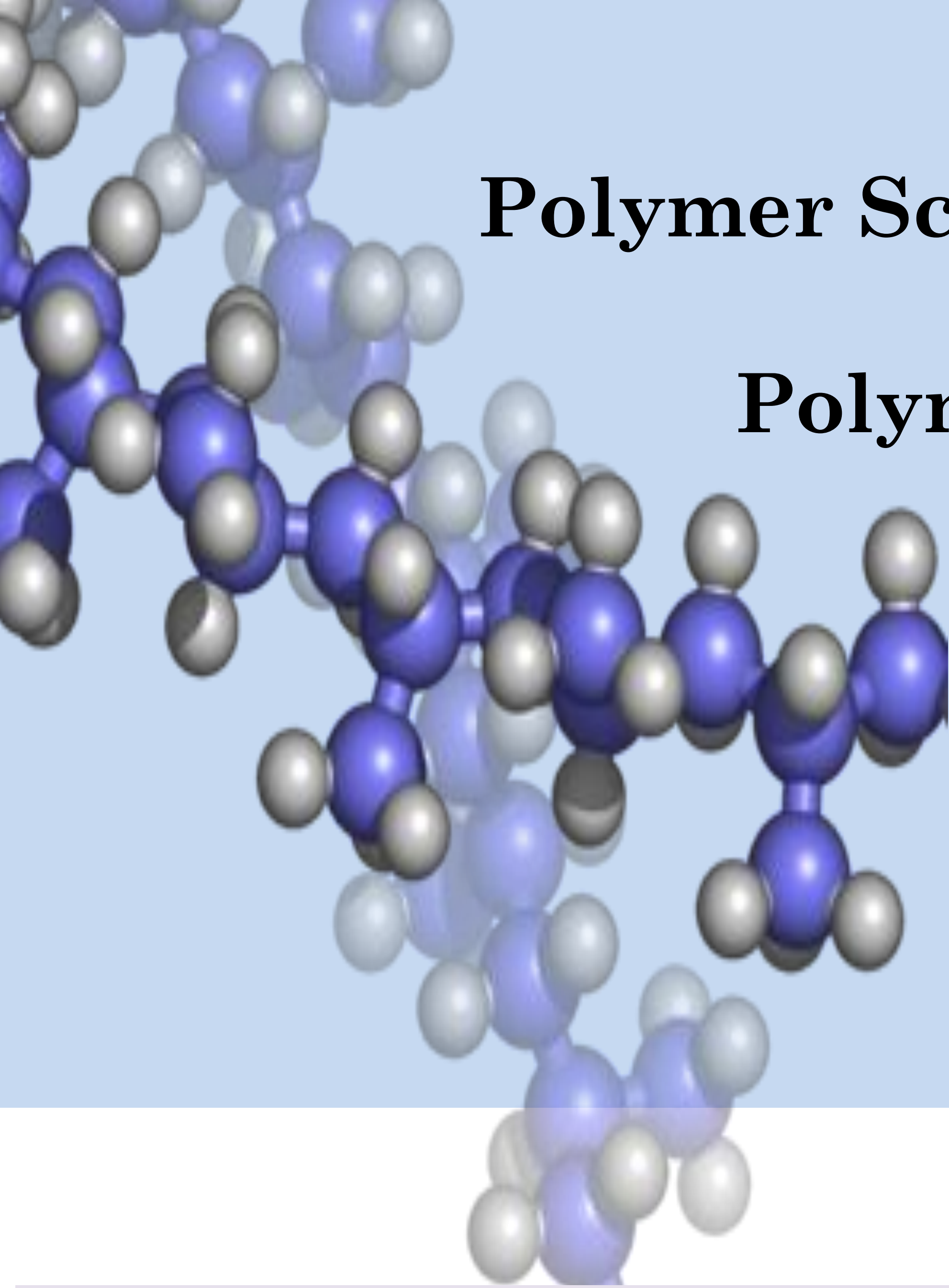


Polymer Science & Engineering

Polymerization

Dr. Motasem Saidan

M. Saidan@gmail.com

Polymerization

- Polymer, meaning literally many parts, is a large organic chemical molecule (macromolecule), consisting of a combination of many small chemical molecules known as monomers.

  - For example, polyethylene (PE), $- CH_2 - CH_2 - CH_2 - \cdots - CH_2 - CH_2 -$, consists of many ethylene, $CH_2 = CH_2$, monomers.

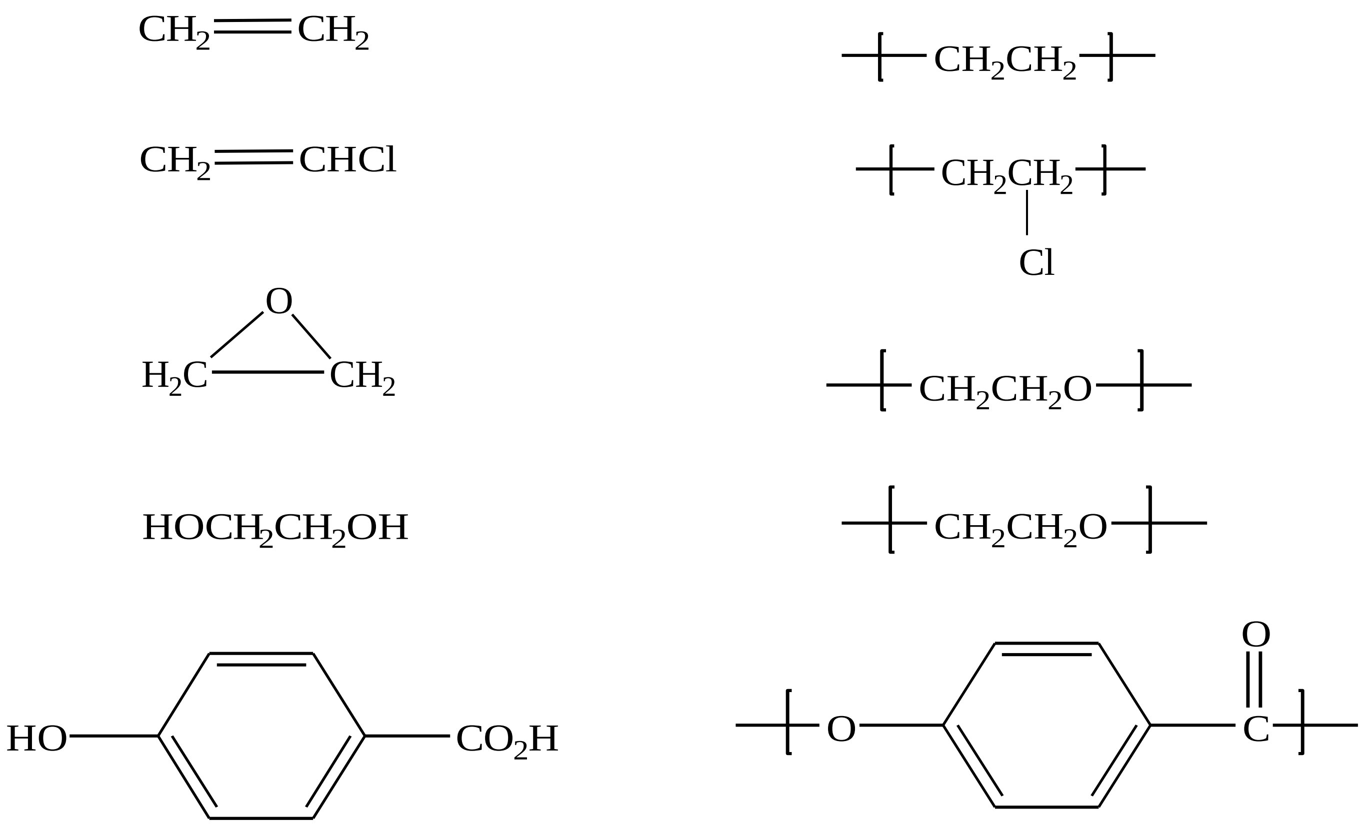
- The process of combining monomers together to yield a macromolecule is known as polymerization.

