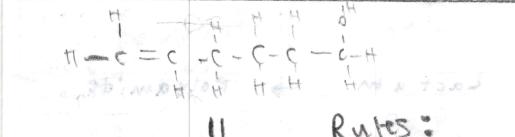


Trees of Materials & Bonding		
Metals	Ceramics	Organics
Metallic Bonding	Ionic bonding	Covalent bonding

Anatomy of Organic Molecule



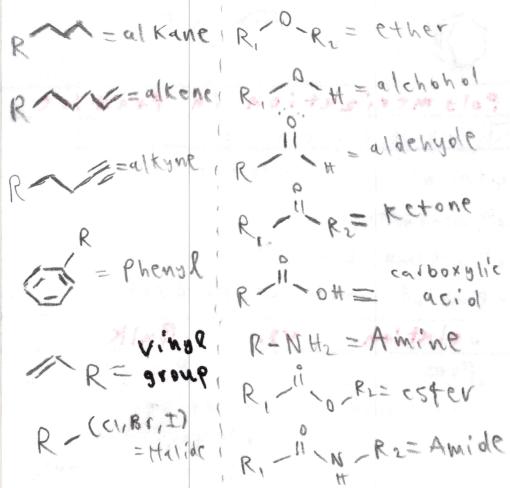
Line/Skeletal Drawing of Molecules



Rates:
 ↓
 1. Denote carbons by points
 2. write explicit if anything but C, H
 3. only write H if functional



Important Functional Groups

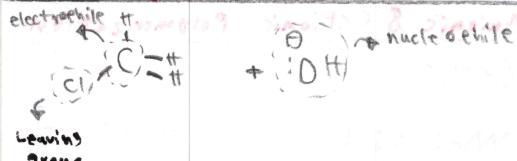


Inter-Molecular Forces

- Hydrogen Bonding (OH, NH)
- Dipole-Dipole ($\text{+x+x+x} (\text{x} \neq \text{C, H})$)
- Aromatic Stacking (aromatic groups)
- Dipole-Induced
- LDF

↳ Relates to Polarity
↳ solubility in (water or oil)

Anatomy of Example organic Rxn



* Factors Affecting Polymer Properties*

- Molecular Weight
- Polydispersity
- composition of Monomers
- Topology
- Method of synthesis/processing

3.034 (2) May 997

Summary Sheet

Polymer Nomenclature

-A-A-A-A-A-A-	Homopolymer Poly A
-A-B-A-B-A-B-A-	Alternating co-Polymer
-A-A-A-A-A-A-	Graft Copolymer
B-B-B	Poly(A-g-B)
B-B-B	Block Copolymer

Polymers: Big Picture

- Polymer chains move via "creep" - sliding of chains past one another

Polydispersity Index (PDI or f)

$$f = \frac{M_w}{M_n}$$

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

↳ M_n = Number average mass

$$M_w = \frac{\sum N_i M_i}{\sum N_i M_i}$$

↳ M_w = weight Average Mass

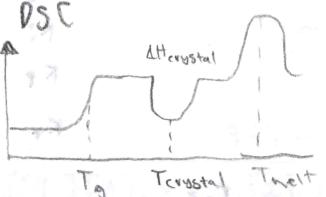
↳ controlling & minimizing dispersity is important

