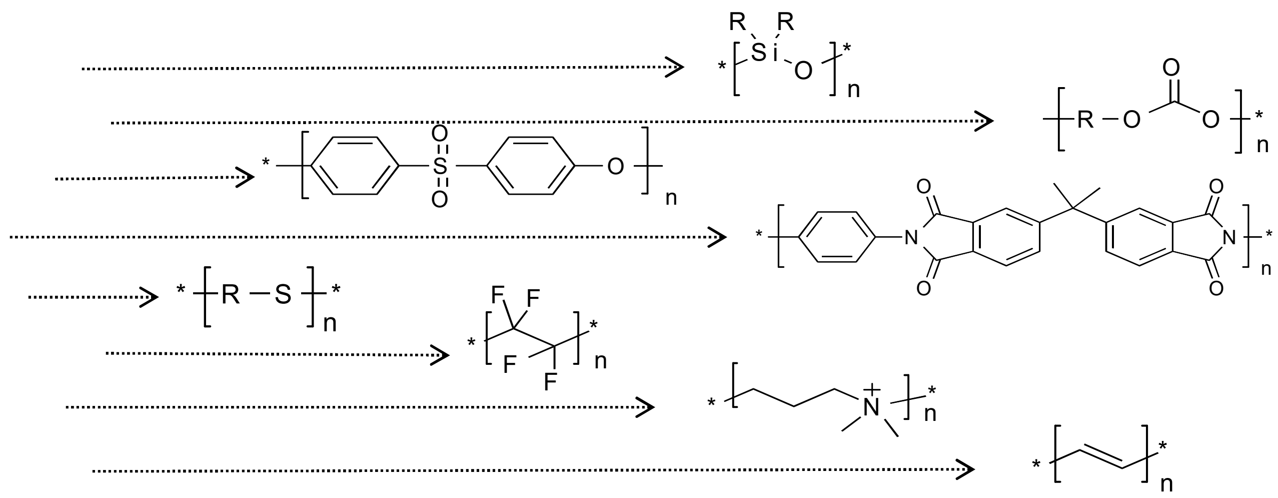
Polymer Functionality

Polysiloxanes
Polycarbonates
Polysulfones
Polyimides
Polysulfides
Fluoropolymers
Polyionomers
Polyacetylenes



Some Definitions

Plastic: A polymer that can be molded when hot and retains its shape when cooled.

THERMOPLASTICS

1. Set & Reset
2. Recycling
3. common in Additions Polymer

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THERMOPLASTICS

Thermoplastics can be softened or melted by heat and reformed (molded) into another shape.

Most addition polymers are thermoplastics.

The polymer chains are held together by weak interactions (noncovalent bonds) such as :

van der Waal's forces,
London dispersion forces and
Dipole-dipole attractions.

THERMOSET PLASTICS

Thermoset plastics : Once set set for ever. Can’t be recycled

Once formed, thermoset plastics cannot be remolded.

On heat get cross linked
Property of Condensation Polymer

HIGH-DENSITY POLYMERS

Linear polymers with chains that can pack closely together. These polymers are often quite rigid.

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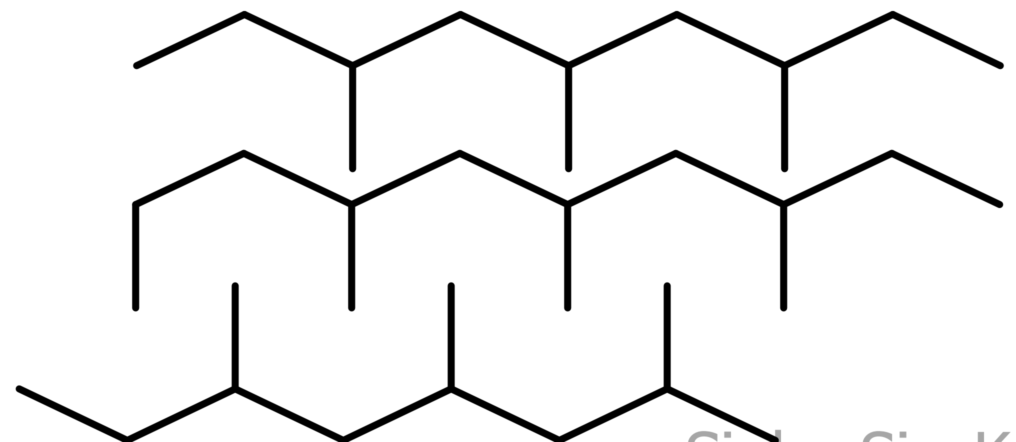
LOW-DENSITY POLYMERS

Branched-chain polymers that cannot pack together as closely.

There is often a degree of cross-linking.



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Homo & Co-Polymers

A polymer prepared from a single monomer is a *homopolymer: Polystyrene*

If two or more monomers are employed, the product is a *Copolymer: Nylon-6.6*

Linear polymer has no branching

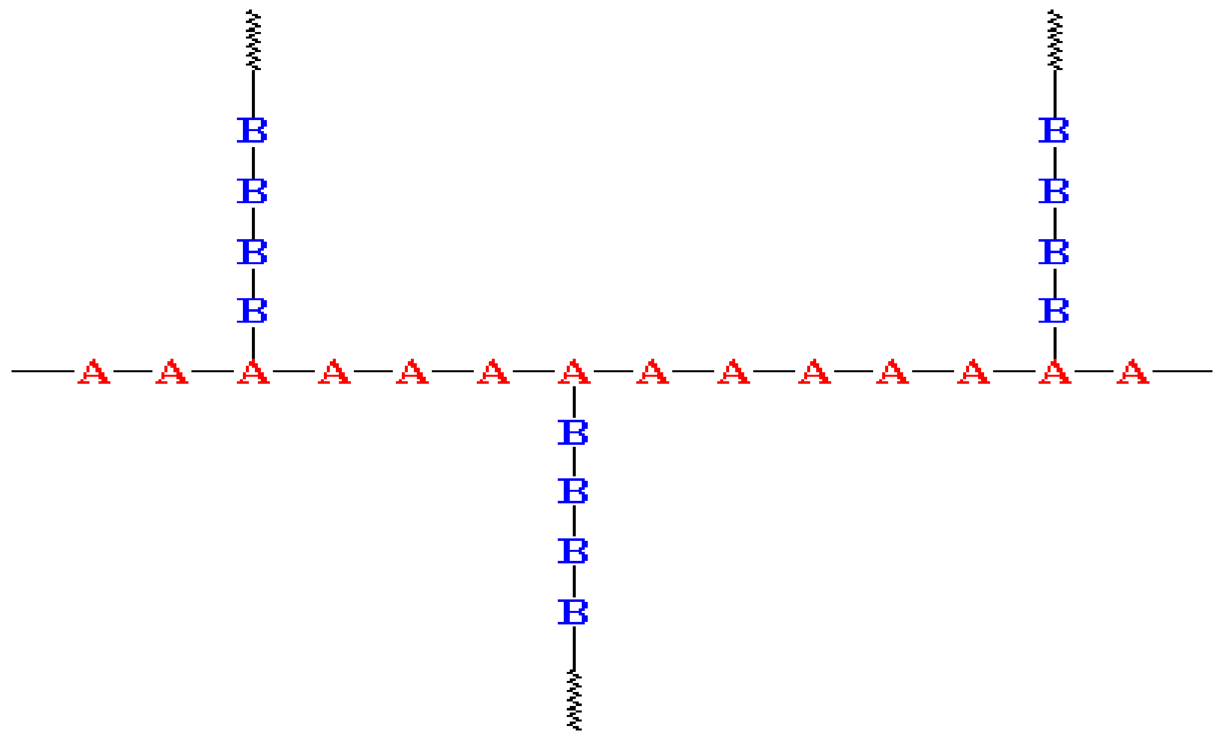
If two or more monomers are employed, the product is a *copolymer*

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—

alternating copolymer

—A—A—B—A—B—B—A—B—A—A—B—B—B—A—

random copolymer



graft copolymer

Graft copolymer is an example of a branched network

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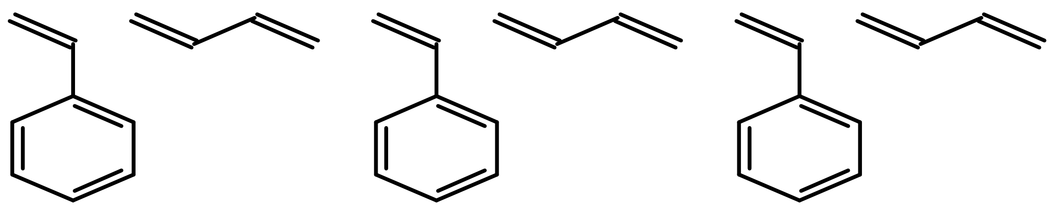
COPOLYMERS

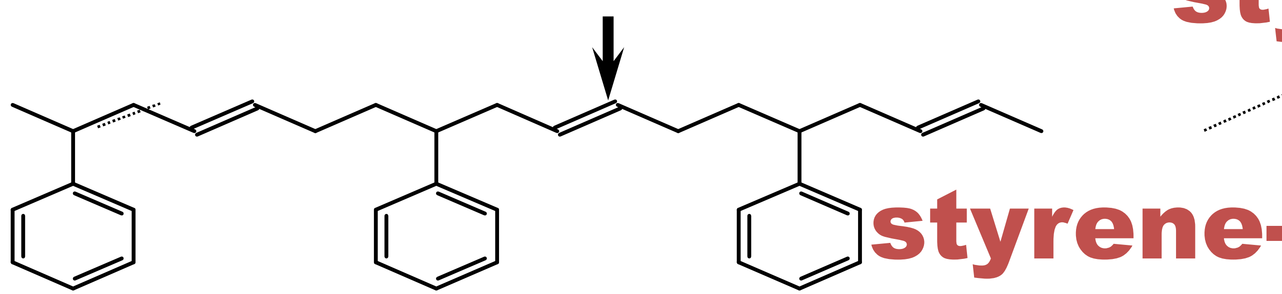
Polymers which are formed by combining two Different monomers in alternating fashion are called copolymers.

A + B + A + B ⟶ A – B – A – B



butadiene

styrene



styrene-butadiene rubber (SBR)

Two main classifications of Polymerization

Addition reaction or Chain growth:
Molecular weight increases by successively adding monomers to a reactive polymer chain end resulting in high molecular weights at low conversions.

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Two main classifications of Polymerization

STEP reaction or growth

Polymers are formed by linking monomer molecules to form dimers, trimers and higher species in a step-wise fashion. The most abundant species react, and thus high molecular weight formed only beyond 99% conversion.

ADDITION POLYMERS

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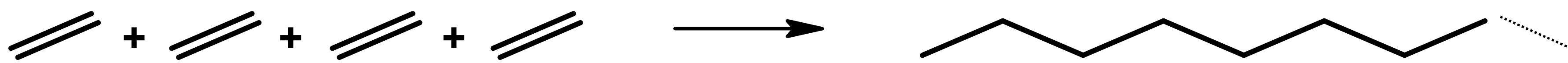
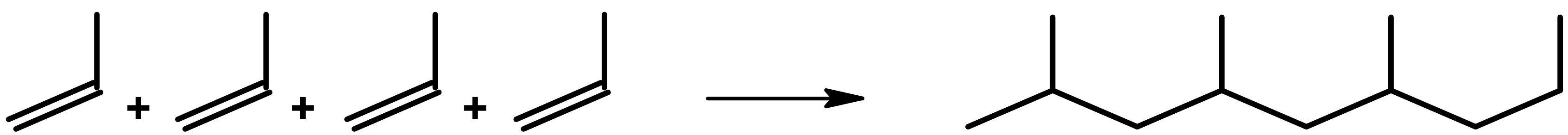
ADDITION POLYMERS

A + A + A + A ⟶ A– A– A– A

monomers　　　polymer



ethylene (ethene)　polyethylene linear



branched

propylene (propene) polypropylene

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PREPARATION OF ADDITION POLYMERS CATIONIC AND FREE-RADICAL PROCEDURES

MECHANISMS

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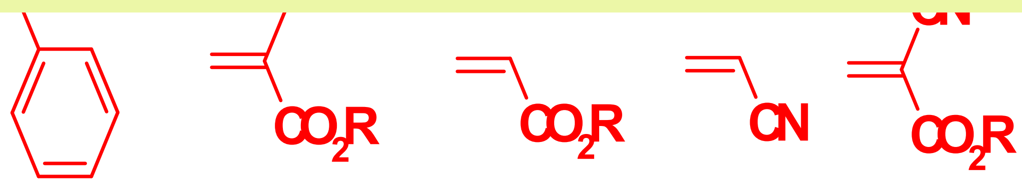
Ionic Chain (addition)-Growth Polymerization

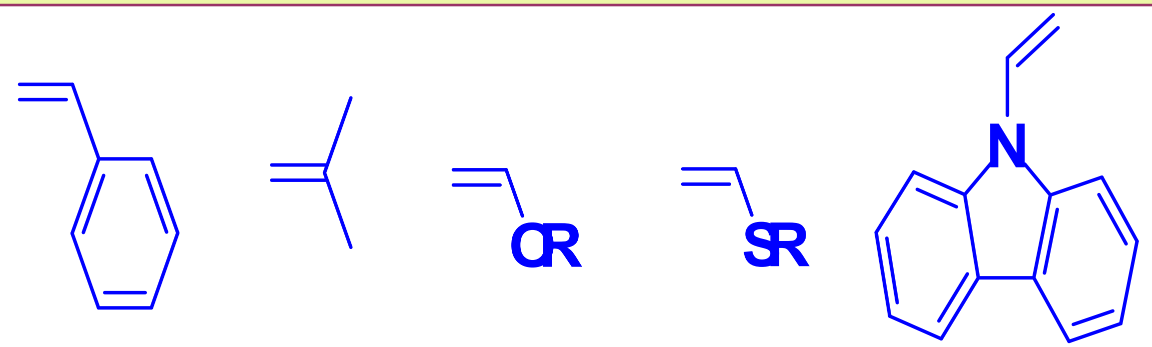
The choice of ionic procedure depends greatly on the electronic nature of the monomers to be polymerized