Development of civilization

Stone age → Bronze age → Iron age → Polymer age

Examples of monomers and polymers

Monomer **Polymer**



Polymerization mechanisms

There are two main types of polymerization mechanisms:

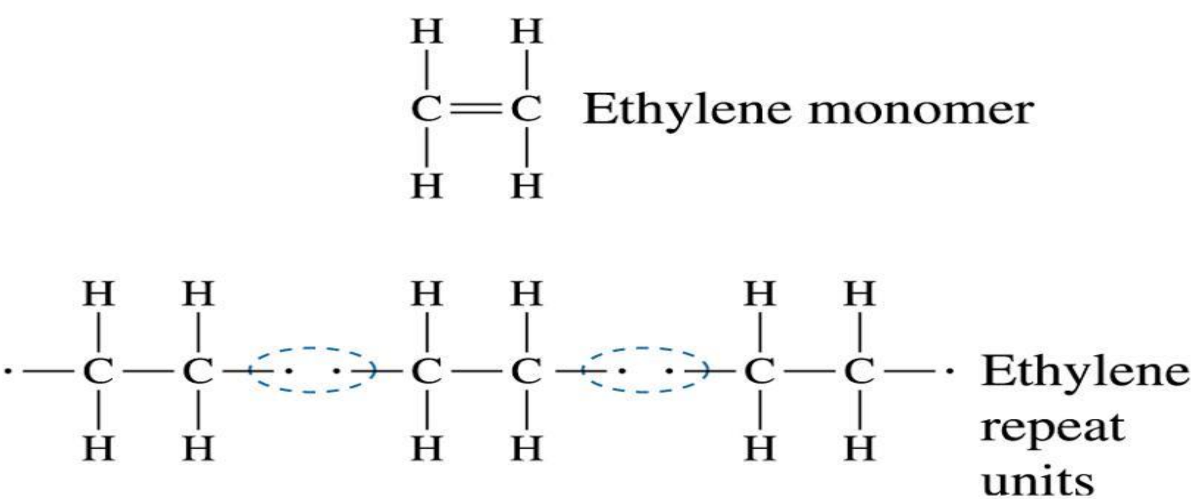
- ✓ **Addition (chain-growth) polymerization**, and
- ✓ **Condensation (step-growth) polymerization**.

- In chain-growth reaction the polymerization proceeds in a chain-like fashion in only one direction.
- In chain-growth: repeating units and monomers are same
- In condensation reaction, the chain growth is not spontaneous and usually occurs slowly: the monomers first form dimers, trimers, tetramers and oligomers.
- In condensation: repeating units and monomers are not equal, to be split out small molecule

➢ Long reaction times are necessary in order to reach polymers with high average molecular weights.

Addition (chain-growth) polymerization

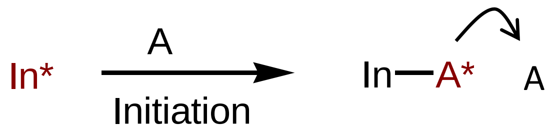
- Addition polymerization - Process by which polymer chains are built up by adding monomers together without creating a byproduct.
- Unsaturated bond - The double- or even triple-covalent bond joining two atoms together in an organic molecule.
- Functionality - The number of sites on a monomer at which polymerization can occur.



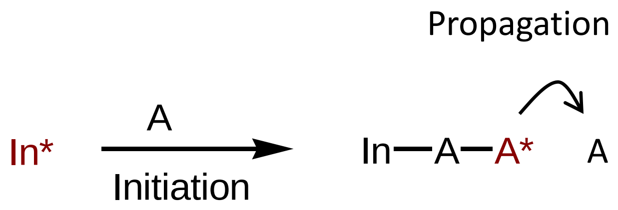
The addition reaction for producing polyethylene from ethylene molecules:

The unsaturated double bond in the monomer is broken to produce active sites, which then attract additional repeat units to either end to produce a chain.