Techniques of Measurement

- Gel Permeation Chromatography

↳ Dispersity, MW

- DSC

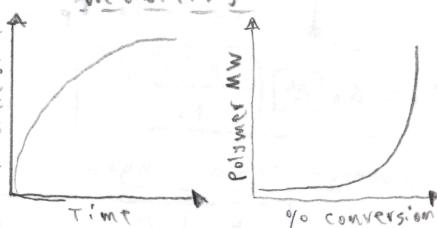


Step-Growth Polymerization

--X-O--Y-C--A--
Homo-Bifunctional Mono mer Hetero-Bifunctional monomer

- Polymer chain length grows exponentially

- Reaction Rate via S-G Polymerization depends on concentration & mobility



* Kinetics of Step Growth *

-A-

P = probability an end group

(\bullet) has reacted

(\circ) unreacted

$$P = \frac{N_A - N_p}{N_A}$$

$$X_n = \frac{N_p}{N_A}$$

$$X_n = \frac{1}{1 - P}$$

$$M_n = (X_n)(\text{MW of Repeat unit})$$

hetero
bi-functional

$$(X_n/2)(\text{MW of Repeat unit})$$

homo
bi-functional

Implications of step Growth

- To make long polymers
↳ reaction must be robust
- f increases w/ growth

$$f = 1 + P$$

Step Growth: Excess Reagent

$$X_n = \frac{1+r}{1+r-2rp}$$

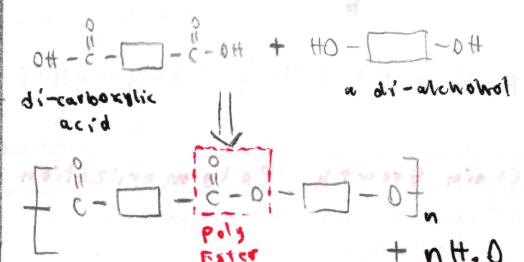
$r = \frac{N_p}{N_x}$

$$M_n = \left(\frac{X_n-1}{2} \right) (\text{MW of Repeat unit}) + (\text{MW}_x - \text{MW}_{LG})$$

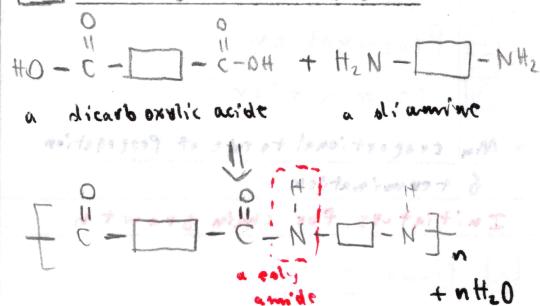
↳ x is in excess

Step Growth: Specific Mechanisms

- Polyesters

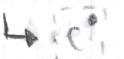


- Polyamides



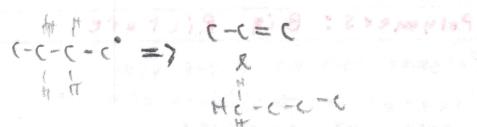
Free Radical Polymerization

- Most Monomers Polymerize using Vinyl Group

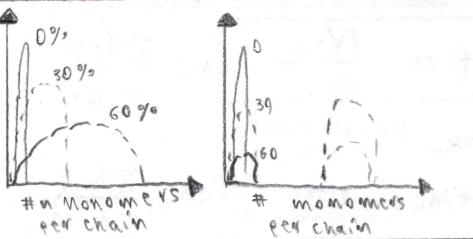


METHODS of Chain Termination

1. Undesirable Side Reaction
2. Chain-Chain Coupling
 - ↳ two radical initiators bond
3. Disproportionation



Step Growth vs. Chain Growth



Kinetics of Chain Growth Polymerization

4 steps:

Reaction Step	Rate constant
1. Decomposition	k_d
2. Initiation	k_i
3. Propagation	k_p
4. Termination	k_t