Vinyl monomers with electron-withdrawing groups



Anionic Polymerization

Ionic Chain (addition)-Growth Polymerization



Vinyl monomers with electron-donating groups

Cationic Polymerization

Monomers and reagents should be scrupulously purified; Polymerizations carried out at very low temperatures

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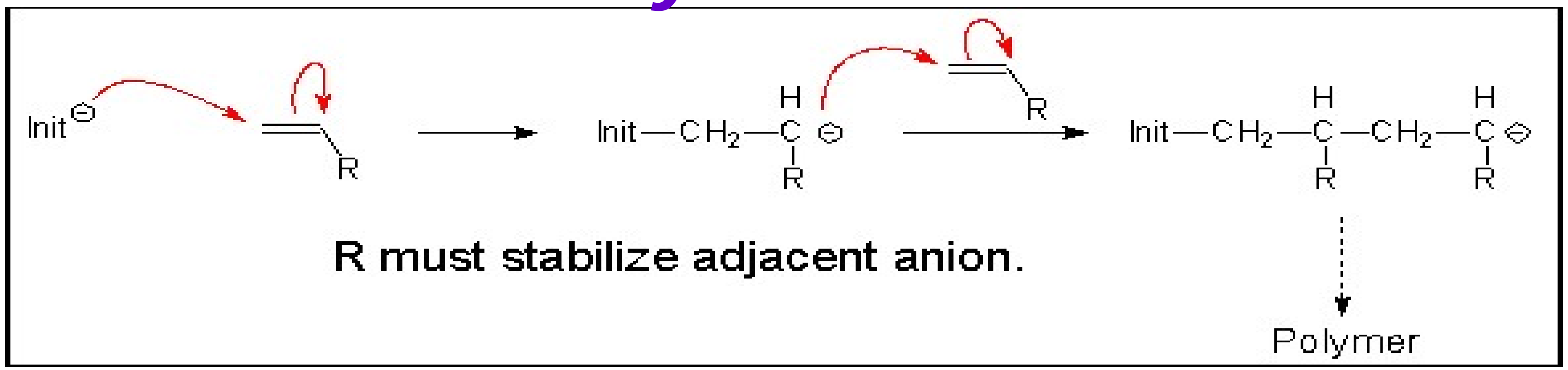
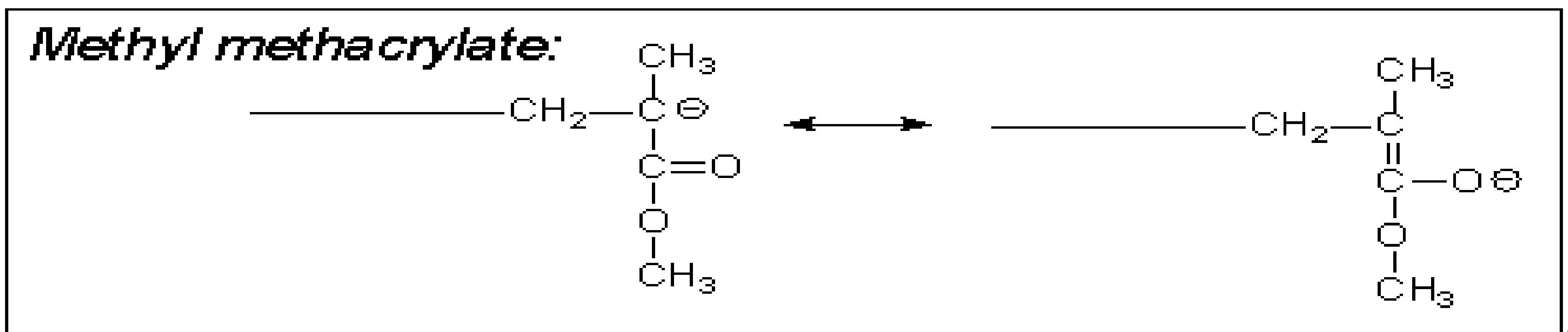
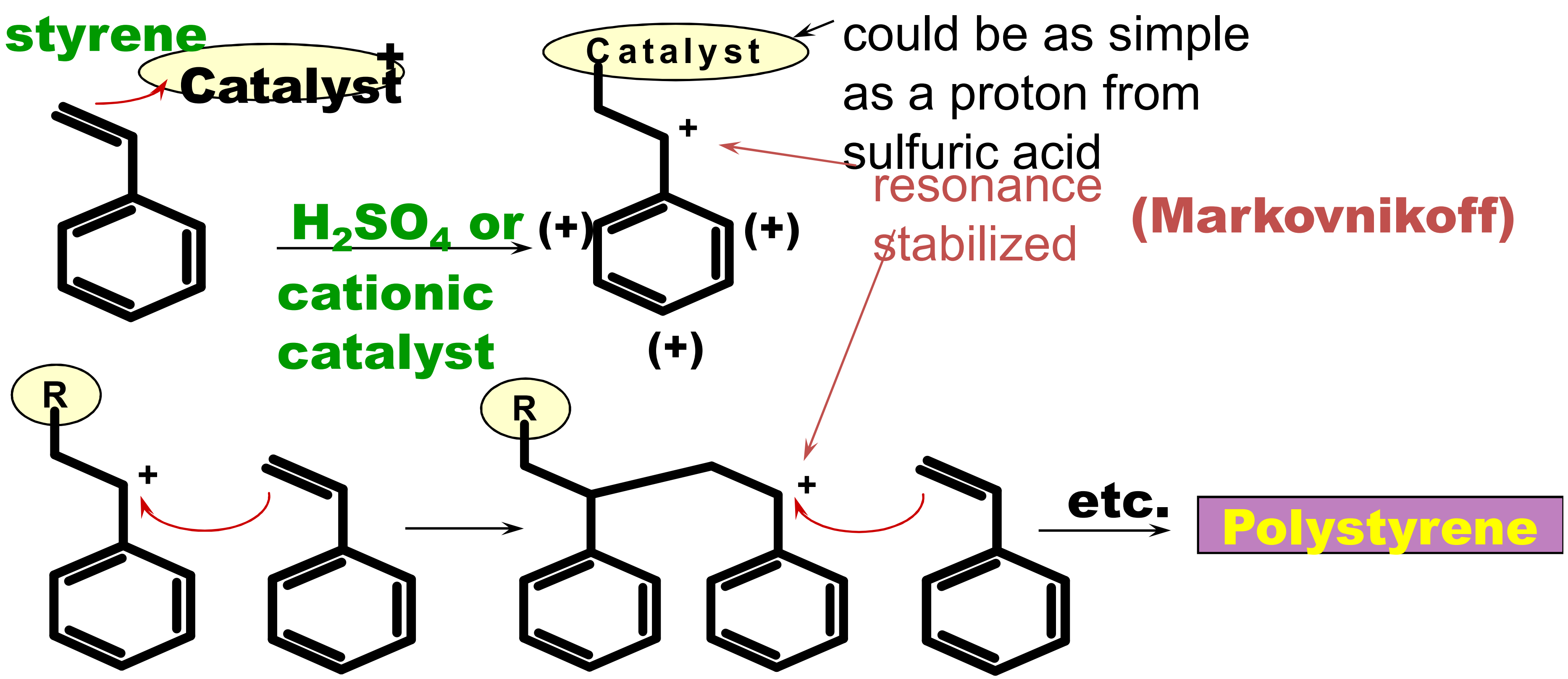
Anionic Polymerizations

Initiators include alkyl lithiums and sodium amide





CATIONIC MECHANISM



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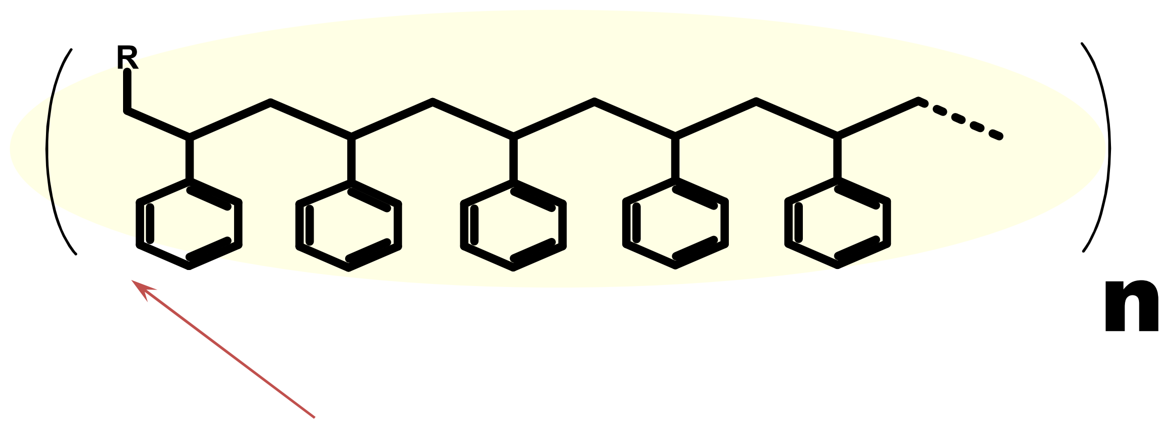
POLYSTYRENE



repeating unit

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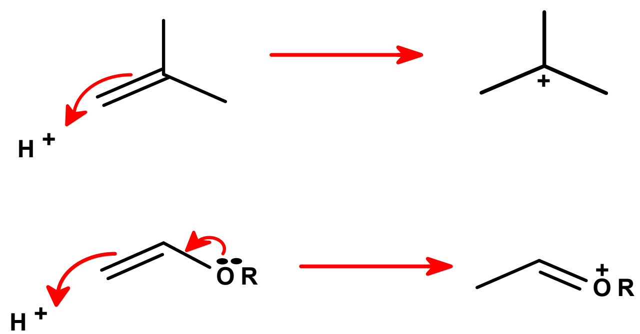
Cationic Polymerization

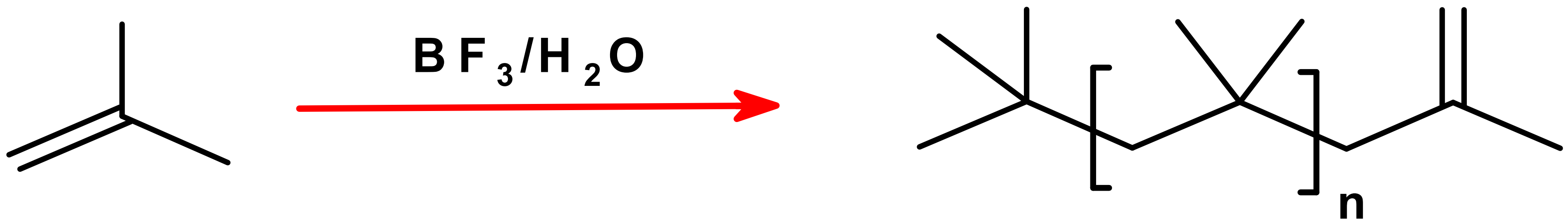
-- the formed carbocation must be quite stable



Stable tertiary carbocation

stable oxonium ion

E.g. proton initiates polymerization of isobutane (2-methylpropene)