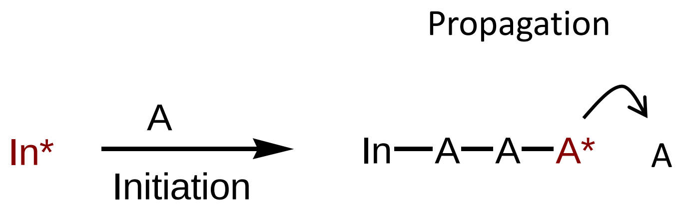
Addition Polymerization



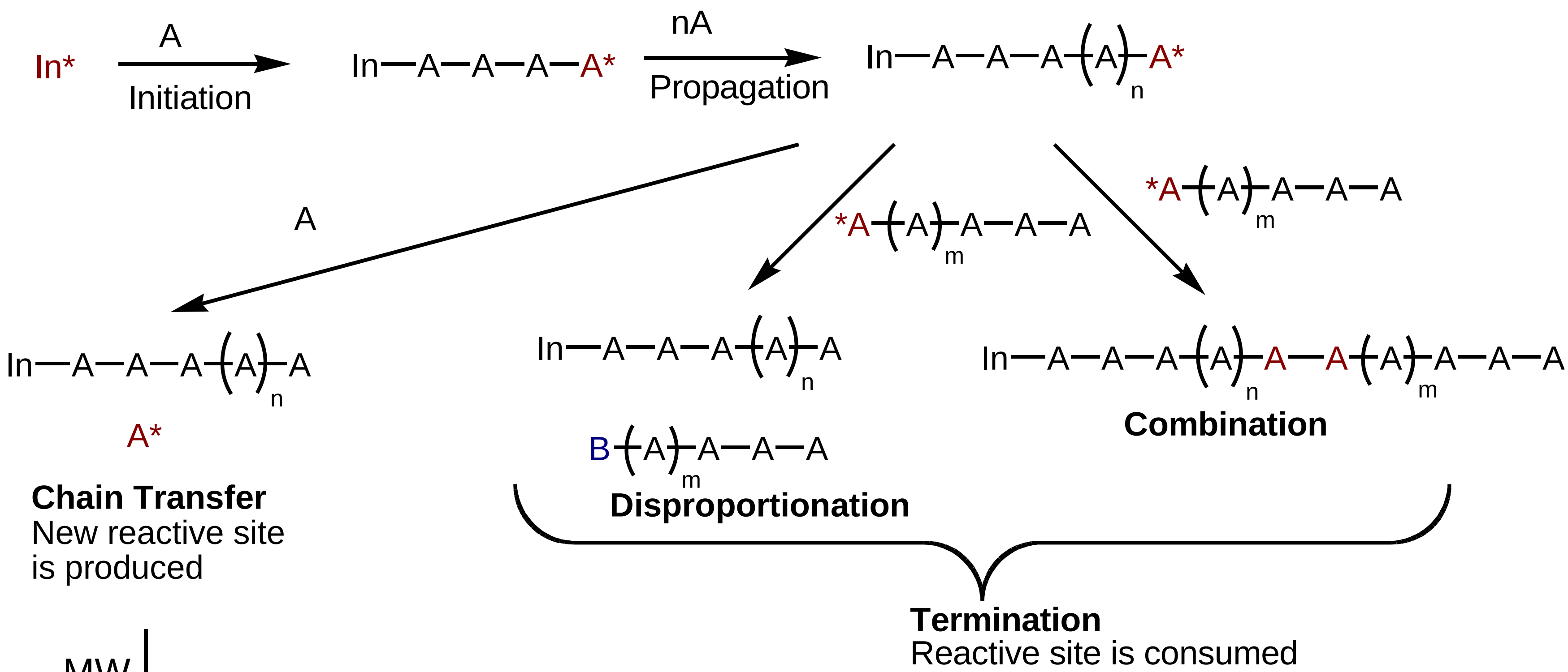
Addition Polymerization

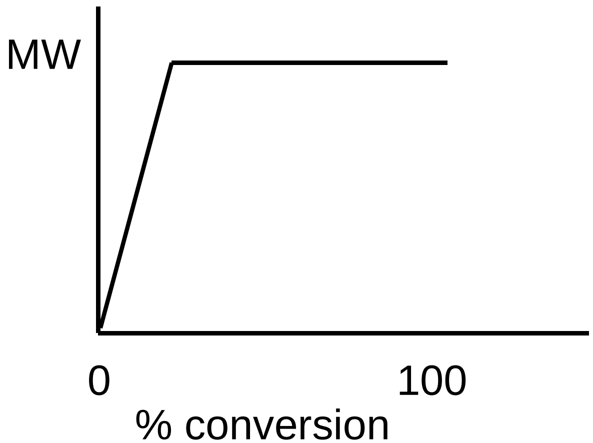


Addition Polymerization



Addition Polymerization

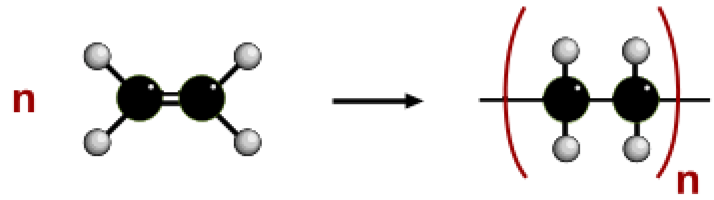




$$MW \propto \frac{k_{propagation}}{k_{termination}}$$

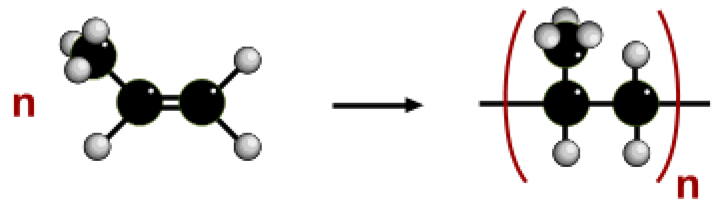
Examples on addition polymerization

ETHENE



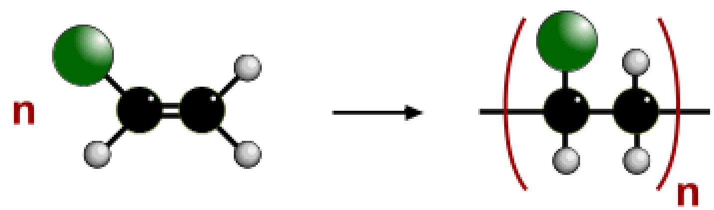
POLY(ETHENE)

PROPENE



POLY(PROPENE)

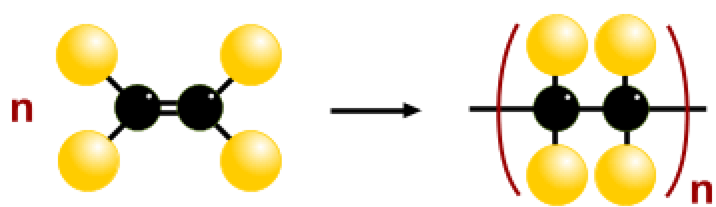
CHLOROETHENE



POLY(CHLOROETHENE)

POLYVINYLCHLORIDE PVC

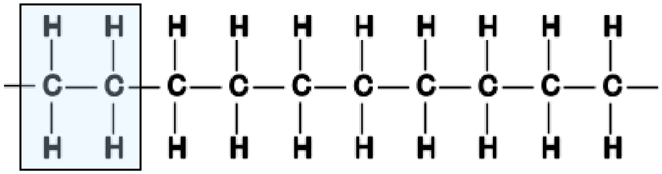
TETRAFLUOROETHENE

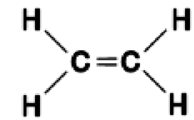


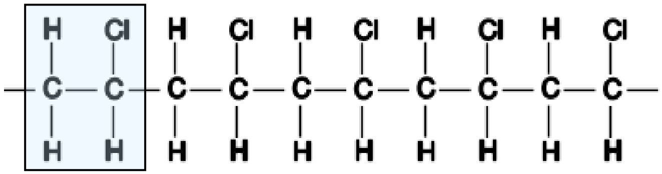
POLY(TETRAFLUOROETHENE)

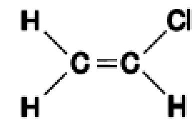
PTFE “Teflon”