$$r_i = 2f k_d [I]$$

$$r_p = K_p [M] [P^{\bullet}]$$

f = fraction of radicals that initiate

$$r_t = 2K_t [P^{\bullet}]^2$$

$$[P^{\bullet}] = \left(\frac{f K_d [I]}{K_t} \right)^{1/2}$$

Plugging in for r_p

$$r_p = K_p [M] \left(\frac{f K_d [I]}{K_t} \right)^{1/2}$$

\bar{J} = Average Chain Length

$$\bar{J} = \frac{r_p}{r_t} = \frac{K_p [M]}{2(f K_d [I])^{1/2}}$$

Ring Opening Polymerization



- ↳ ROP opens up a ring into a growing chain

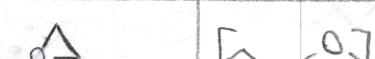
Lactone \rightarrow Poly ester



Lactam \rightarrow Polyamide



Epoxyde \rightarrow Poly-Ether



Ring Opening Metathesis Polymerization

- involves cyclic alkene



Polymerization in Practice

1. Solvent Choice for Solution Phase

- Solubility of components

- Inertness

- Thermal stability

- Ease of retrieving Product

Solution vs. Bulk

Pros

- Easy to control
- Purity
- High Yield
- Lack of solvent
- can mold to shape

Cons

- difficult to purify
- Less control
- Needs to run slowly
- Lot of Solvent

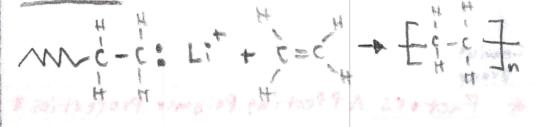
Interface & Emulsion Polymerization

Emulsion

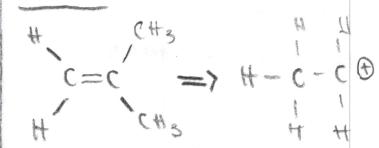
small molecules polymerize in a matrix of solvent

Anionic & Cationic Polymerization

Anionic

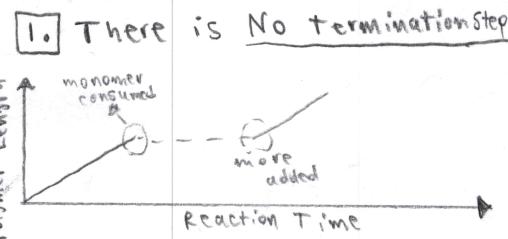


Cationic



Living Polymerization

Key Aspects:



2. $r_p < r_I$

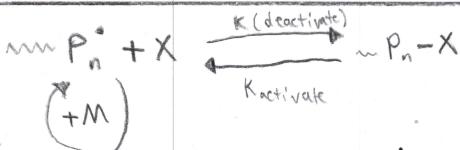
$$r = \frac{[M]}{[I]}$$

"Pseudo-living" Polymerization

Termination is inevitable

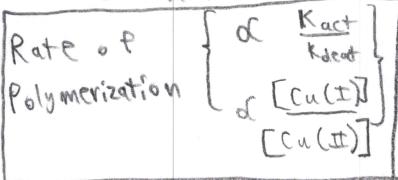
- 1. Must Eliminate Termination as much as possible
- 2. Make sure all grow at same rate

Atom Transfer Radical Polymerization (ATRP)



↳ X is molecular species that can stabilize a radical (usually a halide)

↳ A metal-ligand complex attaches & removes complex



Solubilized Polymers

1. Processing considerations

2. Applications require liquid phase

* Polymer Solubility rules *

- 1. "Like" dissolves "Like"
- ↳ IMF dictate solubility

- 2. Increasing MW Decreases solubility

- 3. Crosslinking decreases solubility

- 4. The rate of solubilization

- Decreases w/ \uparrow MW
- Increases w/ short Polymer Branches
- Decreases w/ long Branches

Thermodynamics of Solubility

$$\Delta G = \Delta H - T \Delta S$$

(-) ? (+) (+)

↳ $\Delta H (+/-)$ depending on IMF

- 1. The longer the polymers, the smaller the entropy increase

Enthalpy of Solubilization

$$\Delta H = \Delta E = \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2$$

↳ ΔH = Enthalpy of mixing

↳ ΔE = internal Energy change

↳ φ = volume fractions of phases
1.82

$$\delta = \text{Solubility Parameters of 1.82}$$

Solubility Parameter

$$\delta = (CED)^{1/2} = \left(\frac{\Delta E_v}{V} \right)^{1/2}$$

↳ δ = Hildebrand solubility parameter

↳ CED = cohesive energy density

↳ ΔE_v = change in internal energy upon vaporization

↳ V = Molar volume of liquid

Hansen Solubility parameter

σ_H - H-Bonding character

σ_P - The Dipole character

σ_D - The LDF character

Polymer soluble if

$$R^2 \geq \left(\sigma_{H,\text{Polymer}} - \sigma_{H,\text{Solv}} \right)^2 + \left(\sigma_{P,\text{Poly}} - \sigma_{P,\text{Solv}} \right)^2 + \left(\sigma_{D,\text{Poly}} - \sigma_{D,\text{Solv}} \right)^2$$