Adhesive, sealant, insulating oil, lubricating oil

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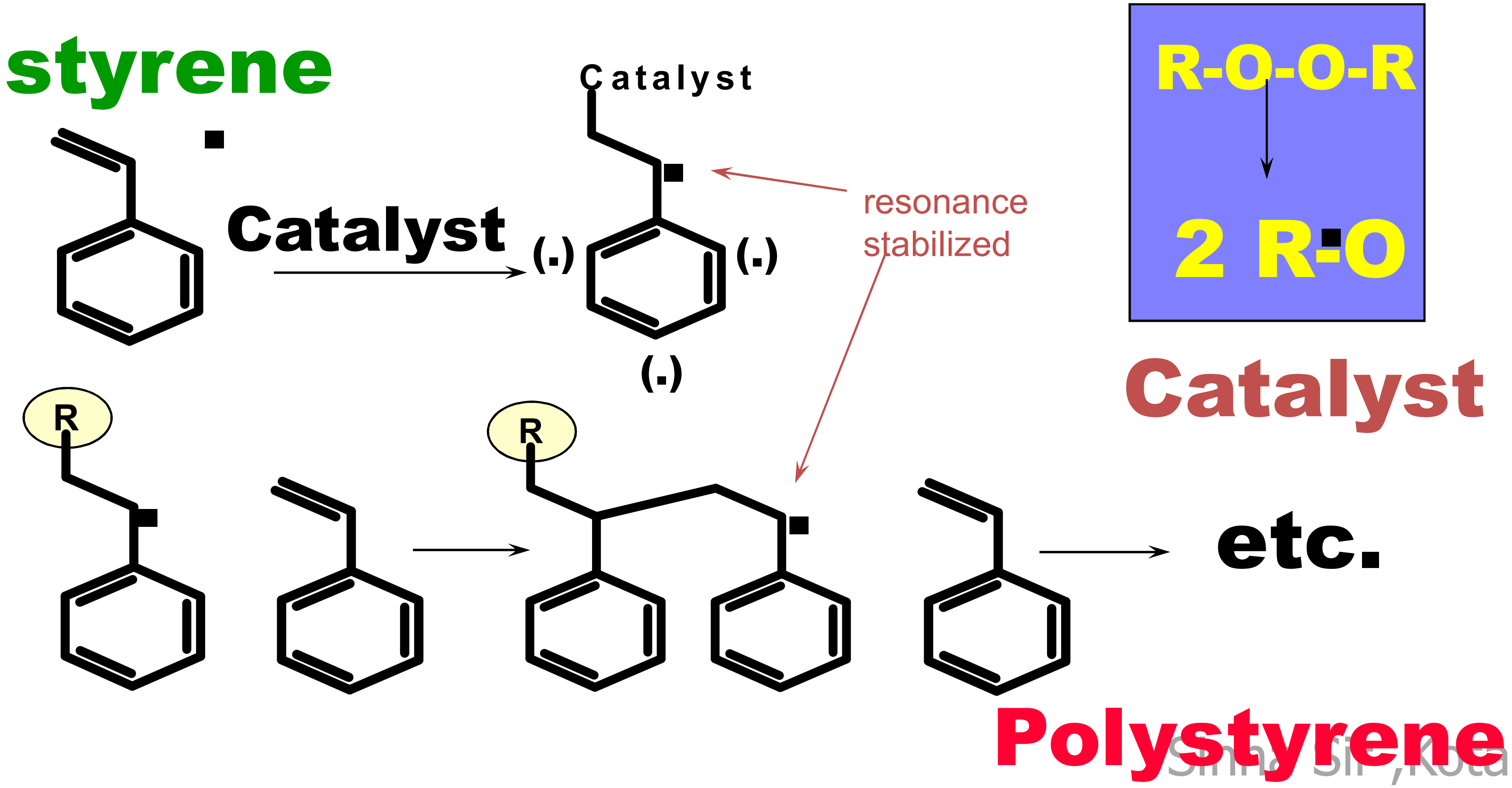
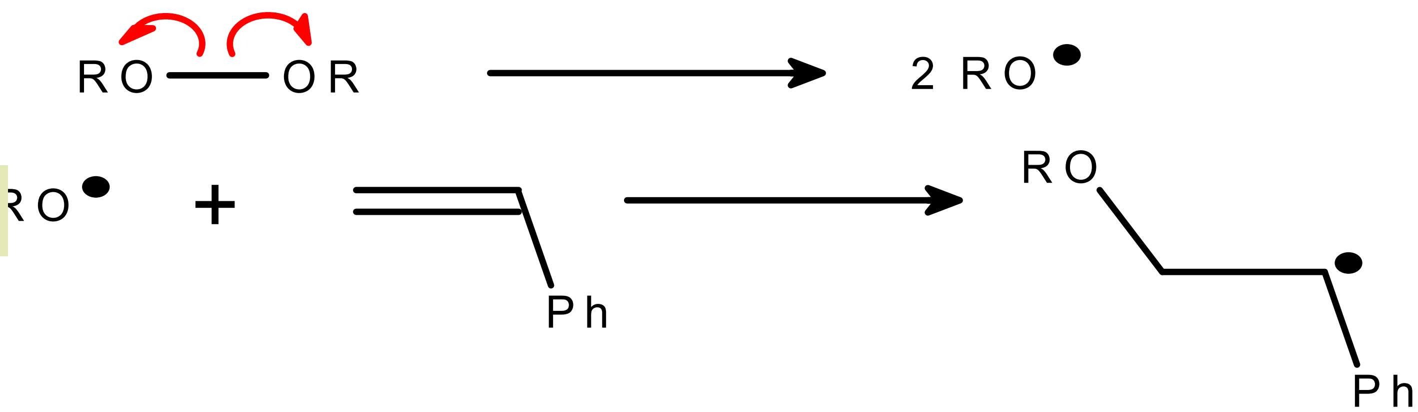
RADICAL MECHANISM

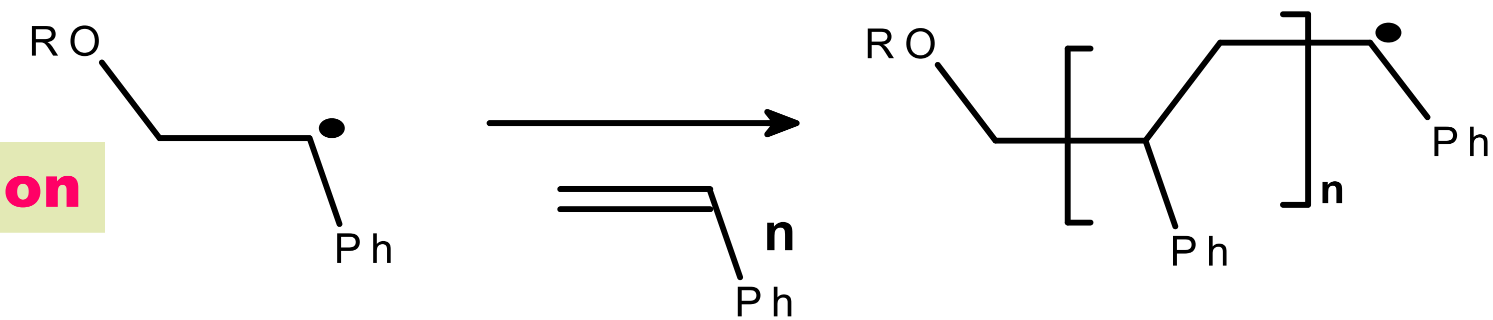


Chain Reaction: Free Radical Polymerization

Initiation



Propagation



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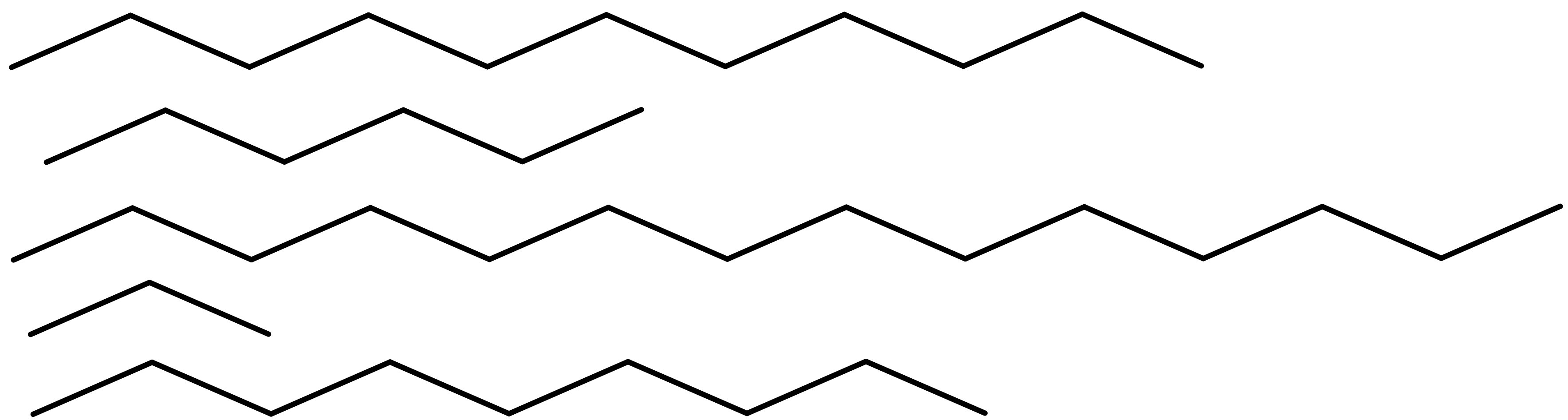
Random Termination



Dead chains

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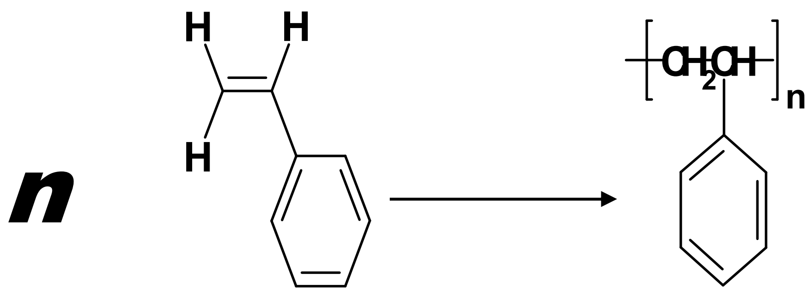
Examples of Polymers Prepared by Radical Polymerization

Monomer | **Polymer**



Poly(styrene)

Poly(acrylonitrile)

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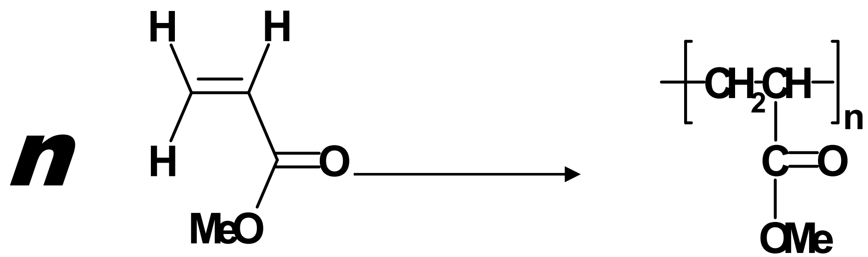
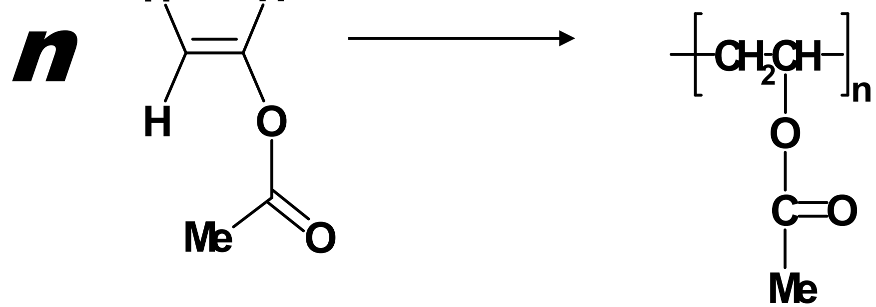
Poly(methylacrylate)

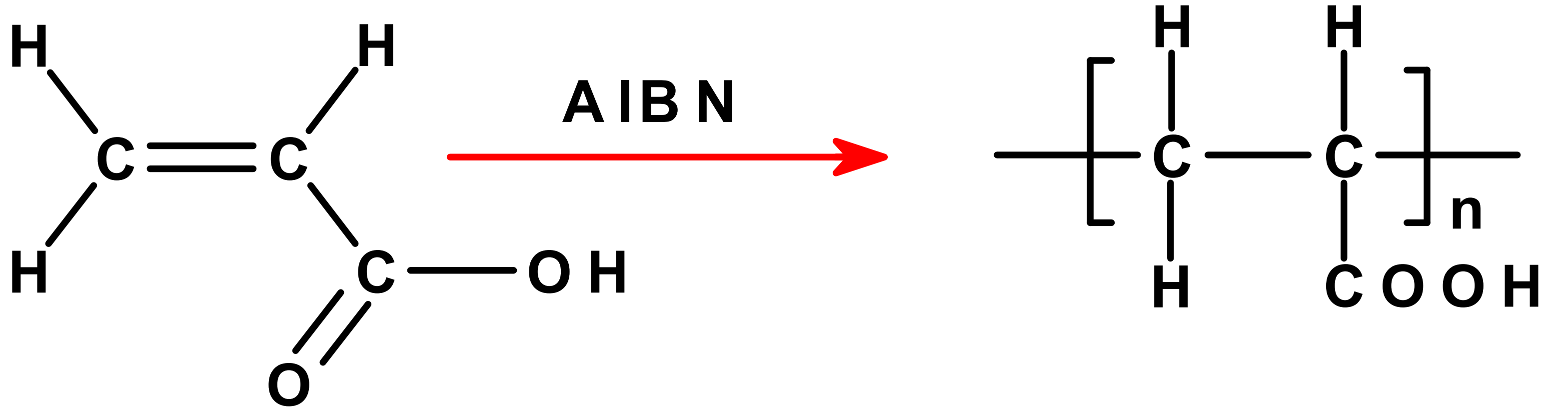


Poly(vinylacetate)



Ion-exchange resins, smart polymers

Some monomers can only be polymerized by radical means, e.g. acrylic acid (AA)