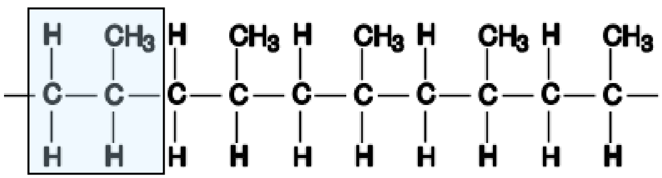
Examples on addition polymerization

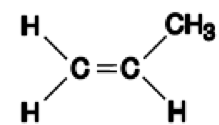


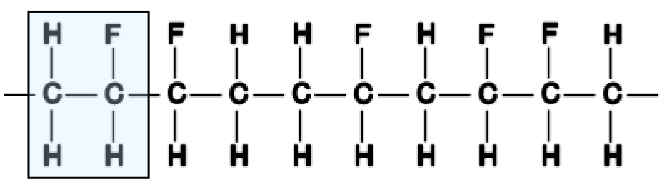


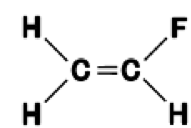


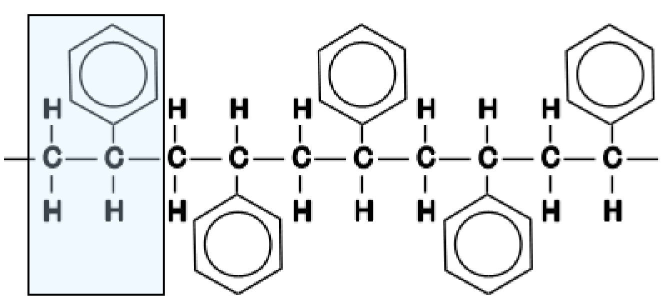


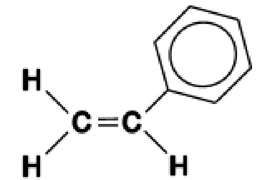








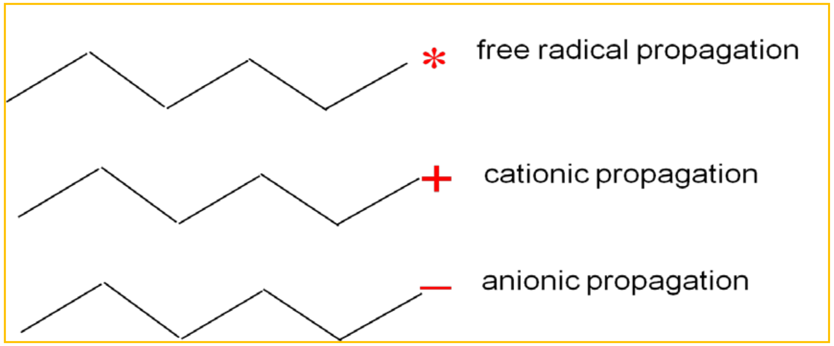




Addition polymerization mechanisms

- The mechanisms for addition polymerization are:

  - Free radical,
  - Anionic and
  - Cationic,
  - Coordination or stereoregular polymerization



- Free-radical, anionic and cationic polymerizations all include three stages:

initiation, propagation and **termination**.

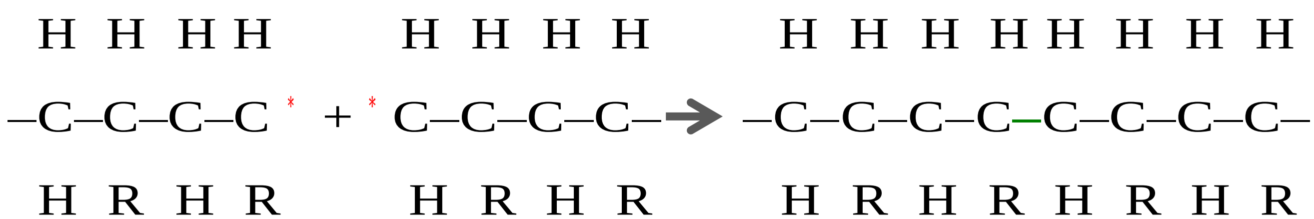
- **Initiation** involves the splitting up of the initiator molecules into free radicals by application of heat at a certain temperature, the initiator free radicals then react with monomer molecules, beginning the formation of polymer chains.

- The addition of monomers during the propagation process is predominantly by **head**(the carbon atom with the R group attached) -to-**tail** (the carbon atom without the R group) bonding due to steric and resonance effects.

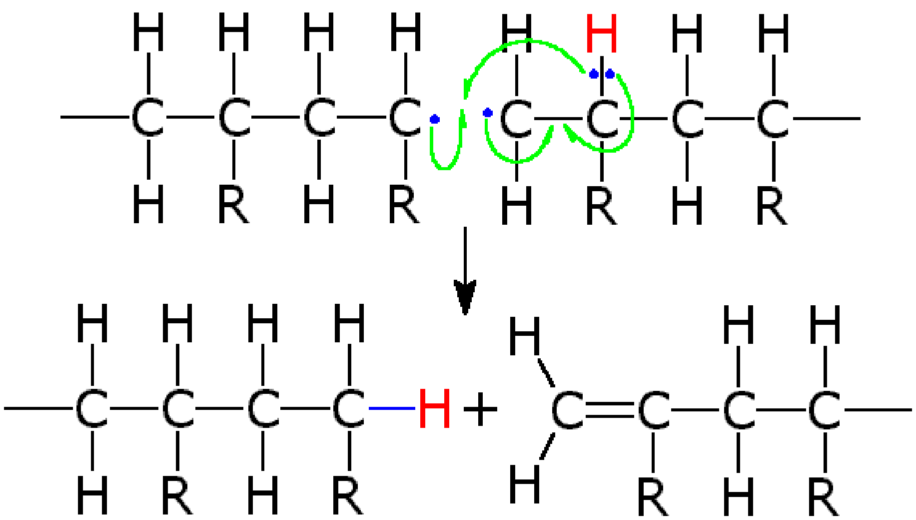
- **Chain transfer to polymer** can also occur as a propagation step in polymerization. This is the process where a growing chain radical is transferred to the middle of another polymer chain, forming **branches** on the polymer chains, which can lead to reduced melting point and mechanical strength for the polymer.

- The **termination** step involves the reaction of any two free radicals with each other, either by combination or disproportionation.

