CHAPTER 5:

1) Step-Growth Polymerization:
  - 2 difunctional monomers
  - forms an intermediate compound with a new functional group

    + intermediate

  - intermediate forms a larger intermediate

    + monomer molecule

  - steps continue until polymer and a byproduct form

Step-Growth examples:

1) polyesters
2) nylons
3) polycarbonates
4) polyurethanes

ex. lactic acid: ester exchange

Step-Growth:

- monomers have 2 reactive functional groups
- polymer backbone is Carbon and usually N or O
- functional groups react without initiator
- can be catalyzed
- often gives off by-product
- intermediates are compounds with 2 reactive functional groups (oligomers)
- polymer develops at a slow rate
- DP and MM increases as reaction proceeds

Step-growth Polymerization:- 3 categories of monomers
`1) 2 monomers with different functional groups
ex: diacid and diol with the byproduct being water
diamine and diacid wioth the byproduct being water
- PETE and nylon 6,6

2) 1 monomer that contains 2 different functional groups
ex: hydroxy acids: lactic acid, amino acids

3) cyclic monomers - cyclic ethers
ex: phthalic anhydride

Polycondensations:
1) melt polycondensation - no solvent used
ex: dimethyl terephthalate and ethylene glycol

2) interfacial polycondensation - using different immisible liquids
ex: nylon

Chain-Growth Polymerization: catonic polymerization
radical polymerization

- think of 1 compound with 1 C-C double bond
- monomer can add only to a reactive intermediate, not to another monomer
- polymer backbone usually contains only carbon atoms
- polymerization proceeds by chain reaction through short lived intermediates (free radical, cation, anion - initiator)
- high polymer is formed very rapidly
- reaction mixture consists only of monomer and high polymer
- MM of polymer formed early in the reaction is approximately the same as that later on - increasing the time increases yield, not MM

A) Free Radical Chain Polymerization: - most prevalent type
free radical is a species having one unpaired electron

Example: polyethylene

1) high pressure (1000-3000-atm)
2) high temperature (100-250°C)
3) radical catalyst - ex. benzoyl peroxide

- all radical chain reaction - 3 steps required

A) Initiation Steps: when trace amounts of radicals are generated by the catalyst

B) Propagation Steps:

C) Termination Steps:

1) Coupling/ Combination

2) Disproportionation

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INDUCTIVE EFFECT:

- the shifting of electrons in a sigma bond in response to the electronegativity of nearby atoms

EDG (**e**lectron **d**onating **g**roups)
  - metals
  - alkyl groups

EWG (**e**lectron **w**ithdrawing **g**roups)
  - Cl, O, N

B) Catonic Polymerization:

- acid (H^+) catalyzed
- effective with electron donating groups
  - methyl, ethyl
- the more groups you have the more stable the cation that is produced

C) Anionic polymerization: (ionic)

- fast
- solvent system
- low temp
- ewg

Dermabond (2-ethylhexyl - cyanoacrylate)

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B) Cationic Polymerization:

- acid (H^+) catalyzed
- effective with electron donating groups
    - methyl, ethyl
- the more groups you have the more stable the cation that is produced
- initiators are often Lewis acids, ex. $AlCl_3$
- ex. isobutylene

C) Anionic polymerization (Ionic):

- usually extremely fast
- carried out in a solvent system
- often at low temperatures
- molar mass is directly proportional to % conversion
- same degree of polymerization (DP)
- molar mass depends on the ratio of monomer to initiator

ex. styrene

Dermabond (2-ethylhexyl α- cyanoacrylate)

Cationic and anionic polymerizations can not terminate by coupling due to like charges and usually don't terminate by disproportionation because they are usually carried out in a solvent system.

'Living' vs 'dead'

Emulsion Polymerization:

- monomer added to an aqueous mixture containing a surfactant (soap) and a water soluble initiator
- colloidial suspension
- ex. latex
  - paints, gloves, adhesives, carpet backing, adhesives

Copolymers:

1) styrene/acrylonitrile	SAN
2) Styrene/butadiene	SBR
3) styrene/acrylonitrile/butadiene	ABS
4) vinyl chloride/vinylidene chloride	saran

Types of Copolymers:

1) Random

2) Alternating

3) Block

4) Graft

- Block: initiating the polymerization of one monomer and then adding an excess of the 2nd monomer

- Graft: made by gamma irradiation of a completed homopolymer chain in the presence of the 2nd monomer. The high radiation knocks hydrogen atoms off the homopolymer chain at random points, thus generating radical sites that can initiate polymerization of the added monomer

<u>Polypropylene:</u>

isotactic

- CH_3 on the same side
- crystalline
- high melting point
- chains are packed together more efficiently - increasing crystallinity
- the greater the crystallinity the better the thermal and mechanical properties, the more resistant to solvents and other chemicals

syndiotactic

- methyl groups alternating front and back

atactic

- random
- soft amorphous polymer
- poor physical and thermal properties

Coordination Polymerization:

- using catalyst of certain transition metal compounds
- electrons of the double bond in the monomer coordinate a complex with a transition metal in the catalyst, influencing the rate of the reaction as well as the stereochemistry during polymerization

ex. ethylene - polymerization at high temperatures & pressure using free radicals produce a highly branched polymer - LDPE

ethylene - polymerized by coordination catalyst gave a denser, less branched polymer - HDPE

Ring Opening Polymerization:

1) ethylene oxide - polyether

2) tetrahydrofuran - polyether

3) caprolactam - polyamide

Dendrimers:

- highly branched - branched so much that it has no main chain
- highly ordered structures
- have reactive groups on outside
- properties dominated by the end groups
- do not entangle
- small molecules can be encapsulated inside

Silicons:

- chain of alternating silicon and oxygen bonds
- use as elastomers - very flexible
- sealants and caulking material