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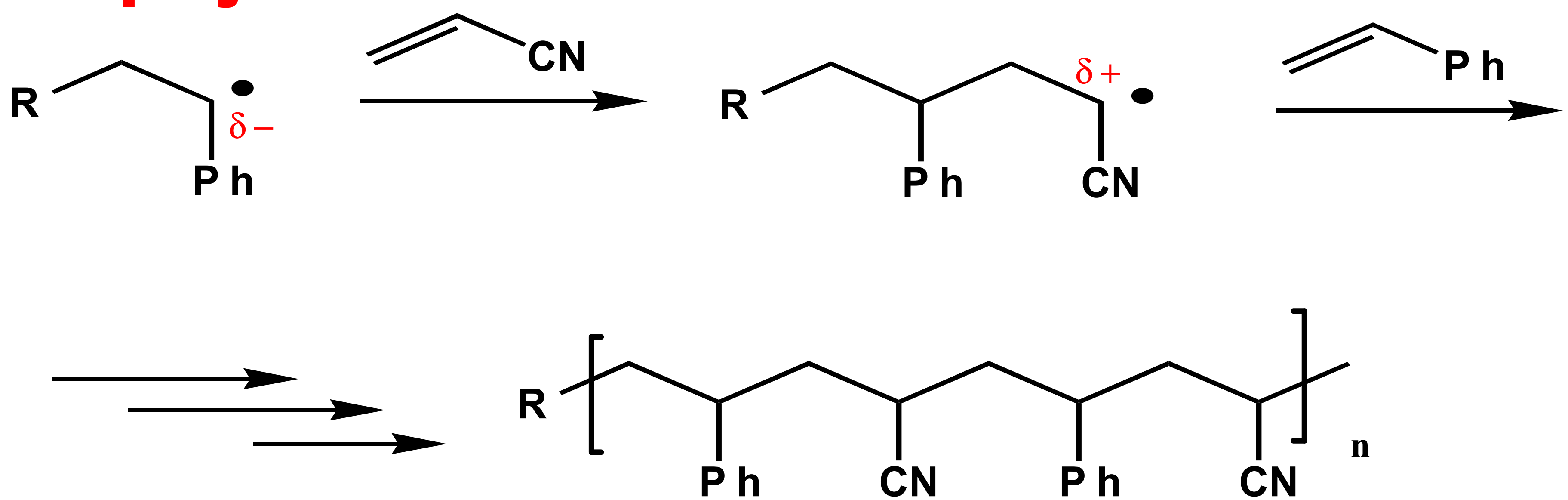
Radical Polarity

Polar Effects are important in radical polymerizations, and can give alternating copolymers



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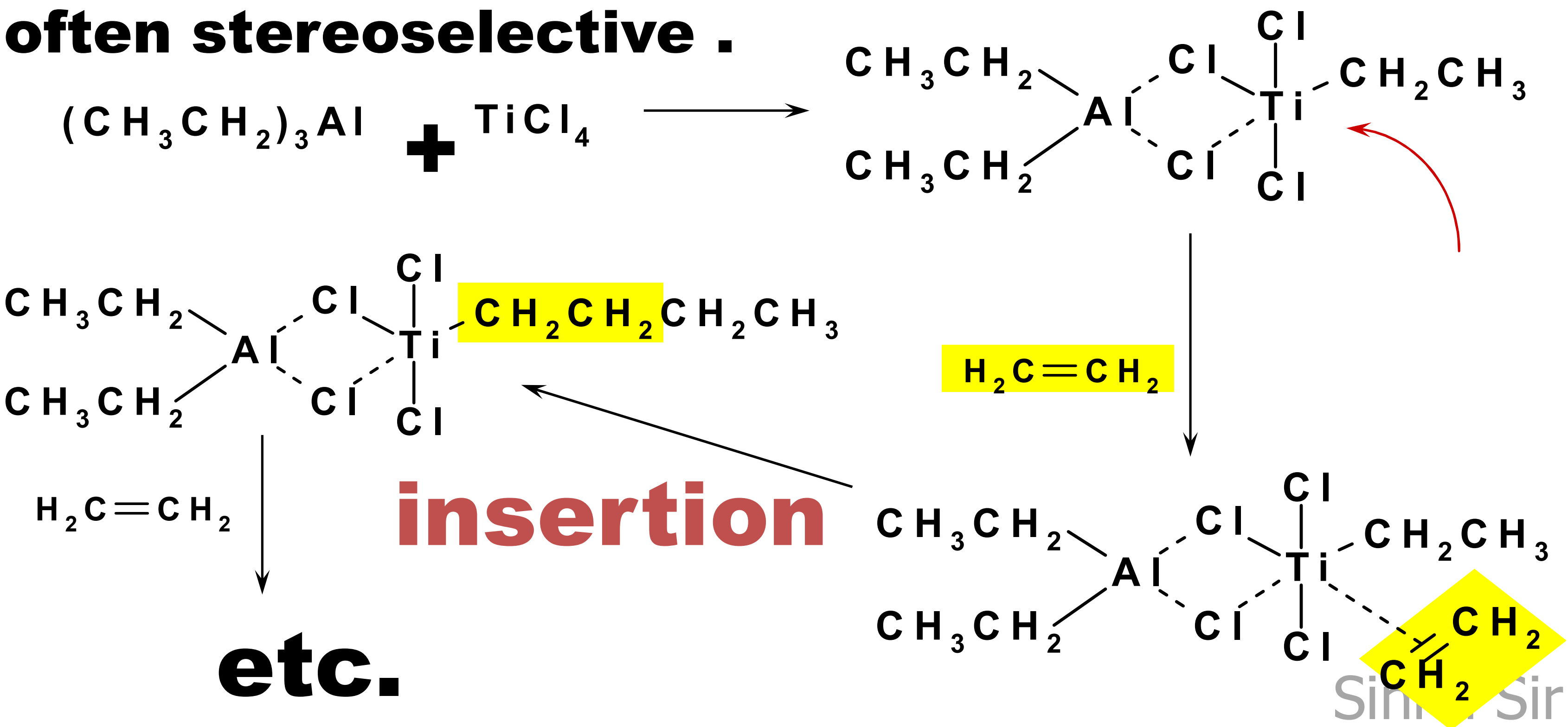
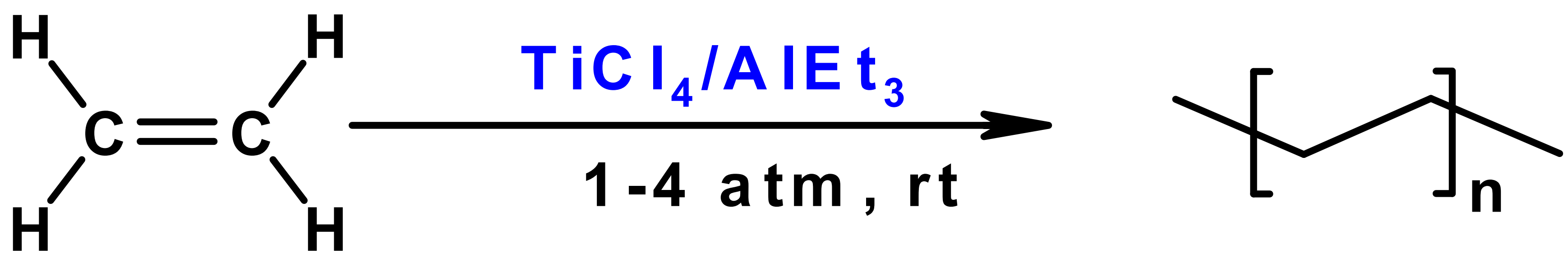
Ziegler-Natta Catalysts

Cationic, anionic or radical processes are not Involved and the polymerization is often stereoselective .



Ziegler-Natta Chain (Addition) Polymerization



Milder conditions than radical polymerization

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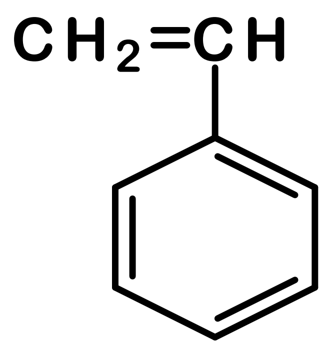
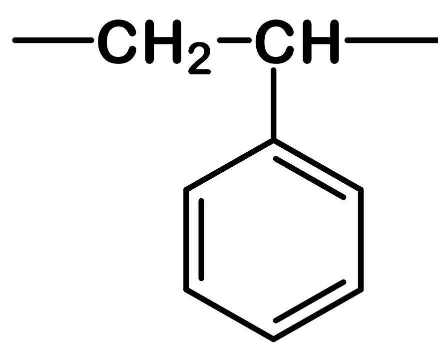
SOME COMMON ADDITION POLYMERS

example	monomer	polymer	uses
polyethylene	$CH_2=CH_2$	$-CH_2-CH_2-$	**most common polymer bags, wire insulation, squeeze bottles**
polypropylene	$CH_2=CH(CH_3)$	$-CH_2-CH(CH_3)-$	**fibers, bottles, indoor-outdoor carpet**
polystyrene			**styrofoam, inexpensive molded objects: household items toys**

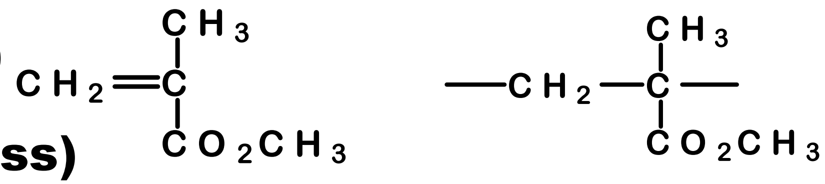
SOME COMMON ADDITION POLYMERS

polyvinyl chloride (PVC)	$CH_2{=}CH(Cl)$	$-CH_2-CH(Cl)-$	**synthetic leather, clear bottles, floor coverings, water pipe**
Teflon	$CF_2{=}CF_2$	$-CF_2-CF_2-$	**non-stick surfaces, chemically resistant items**
polyacrylonitrile (Orlon, Acrilan)	$CH_2{=}CH(C{\equiv}N)$	$-CH_2-CH(C{\equiv}N)-$	**fiber used in sweaters, blankets, carpets**

COMMON ADDITION POLYMERS (cont)

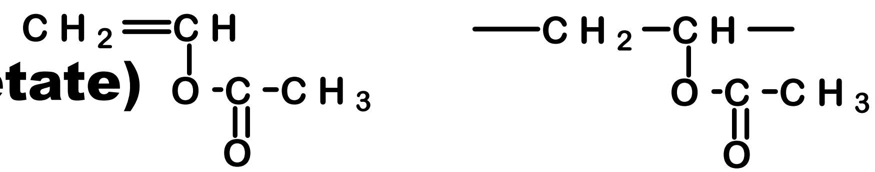
poly(methyl methacrylate)

(Lucite, Plexiglass)



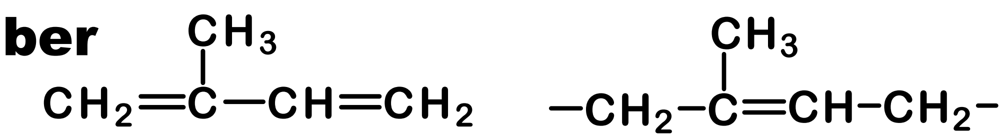
unbreakable glass, latex paint

poly(vinyl acetate)



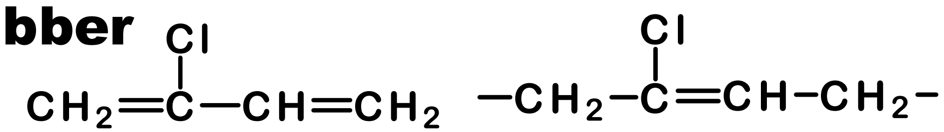
adhesives,
latex paints,
textile coatings
chewing gum

natural rubber



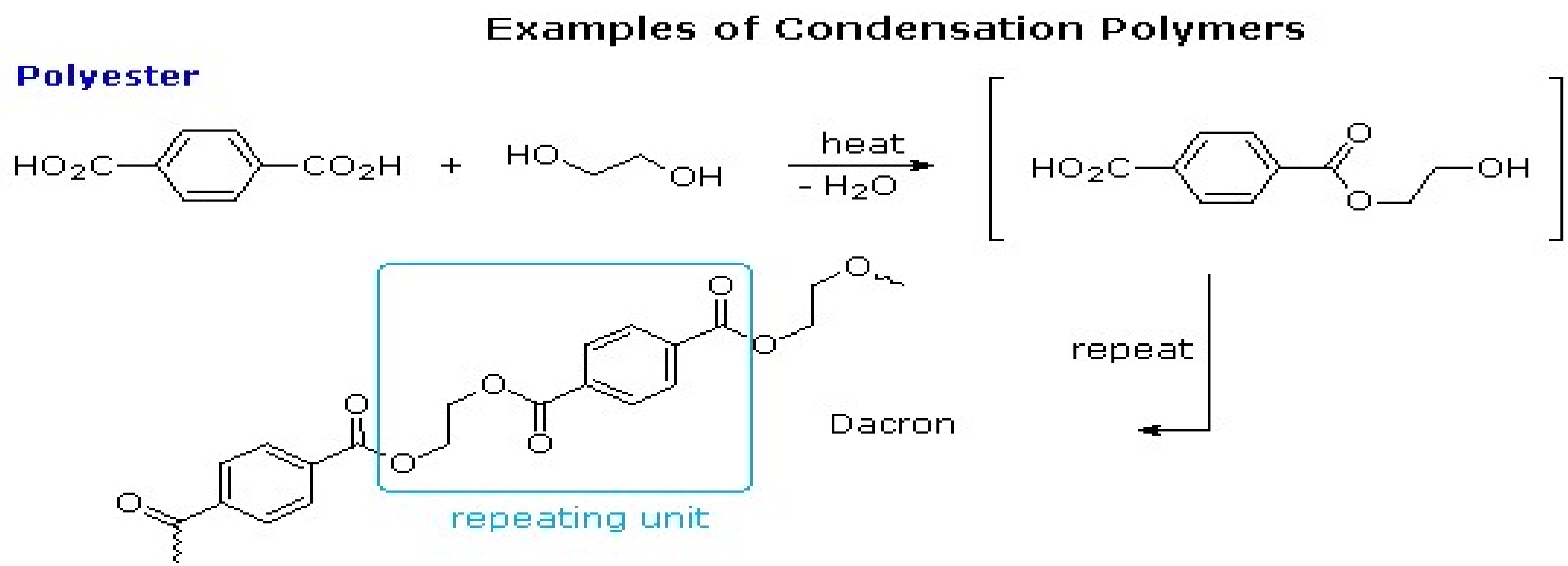
the polymer is cross-linked with sulfur (vulcanization)