- **Combination** involves the coupling of two growing polymer chain radicals as shown below:



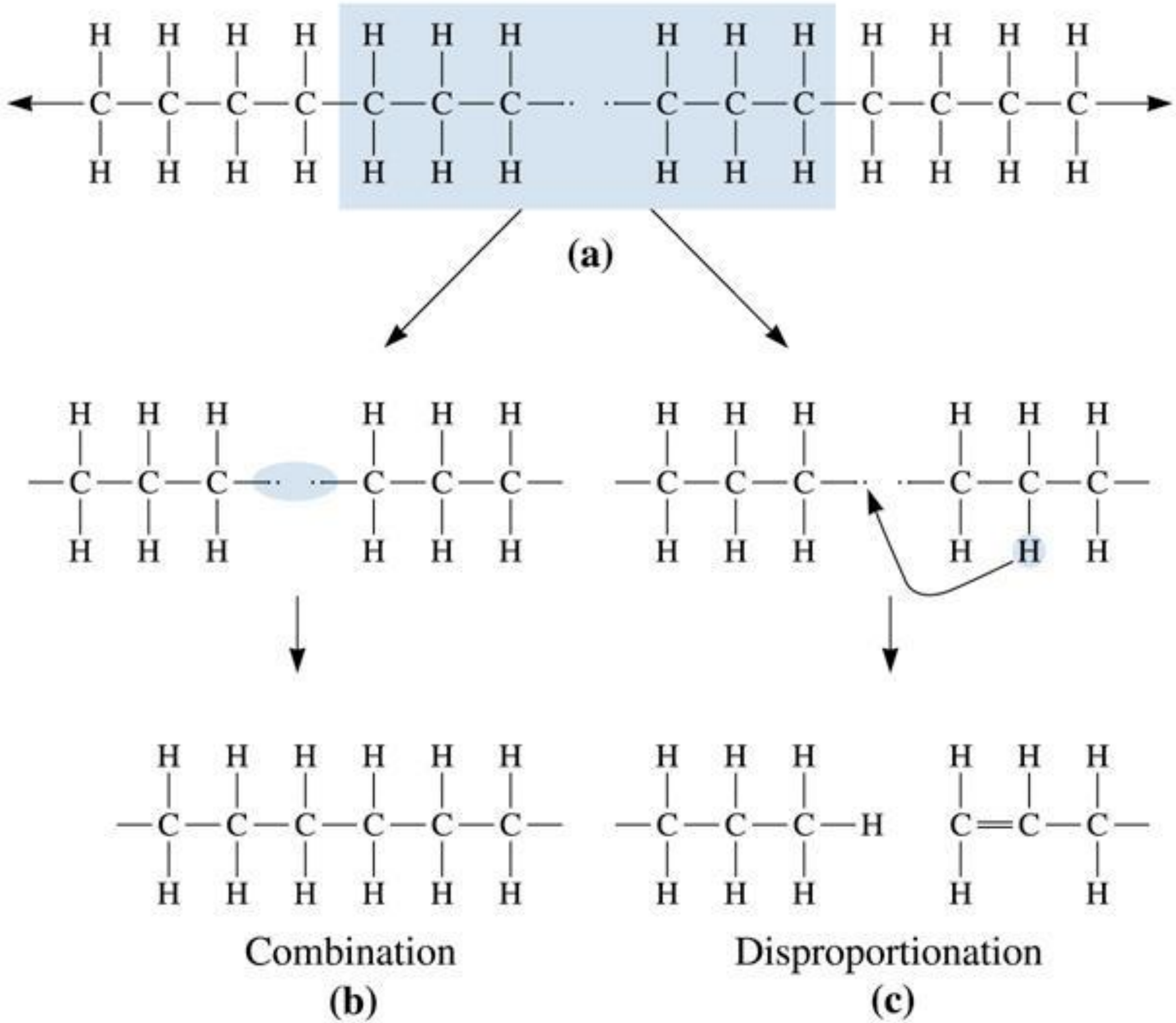
- **Disproportionation** is a rather complicated way in which two growing polymer chains are rendered inactive: when two growing chain ends come close together, the unpaired electron of the chains are exchanged in such a manner that the first chain gains a H element from the second chain, and a double bond forms at the head of the second.



- In free radical polymerization the polymerization site moves progressively away from the initiator and is not influenced by the chemical structure of the initiator, accordingly, it is the type of monomer rather than the initiator that dictates the free-radical polymerization process.

- The flexible and dynamic nature of the free-radical site can cause the formation of side branches by an internal chain transfer process known as backbiting, which generates a free radical site within the growing polymer chain.

Termination of polyethylene chain growth

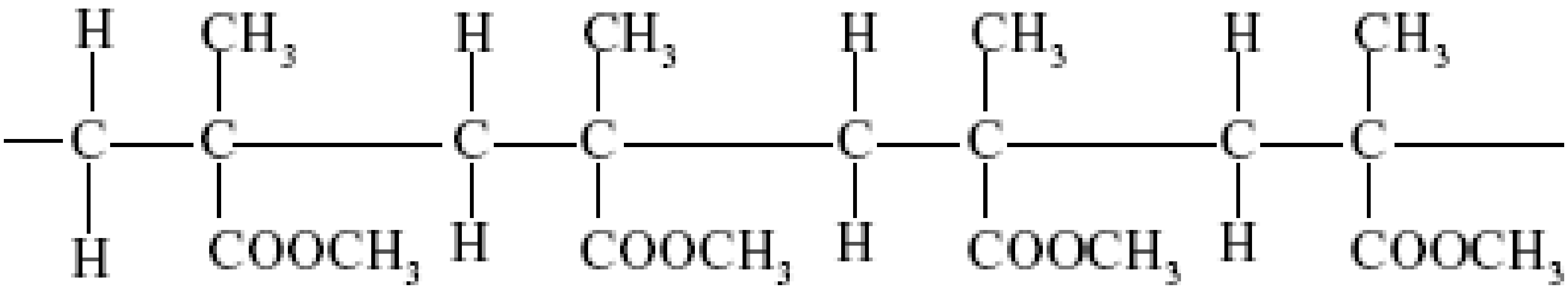


Some Common Addition Polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$–(CH_2\text{-}CH_2)_n–$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$–(CH_2\text{-}CH_2)_n–$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$–[CH_2\text{-}CH(CH_3)]_n–$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$–(CH_2\text{-}CHCl)_n–$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$–(CH_2\text{-}CCl_2)_n–$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$–[CH_2\text{-}CH(C_6H_5)]_n–$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$–(CH_2\text{-}CHCN)_n–$	acrylonitrile $CH_2=CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$–(CF_2\text{-}CF_2)_n–$	tetrafluoroethylene $CF_2=CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$–[CH_2\text{-}C(CH_3)CO_2CH_3]_n–$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$–(CH_2\text{-}CHOCOCH_3)_n–$	vinyl acetate $CH_2=CHOCOCH_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$–[CH_2\text{-}CH=C(CH_3)\text{-}CH_2]_n–$	isoprene $CH_2=CH\text{-}C(CH_3)=CH_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$–[CH_2\text{-}CH=CCl\text{-}CH_2]_n–$	chloroprene $CH_2=CH\text{-}CCl=CH_2$	tough, rubbery solid	synthetic rubber oil resistant

Example

1. Perspex is a polymer with the following structure



(a) Circle the repeating unit

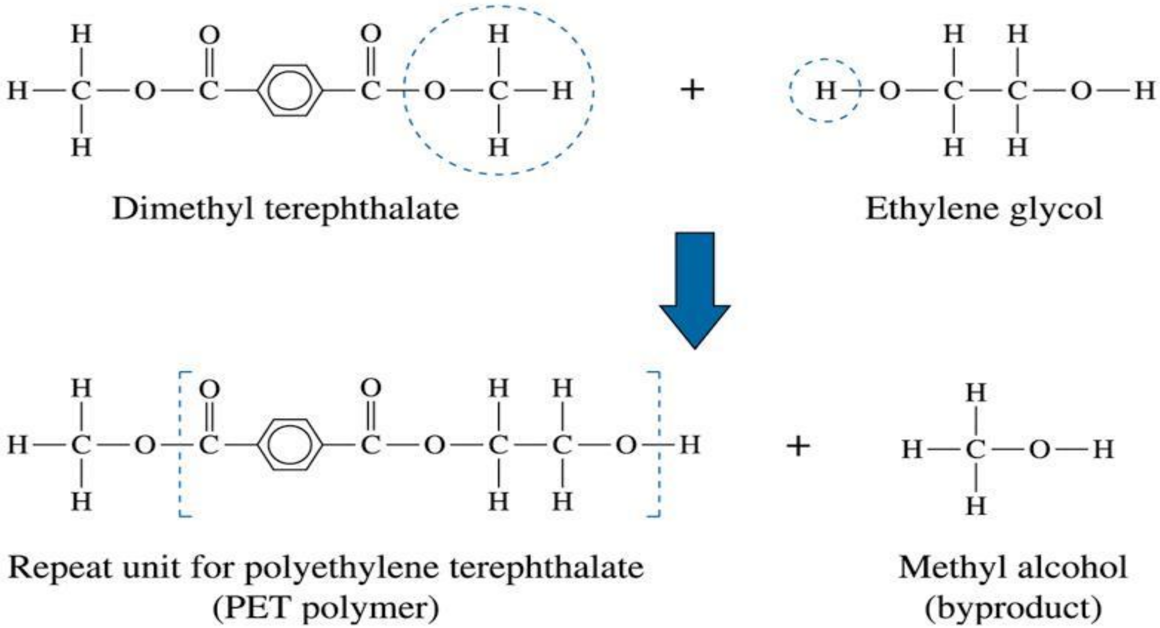
(b) Draw the structural formula of the monomer

(c) Which type of polymerisation has taken place in its formation?

(d) Why is this polymer non-biodegradeable?

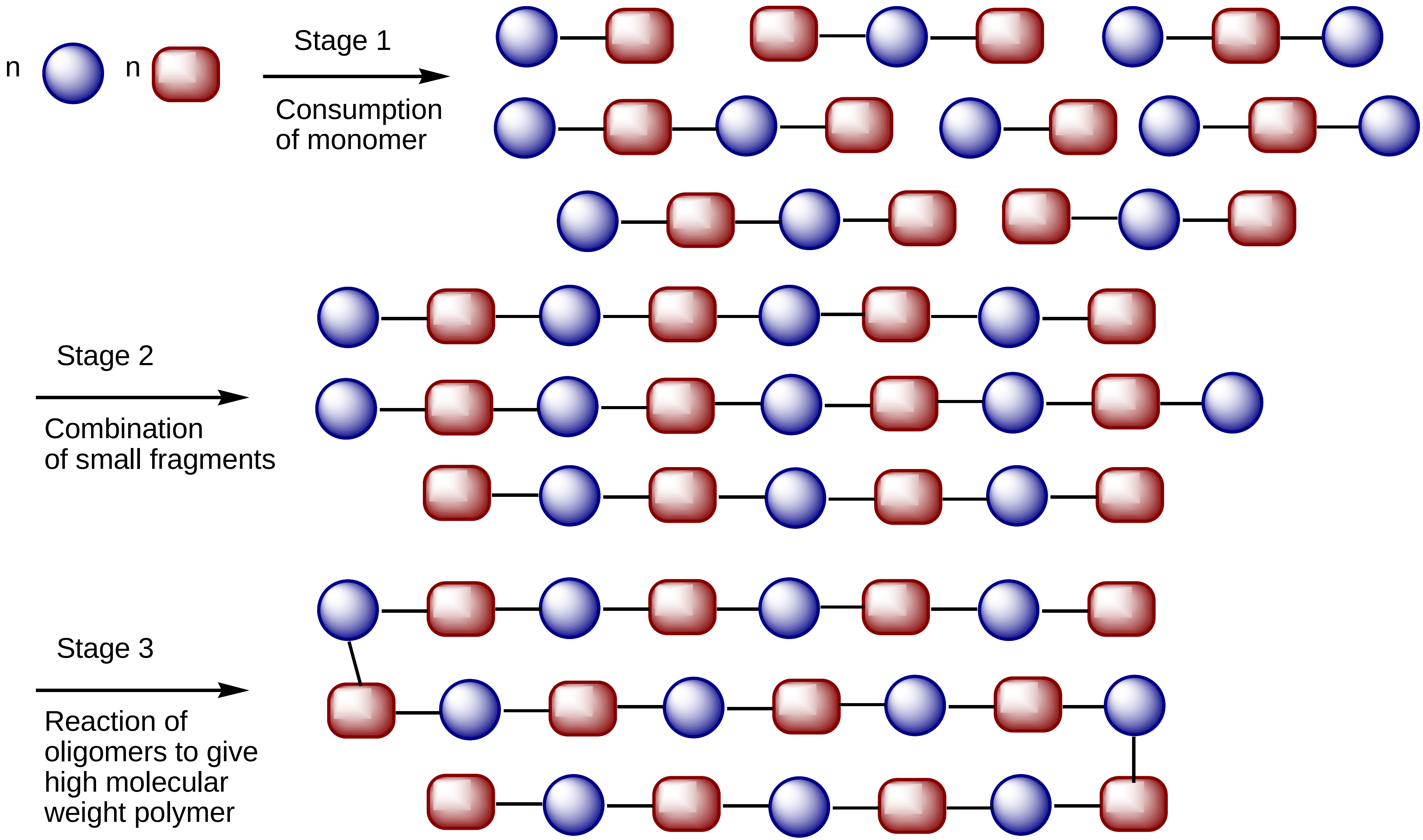
Condensation polymerization

Condensation polymerization - A polymerization mechanism in which a small molecule (e.g., water, methanol, etc.) is condensed out as a byproduct.



The condensation reaction for polyethylene terephthalate (PET), a common polyester. The OCH3 group and a hydrogen atom are removed from the monomers, permitting the two monomers to join and producing methyl alcohol as a byproduct.