neoprene rubber



cross-linked with ZnO, resistant to gasoline and oil

SOME COMMON CONDENSATION POLYMERS



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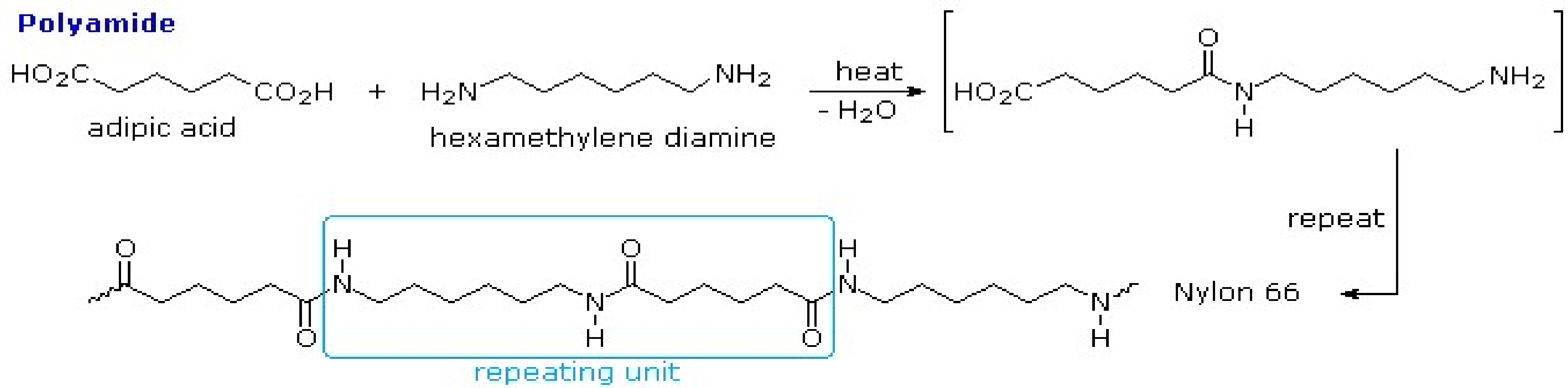
SOME COMMON CONDENSATION POLYMERS



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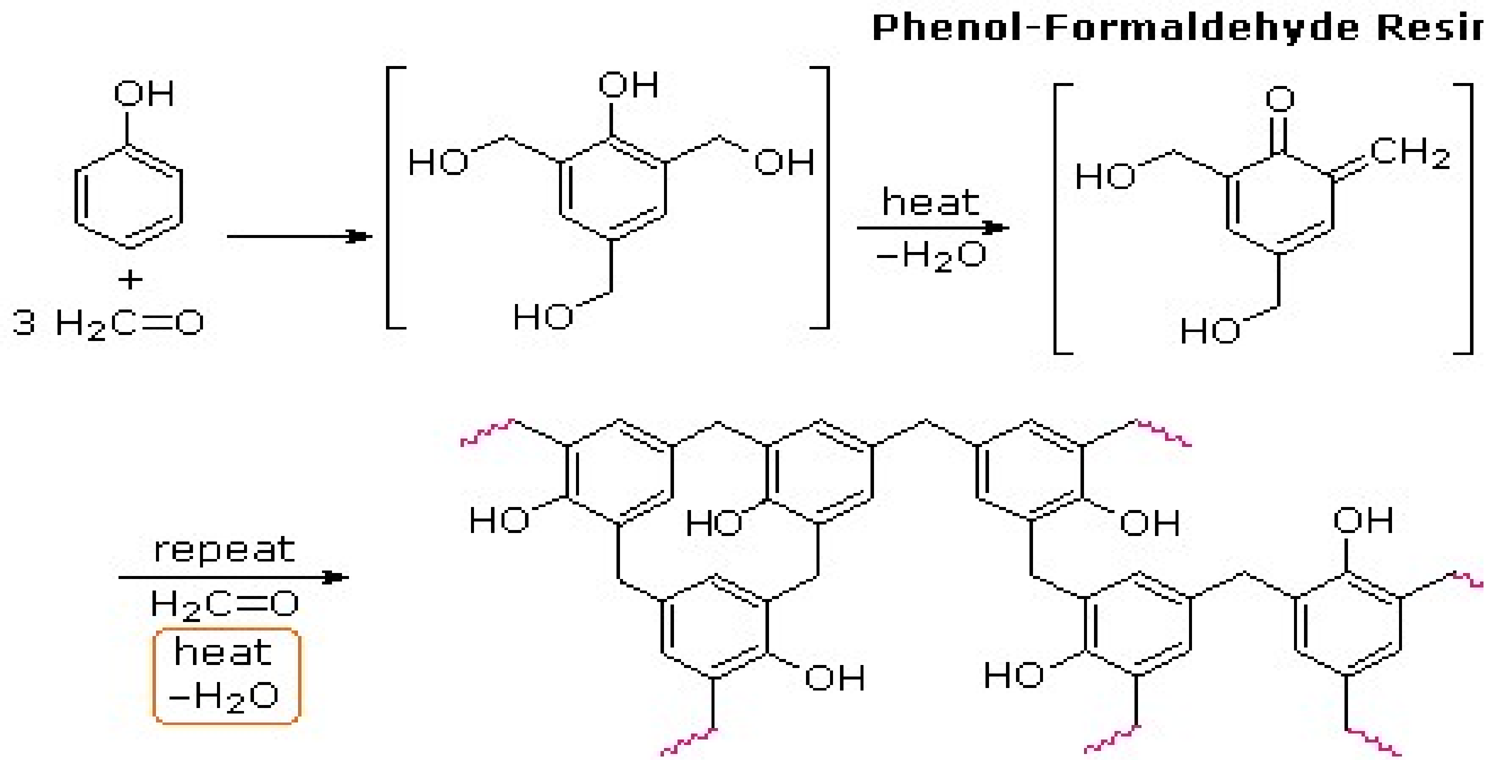
SOME COMMON CONDENSATION POLYMERS



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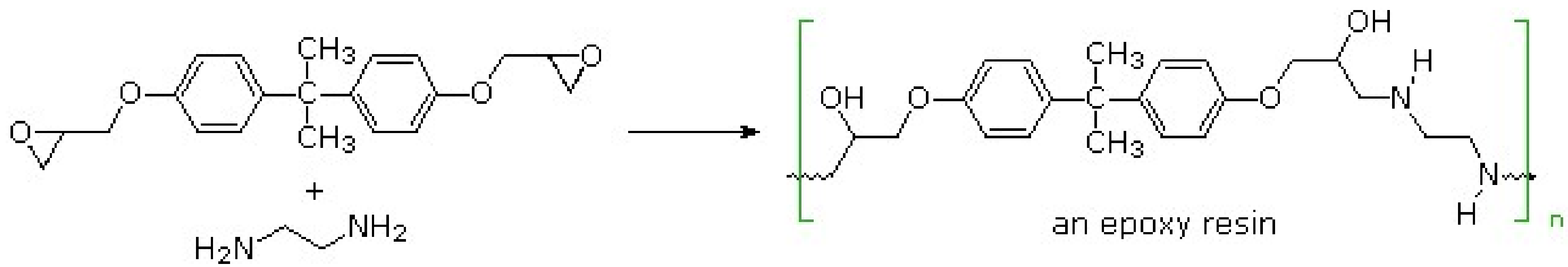
SOME COMMON CONDENSATION POLYMERS



Bisphenol A is prepared by the acid-catalyzed condensation of acetone with phenol.

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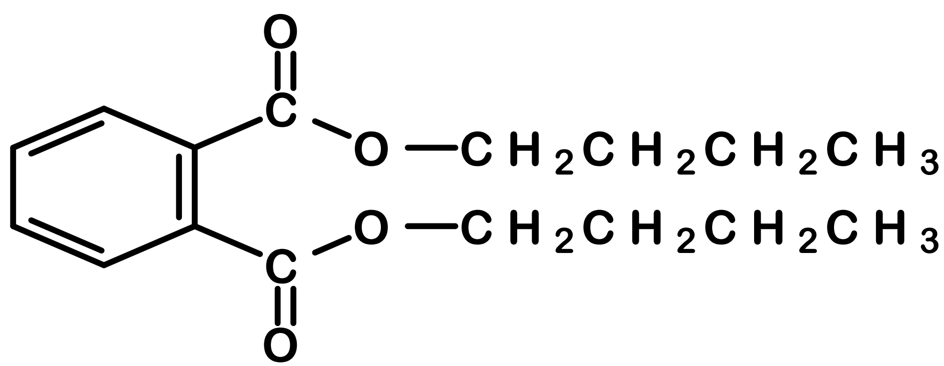
PLASTICIZERS

Most polymers of high molecular weight are quite rigid. These polymers can be softened and made flexible by adding **plasticizers**, usually dialkyl phthalate esters, such as dibutyl phthalate, a high boiling liquid.



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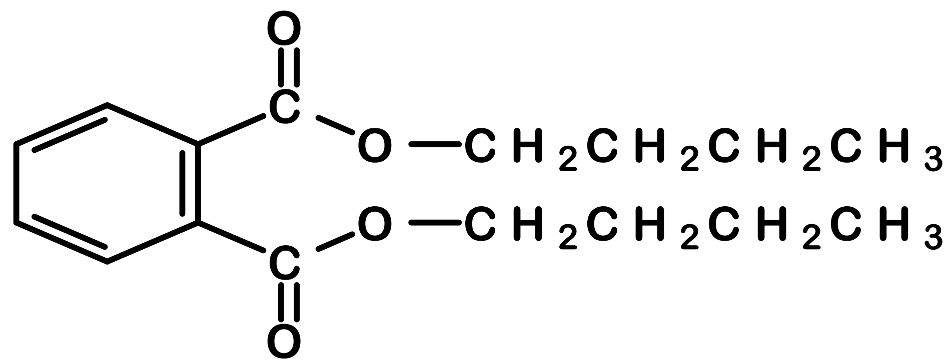
PLASTICIZERS



dibutyl phthalate

The plasticizer separates the individual polymer chains from one another. It acts as a lubricant which reduces the attractions between the polymer chains.

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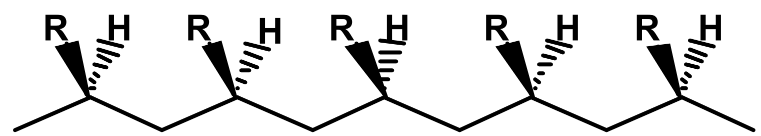
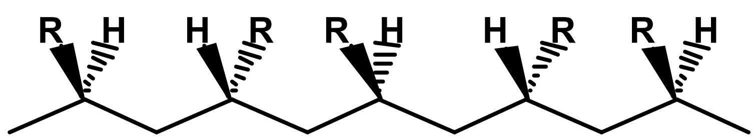
Stereochemistry

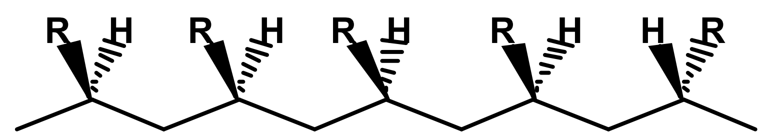
- There are three alternatives for the relative configurations of stereocenters along the chain of a substituted ethylene polymer.



Isotactic polymer
(identical configurations)



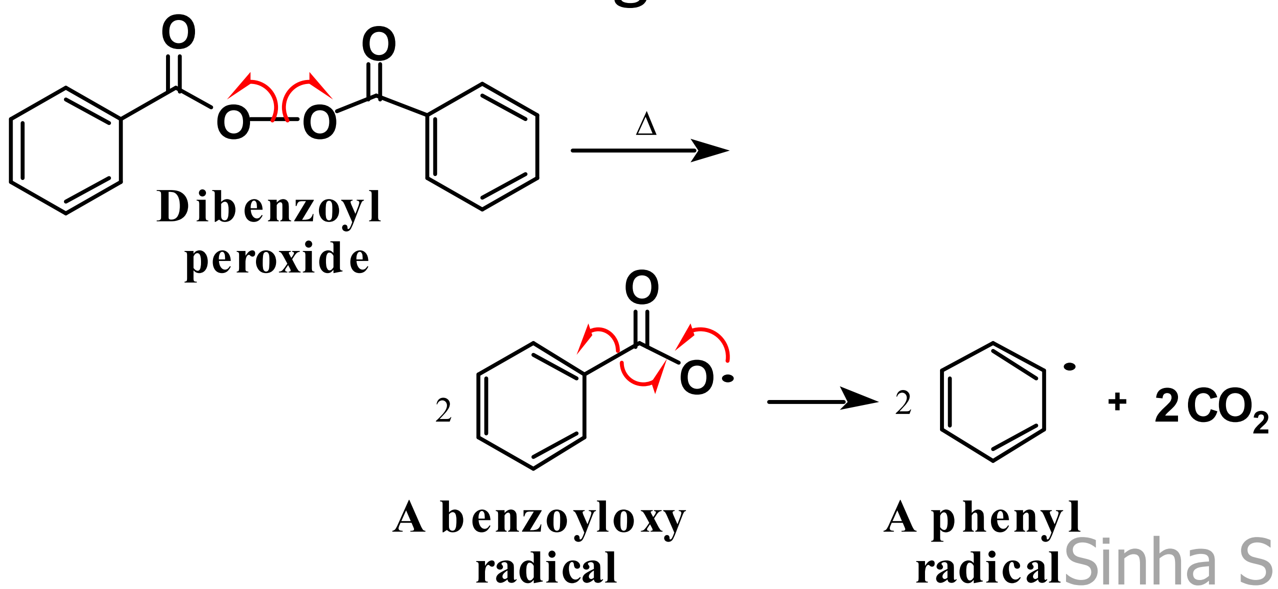
Syndiotactic polymer
(alternating configurations)



Atactic polymer
(random configurations)

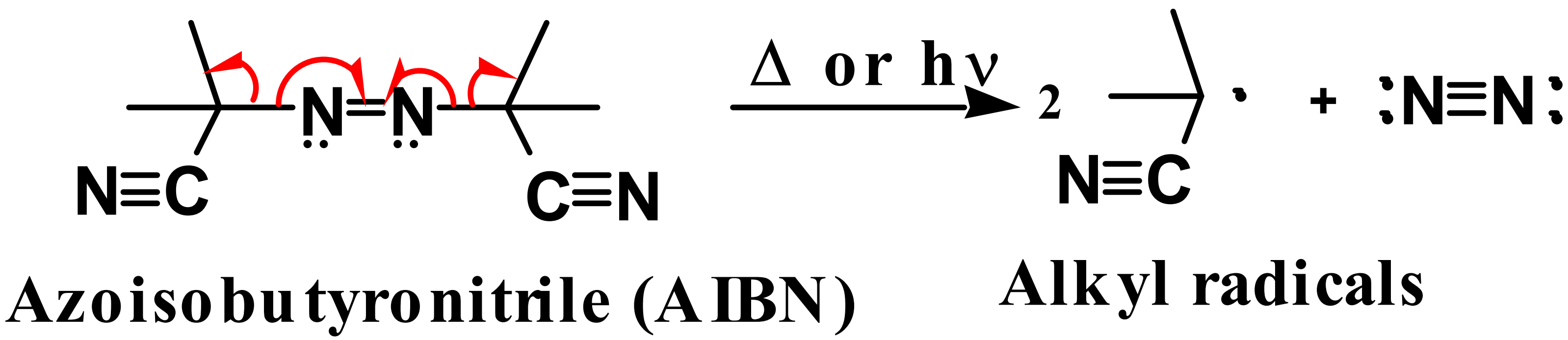
Radical Mechanism

- Among the initiators used for radical chain-growth polymerization are diacyl peroxides, which decompose on mild heating.



Radical Mechanism

- Another common class of initiators are azo compounds, which also decompose on mild heating or with absorption of UV light.



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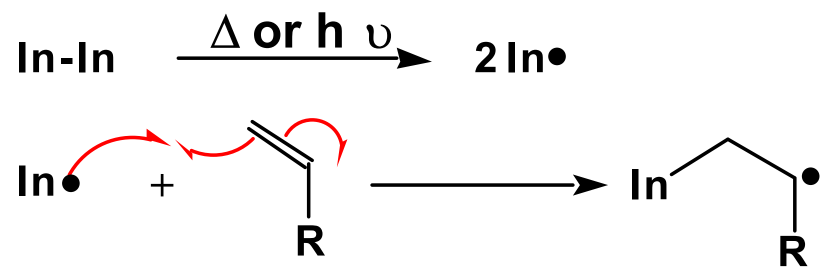
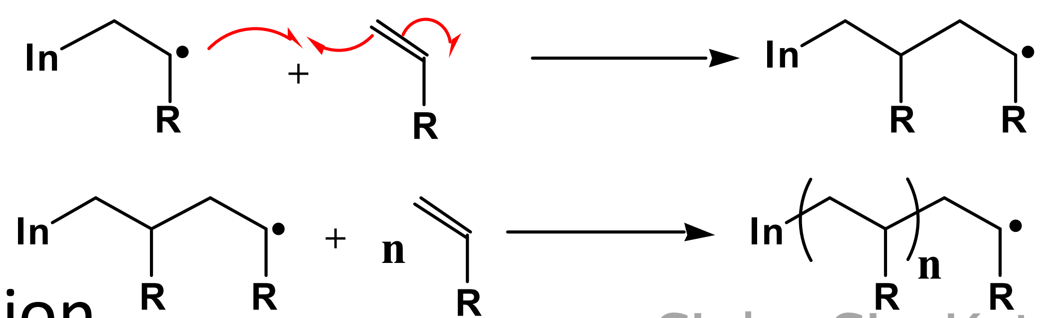
Radical Mechanism

- Radical polymerization of a substituted ethylene.
  - chain initiation

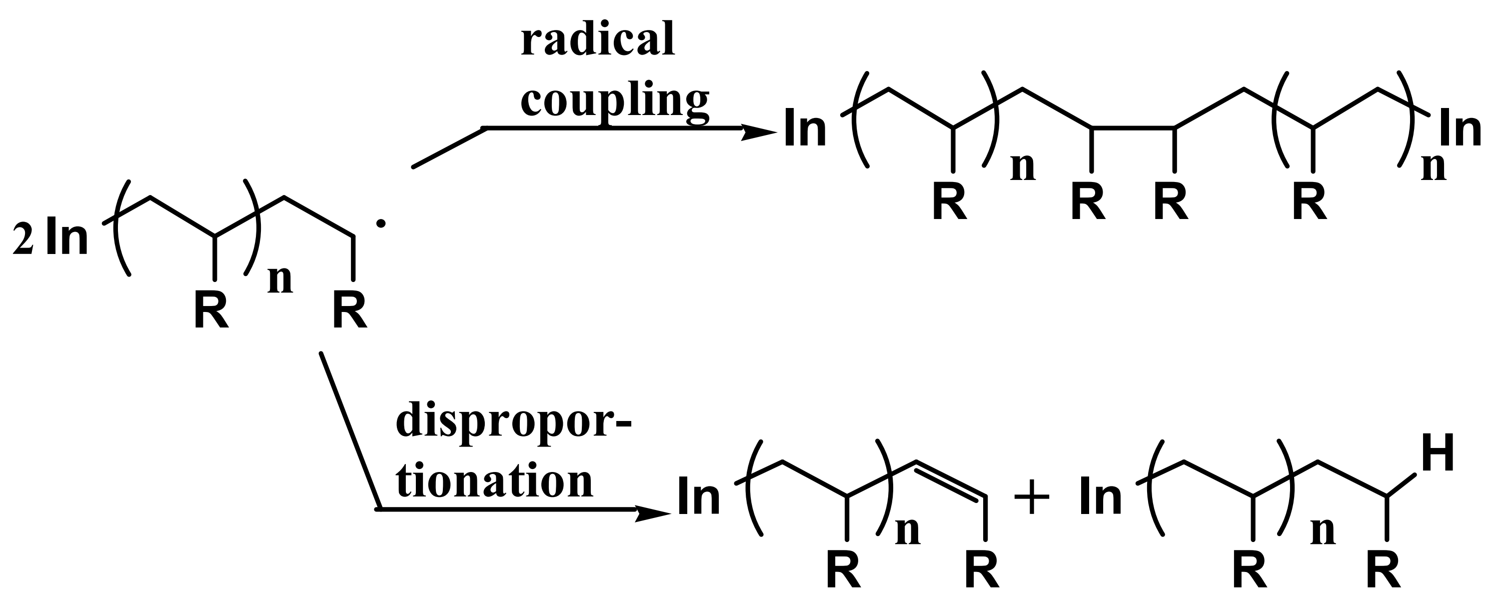




  - chain propagation

Radical Mechanism

–Chain termination.



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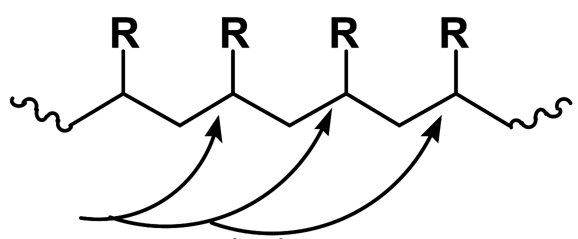
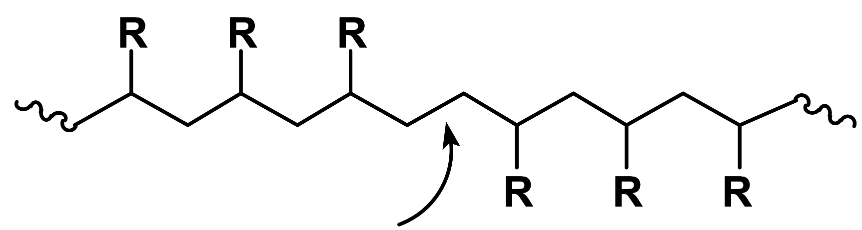
Radical Mechanism

- Radical reactions with double bonds almost always gives the more stable (the more substituted) radical.
- Because additions are biased in this fashion, polymerizations of vinyl monomers tend to yield polymers with head-to-tail linkages.



head-to-tail linkages



head-to-head linkage

Mechanism

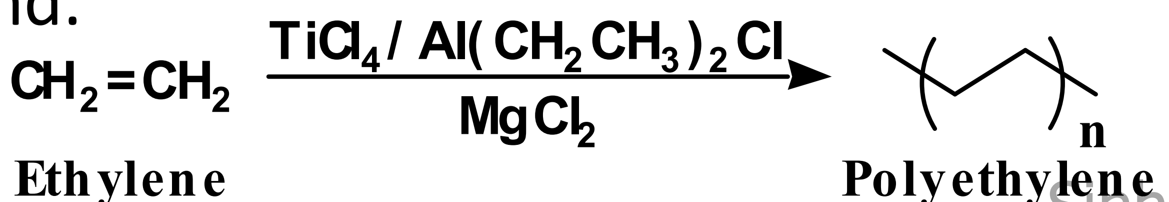
- The first commercial polyethylenes produced by radical polymerization were soft, tough polymers known as low-density polyethylene (LDPE).
- LDPE chains are highly branched due to chain-transfer reactions.

Because this branching prevents polyethylene chains from packing efficiently, LDPE is largely amorphous and transparent

Mechanism

Ziegler-Natta Polymers

- Ziegler-Natta chain-growth polymerization is an alternative method that does not involve radicals.
  - Ziegler-Natta catalysts are heterogeneous materials composed of a $MgCl_2$ support, a Group 4B transition metal halide such as $TiCl_4$, and an alkylaluminum compound.

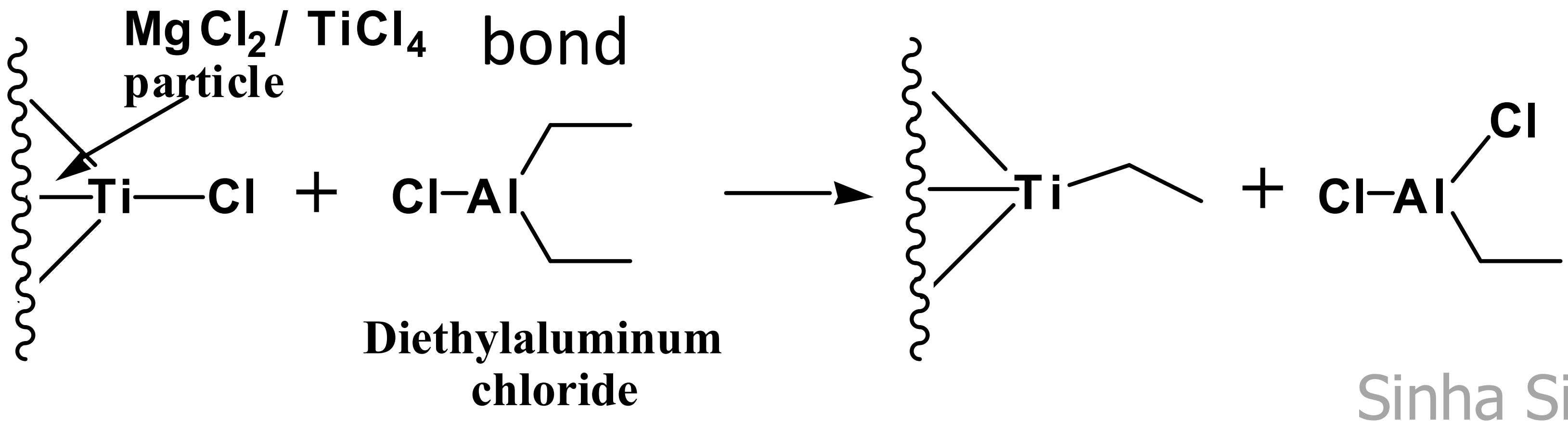


Mechanism

Ziegler-Natta Polymers

- Mechanism of Ziegler-Natta polymerization.

Step 1: Formation of a titanium-ethyl bond

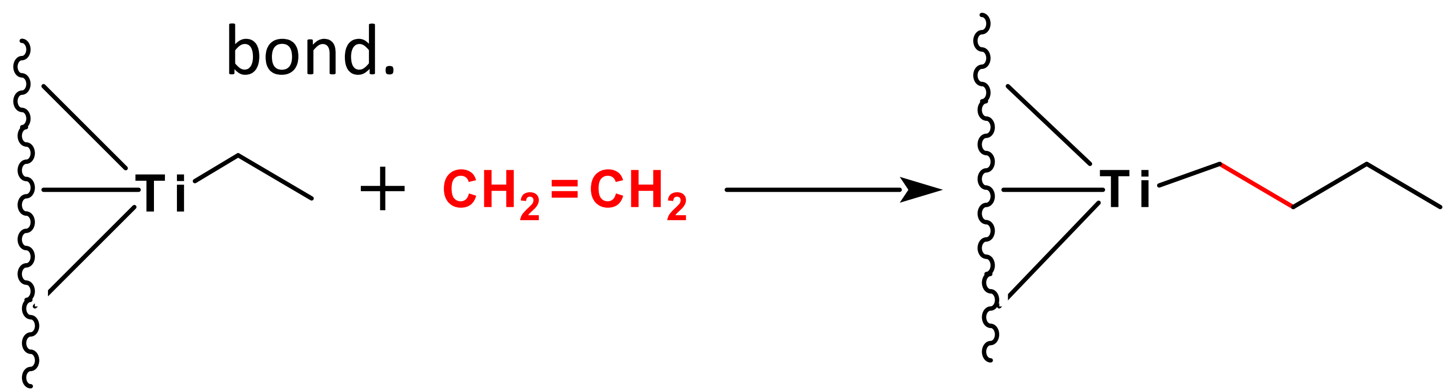


Mechanism

Ziegler-Natta Polymers

- Mechanism of Ziegler-Natta polymerization.