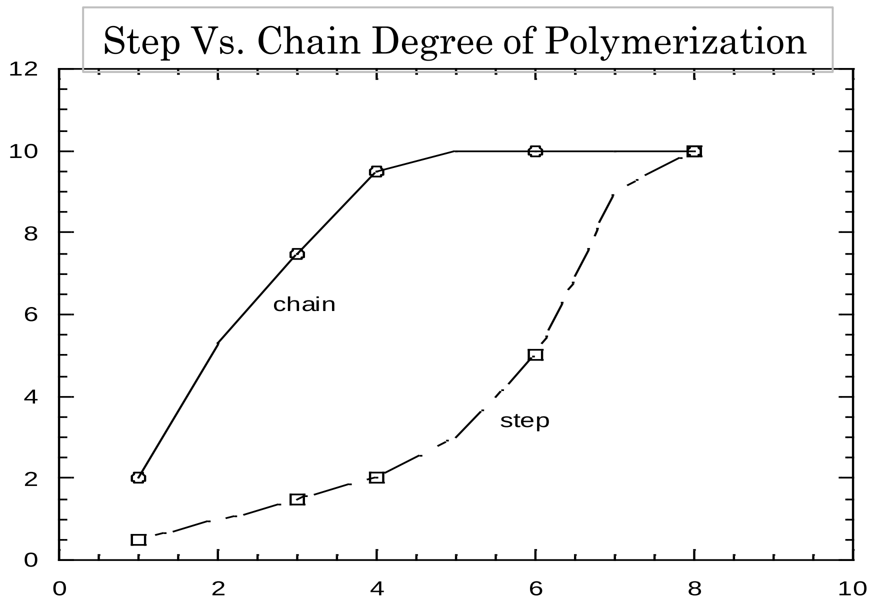
Condensation (step-growth) polymerization



Basic kinetics

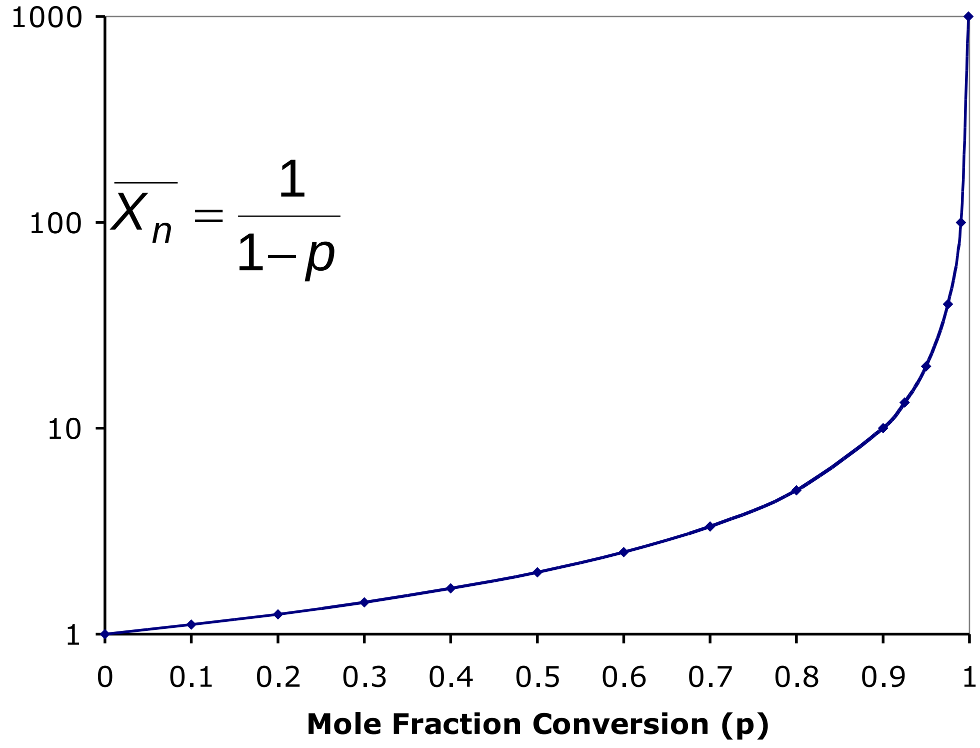
Monomer	+	monomer	$\longrightarrow$	dimer
Dimer	+	monomer	$\longrightarrow$	trimer
Dimer	+	dimer	$\longrightarrow$	tetramer
Trimer	+	monomer	$\longrightarrow$	tetramer
Trimer	+	dimer	$\longrightarrow$	pentamer
Trimer	+	trimer	$\longrightarrow$	hexamer
Tetramer	+	monomer	$\longrightarrow$	pentamer
Tetramer	+	dimer	$\longrightarrow$	hexamer
Tetramer	+	trimer	$\longrightarrow$	heptamer
Tetramer	+	tetramer	$\longrightarrow$	octamer
Pentamer	+	trimer	$\longrightarrow$	octamer
Pentamer	+	tetramer	$\longrightarrow$	nonamer

$$n\text{-mer} + m\text{-mer} \longrightarrow (n+m)\text{-mer}$$



Step-growth

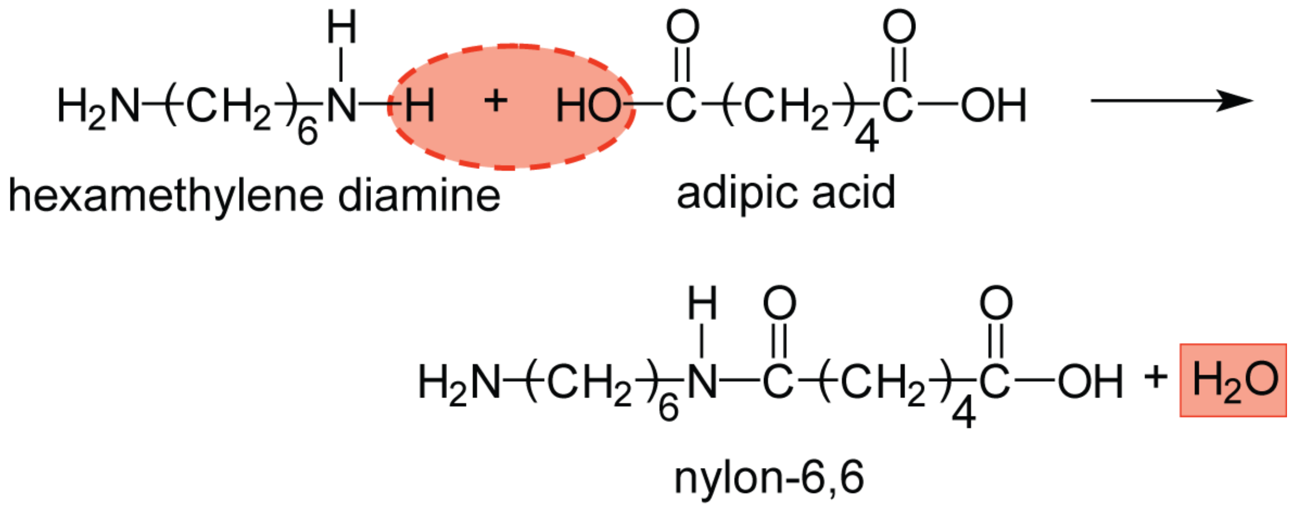
- Because high polymer does not form until the end of the reaction, high molecular weight polymer is not obtained unless high conversion of monomer is achieved.