Step 2: Insertion of ethylene into the Ti-C bond.



Mechanism

Ziegler-Natta Polymers

- Polyethylene from Ziegler-Natta systems is termed high-density polyethylene (HDPE).
  - It has a considerably lower degree of chain branching than LDPE and a result has a higher degree of crystallinity, a higher density, a higher melting point, and is several times stronger than LDPE.

Mechanism

Ziegler-Natta Polymers

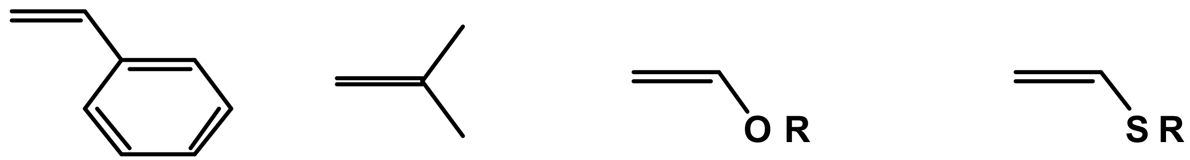
–Appox. 45% of all HDPE is molded into containers.

–With special fabrication techniques, HDPE chains can be made to adopt an extended zig-zag conformation. HDPE processed in this manner is stiffer than steel and has 4x the tensile strength!

Mechanism

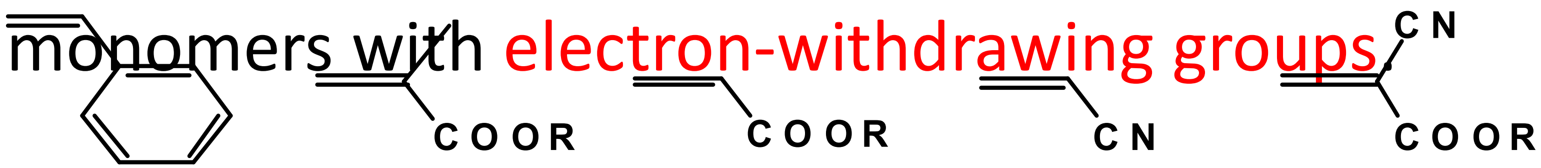
Ionic Chain Growth

- Either anionic or cationic polymerizations
  - Cationic polymerizations are most common with monomers with electron-donating groups.



Styrene Isobutylene Vinyl ethers Vinyl thioethers

  - Anionic polymerizations are most common with monomers with electron-withdrawing groups.

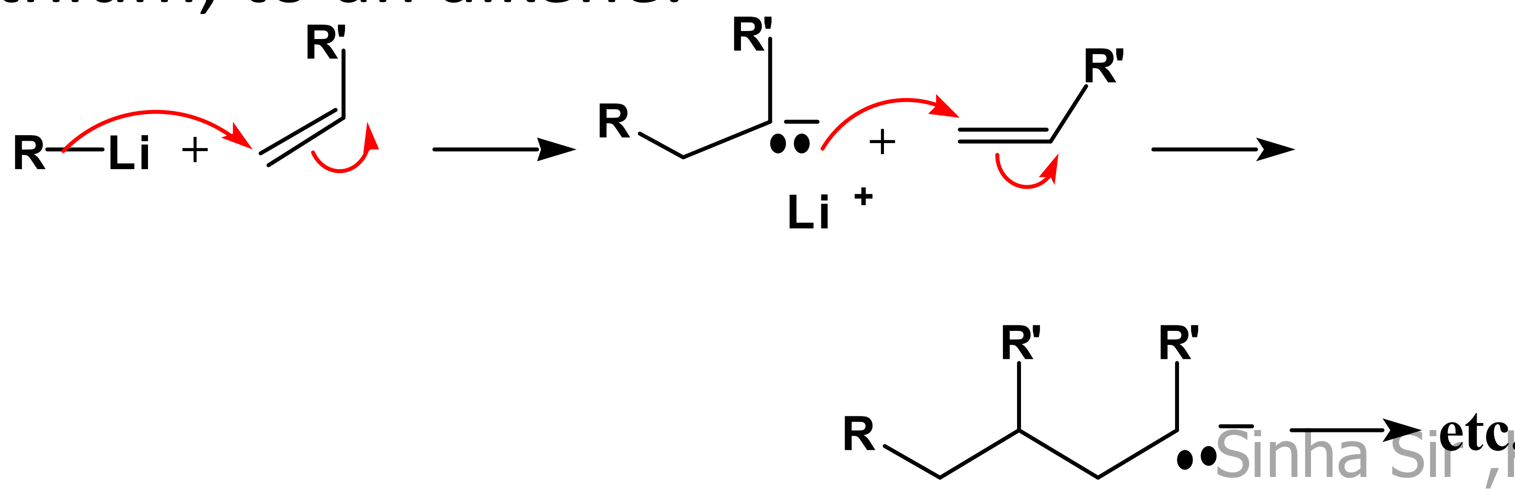


Styrene Alkyl methacrylates Alkyl acrylates Acrylonitrile Alkyl cyanoacrylates

Mechanism

Anionic Chain Growth

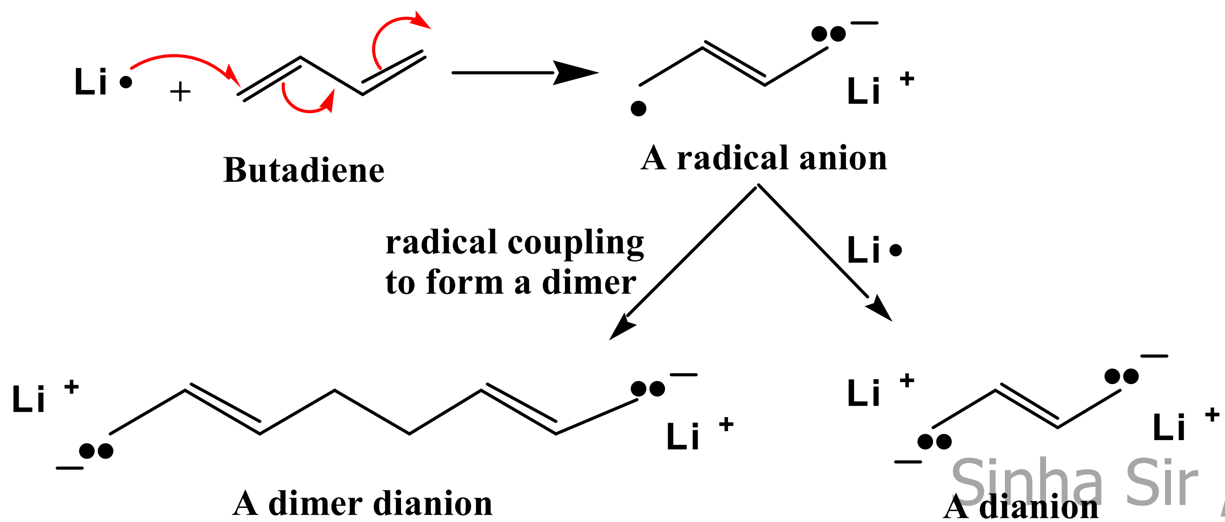
- Anionic polymerization can be initiated by addition of a nucleophile, such as methyl lithium, to an alkene.



Mechanism

Anionic Chain Growth

- An alternative method for initiation involves a one-electron reduction of the monomer by Li or Na to form a radical anion which is either reduced or dimerized to a dianion.



Mechanism

Anionic Chain Growth

- Sodium naphthalide may be used.

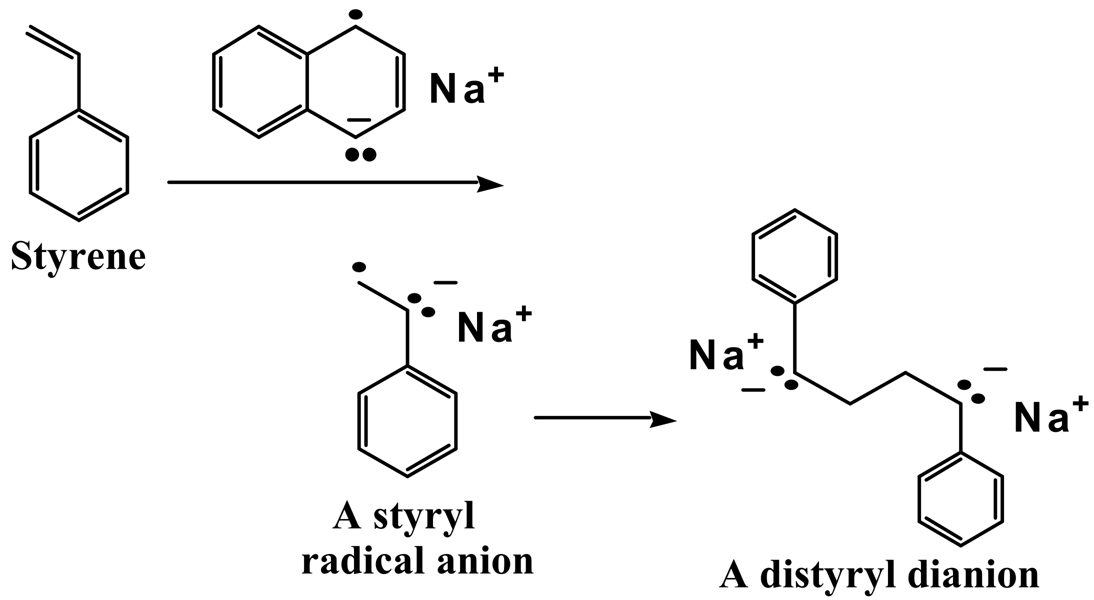
Naphthalene

Sodium naphthalide
(a radical anion)

The naphthalide radical anion is a powerful reducing agent and, for example, reduces styrene to a radical

Mechanism

Anionic Chain Growth



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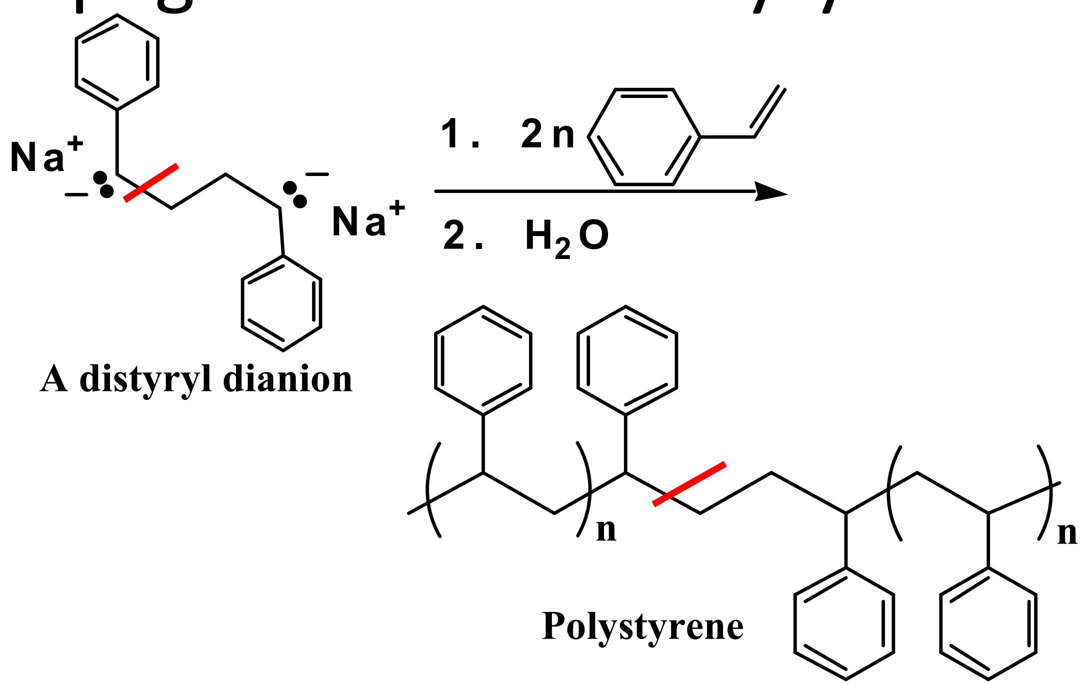
Mechanism

Anionic Chain Growth

- Propagation of the distyryl dianion.



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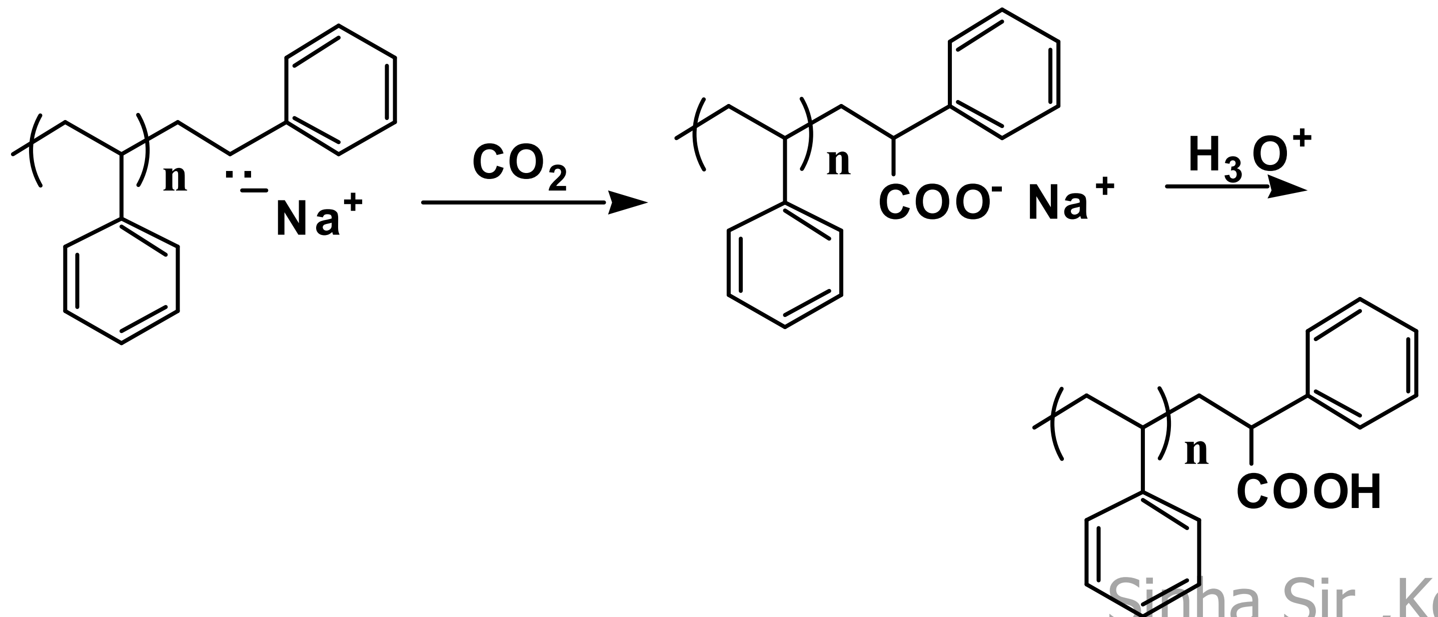
Mechanism

Anionic Chain Growth

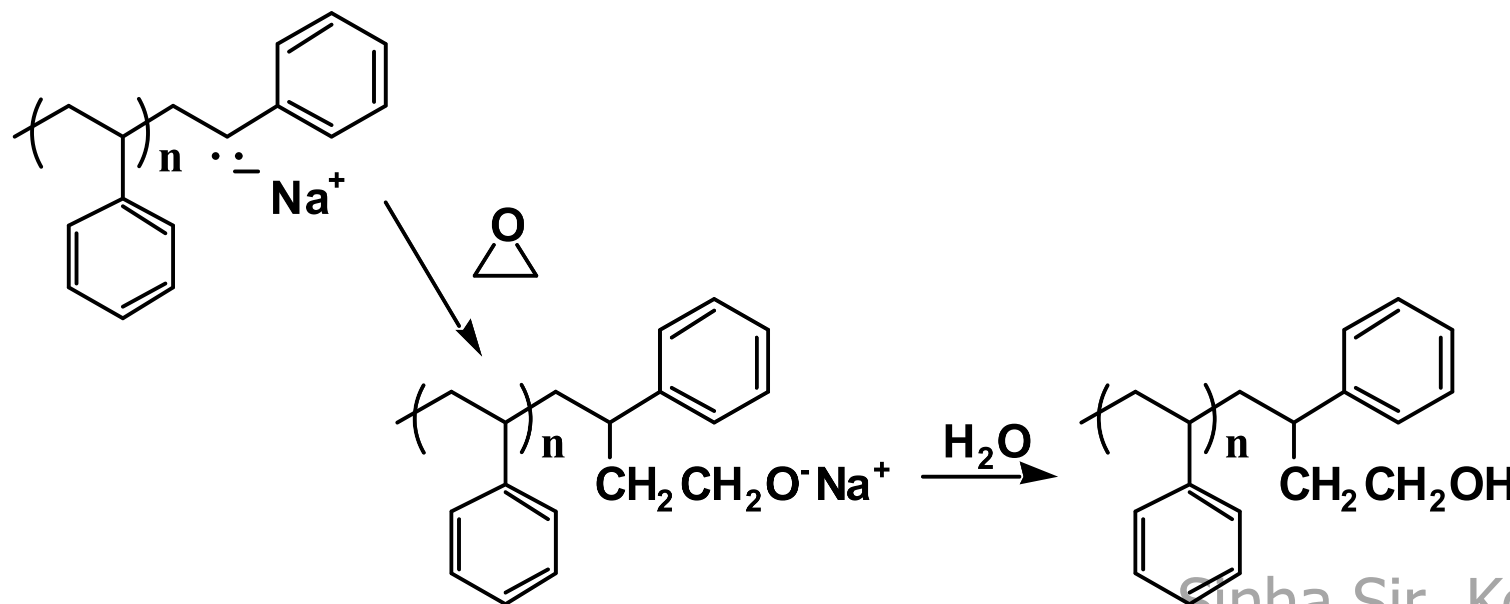
Termination by carboxylation.



Mechanism

Anionic Chain Growth

Termination by ethylene oxide.



Mechanism

Cationic Chain Growth

- The two most common methods for initiating cationic polymerization are:
  - –Addition of H^+. Reaction of a strong proton acid with the monomer.
  - –Ionization, as in S_N1. Abstraction of a halide from the organic initiator by a Lewis acid.

Mechanism

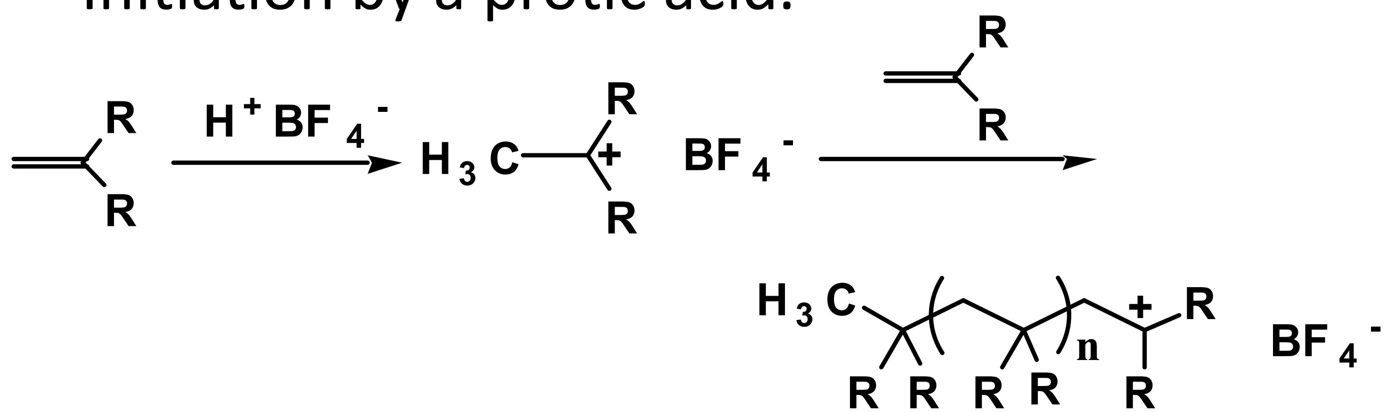
Cationic Chain Growth

- Initiation by a proton acid requires a strong acid with a nonnucleophilic anion in order to avoid completion of the addition to the double bond
  - –Suitable acids include HF/AsF_5 and HF/BF_3.

Mechanism

Cationic Chain Growth

– Initiation by a protic acid.



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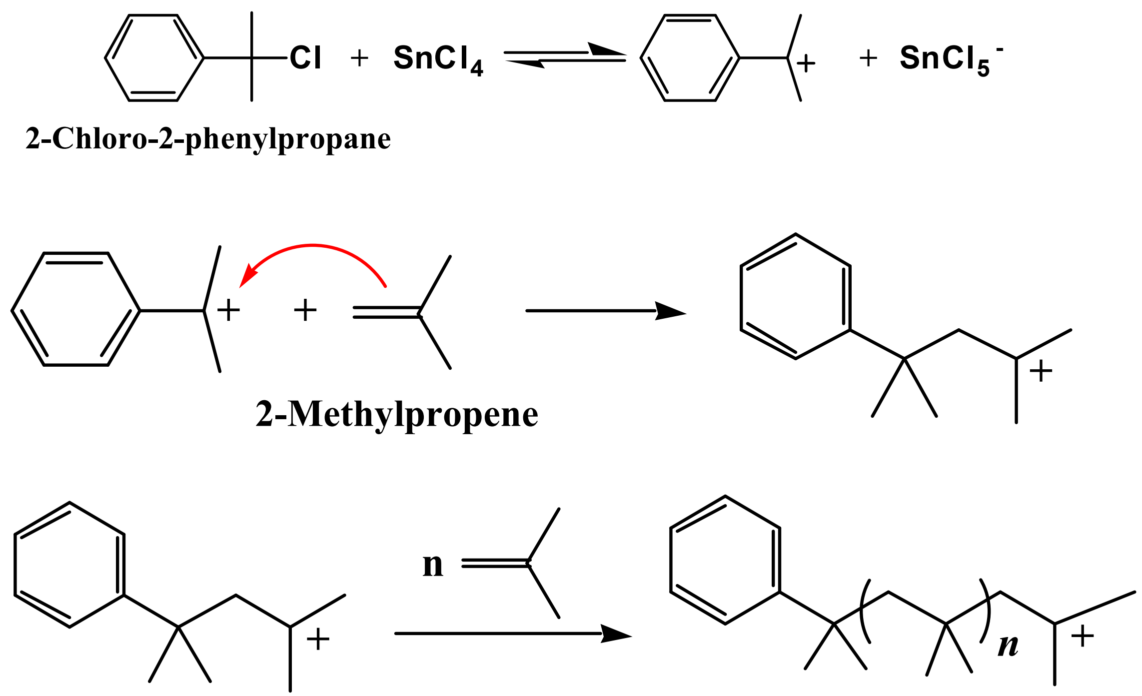
Mechanism

Cationic Chain Growth

– initiation

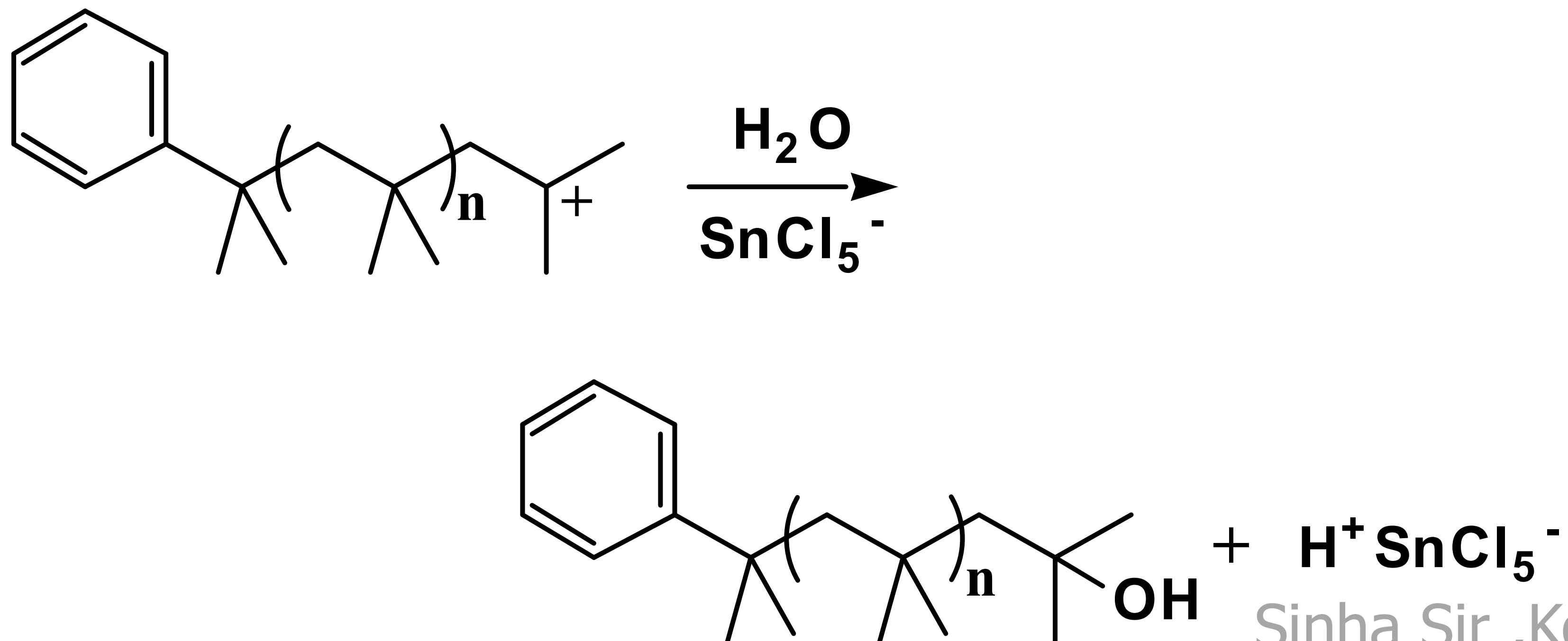
– propagation



Mechanism

Cationic Chain Growth

– Chain termination



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