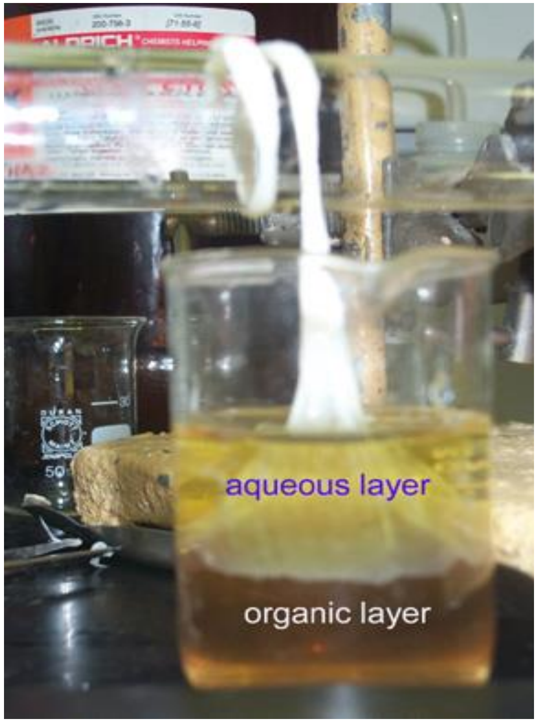


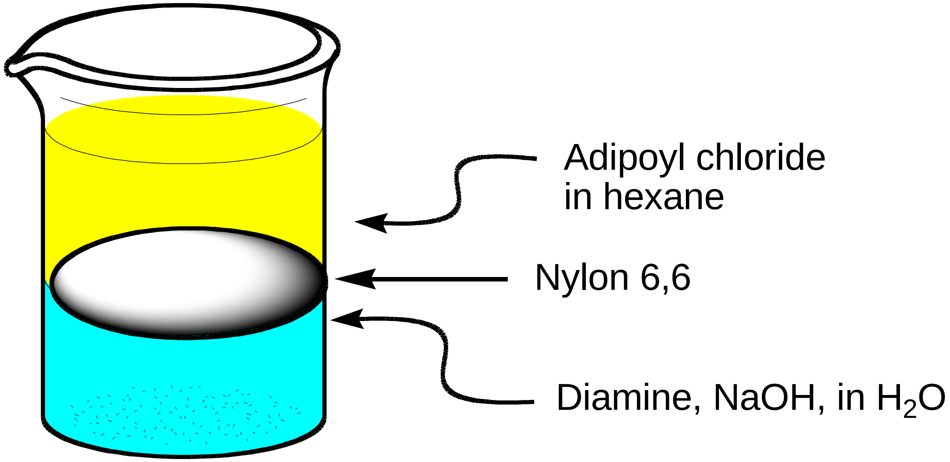
$$\overline{X_n} = \frac{1}{1-p}$$

$\overline{X_n}$ = Degree of polymerization
p = mole fraction monomer conversion

Example

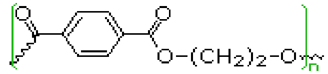
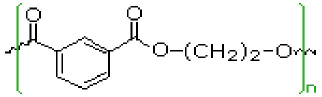
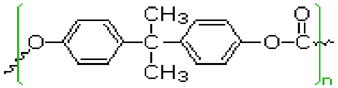
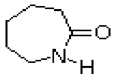
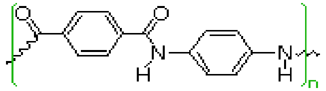
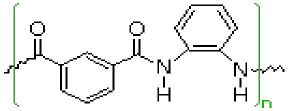
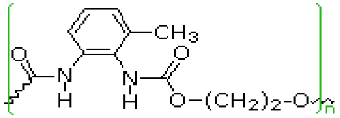
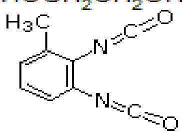






Since the reactants are in different phases, they can only react at the phase boundary. Once a layer of polymer forms, no more reaction occurs. Removing the polymer allows more reaction to occur.

Some Condensation Polymers

Formula	Type	Components	T_g °C	T_m °C
$\sim[CO(CH_2)_4CO\text{-}OCH_2CH_2O]_n\sim$	**polyester**	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	< 0	50
	**polyester** Dacron Mylar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	70	265
	**polyester**	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ $HO\text{-}CH_2CH_2\text{-}OH$	50	240
	**polycarbonate** Lexan	$(HO\text{-}C_6H_4\text{-})_2C(CH_3)_2$ (Bisphenol A) $X_2C{=}O$ (X = OCH_3 or Cl)	150	267
$\sim[CO(CH_2)_4CO\text{-}NH(CH_2)_6NH]_n\sim$	**polyamide** Nylon 66	$HO_2C\text{-}(CH_2)_4\text{-}CO_2H$ $H_2N\text{-}(CH_2)_6\text{-}NH_2$	45	265
$\sim[CO(CH_2)_5NH]_n\sim$	**polyamide** Nylon 6 Perlon		53	223
	**polyamide** Kevlar	para $HO_2C\text{-}C_6H_4\text{-}CO_2H$ para $H_2N\text{-}C_6H_4\text{-}NH_2$	---	500
	**polyamide** Nomex	meta $HO_2C\text{-}C_6H_4\text{-}CO_2H$ meta $H_2N\text{-}C_6H_4\text{-}NH_2$	273	390
	**polyurethane** Spandex	$HOCH_2CH_2OH$ 	52	---

Step vs. Chain Polymerization

Chain Polymerization

- Growth occurs *only* by addition of monomer to active chain end.
- Monomer is present throughout, but its concentration decreases.
- High polymer forms immediately.
- MW and yield depend on mechanism details.
- Chain growth is usually very rapid (seconds to microseconds).
- Only monomer and polymer are present during reaction.
- Usually (but not always) polymer repeat unit has the same atoms as had the monomer.
- narrower distribution; just polymer and monomer

Step Polymerization

- Any two molecular species can react.
- Monomer disappears early.
- Polymer MW rises throughout.
- Growth of chains is usually slow (minutes to days).
- Long reaction times increase MW, but yield hardly changes.
- All molecular species are present throughout.
- Usually (but not always) polymer repeat unit has fewer atoms than had the monomer.
- broad molecular weight distribution in late stages