Properties of Dissolved Polymers

• in good solvent Polymers swell

• in bad solvent Polymer contracts

• in terrible solvent Polymer precipitates

* Viscosity depends on dissolution

$$\text{Bad} < \text{Good}$$

Crystallization Driving force

- 1. What IMF Present? \uparrow IMF \uparrow Crystallinity
- 2. Compactness of Monomer? \uparrow \uparrow Crystallinity
- 3. Backbone Flexibility? \downarrow \downarrow Crystallinity
- 4. Regularity of Monomer structure \uparrow \uparrow Crystallinity
- 5. Linear vs. Branching \downarrow Crystallinity
- 6. \downarrow chain, \uparrow crystallinity

$$T_m \propto T_g$$

1. Backbone Flexibility

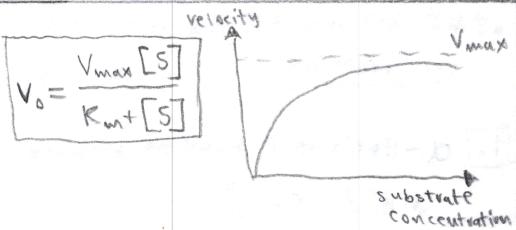
↳ \uparrow Flexible, \uparrow T_g , \uparrow T_m

2. Size of monomer Pendant Group \uparrow size, \uparrow T_g , \downarrow T_m

3. Strength of IMF \uparrow IMF, $\uparrow T_g$, $\downarrow T_m$

Physical effects of crystallinity
Crystallinity, $\uparrow E$, \uparrow Deacity

Enzyme Kinetics

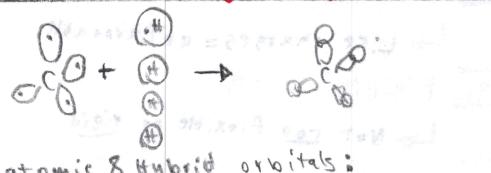


K_m : The $[S]$ where $V_0 = \frac{1}{2} V_{max}$

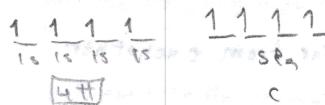
Enzymes most efficient

when $[S] < K_m$

Conducting Polymers



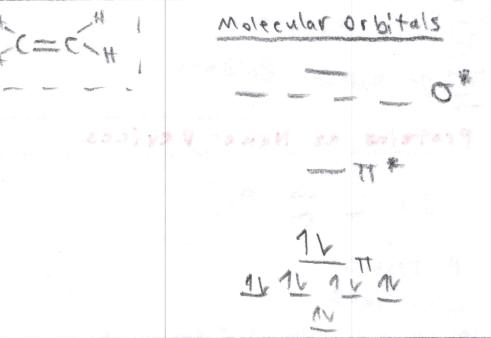
atomic & hybrid orbitals:



Molecular Orbitals:



what Makes a Polymer conductive



As you increase chain length
LUMO \rightarrow lowest unoccupied molecular orbital

HOMO \rightarrow highest occupied molecular orbital

Become smaller \Rightarrow you get a Bandgap

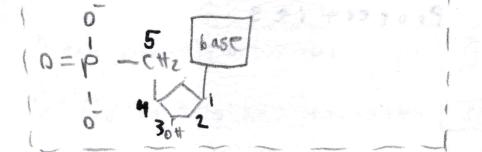
\hookrightarrow in order to be conductive
MUST HAVE CONJUGATED BACKBONE

\hookrightarrow can be altered by doping

Nucleic Acids and Nucleotides

- Store & transmit information
- DNA Monomer:

1. A sugar
2. Phosphate group
3. Nucleobase



- The sugars' carbons are numbered so there is a 3' 5' end

\hookrightarrow DNA written 5' \rightarrow 3'

*Phosphate is always charged
 \hookrightarrow DNA = Poly Electrolyte

Nucleic Acid Terminology

Base = Nucleobase

Sugar+Base = Nucleoside

whole thing = Nucleotide

Oligonucleotide \rightarrow Short synthetic DNA strand (10-100)

Poly Nucleotide \rightarrow Long Repeating String of same Nucleotide

DNA \rightarrow Long string that codes biological info

DNA Properties

- DNA sequences bind in anti-parallel behavior (5' - 3')

Forces that stabilize DNA

1. H-Bonding between Nucleobases
2. Aromatic Stacking
3. Hydrophobic interactions
4. Electrostatic (w/ salt)

\hookrightarrow Duplexes ONLY form when cations present

Naturally occurring variations

1. RNA \rightarrow OH on 2' carbon
2. PNA \rightarrow replaces phosphate/sugar Backbone w/ Polyamide Backbone

Advantages:

- Duplex forms w/o Salt
- Harder to destroy
- Not water soluble

DNA Synthesis

- We make 2 copies of existing strand

Why Use DNA as a Material

- Has just enough diversity to make different forms, but has near-predictable behavior

possible sequences = 4^n / n = # of nucleotides

Duplex Stability

(+) Hydrogen Bonding

(+) Aromatic Stacking

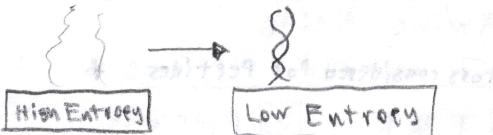
(-) charge-charge Repulsion

Takeaway:

(G-C) \rightarrow contributes more favorably than A-T

Mismatches bring energetic penalties

Entropy



Thermodynamics of DNA Formation

$$\Delta G = \Delta H - T \Delta S$$

At some temperature, the entropic penalty overcomes enthalpic benefit & DNA "melts" or denatures can verify via absorption test

DNA Melting

It's asymptotic relative to length

$$10 \text{ bp} \rightarrow 35^\circ$$

$$20 \text{ bp} \rightarrow 60^\circ$$

$$30 \text{ bp} \rightarrow 70^\circ$$

$$40 \text{ bp} \rightarrow 75^\circ$$

2. improper alignment

\hookrightarrow broadens T_m

3. Base mismatches

\hookrightarrow huge reduction in T_m

4. \uparrow salt concentration

\hookrightarrow T_m increases asymptotically

5. Free Nucleotides

\hookrightarrow decrease in T_m

6. Difference in Solvent

\hookrightarrow decrease in T_m

7. Oligonucleotide concentration

\hookrightarrow increase in T_m w/ concentration

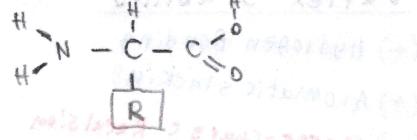
4 classes of organic materials

- 1. Nucleic Acids
- 2. Amino Acids
- 3. Sugars
- 4. Lipids

Advantages of Biomaterials

- 1. better precision than synthetic
- 2. sourcing from nature/Eco-Friendly

* Basic Components of Amino Acid *



Characteristics:

- 1. Polypeptides made of NHC terminus
- 2. COOH & NH₂ usually reactive enough to form peptide bonds

Amino Acids

• 21 Naturally occurring Amino Acids

Factors considered for Peptides: *

- 1. IMF
- 2. Solubility
- 3. Bulkiness
- 4. Reactivity

Hydrophobic Amino Acids

- 1. Alanine
- 2. Valine
- 3. Isoleucine
- 4. Leucine

Properties :

- 1. Point Inwards (away from water)
- 2. Increase Chain Flexibility
- 3. Not Reactive

Hydrophobic(Aromatic) AA's

- 1. Phenylalanine
- 2. Tyrosine
- 3. Tryptophan

Properties:

- 1. Point Inwards
- 2. Decrease Flexibility
- 3. Have Aromatic stacking IMF

Hydrophilic Amino Acids

- 1. Serine
- 2. Threonine
- 3. Asparagine
- 4. Glutamine

Properties :

- 1. Point Outwards
- 2. Decrease Flexibility of chain
- 3. Engage in H-Bonding
- 4. Have greater reaction Potential

3.034 Summary Sheet # 2

Charged Hydrophilic AA

- | Positive | Negative |
|--------------|------------------|
| 1. Arginine | B. Aspartic Acid |
| 2. Histidine | 2. Glutamic Acid |
| 3. Lysine | |

Properties :

- 1. Point outwards (toward water)
- 2. increase Chain Flexibility
- 3. Engage in Electrostatic Interactions
- 4. Have great Reactivity

* Special AA *

- 1. Cysteine → Di-Sulfide Bridges
- 2. Selenocysteine → very uncommon
- 3. Glycine → smallest possible R-Group
- 4. Proline → very rigid

Charge State of Peptides

* when is it in charged state & when neutral

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^+ + \text{H}_3\text{O}^+$$

$$K_a = \frac{[\text{A}^+][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$\text{pK}_a = -\log_{10}(K_a)$$

smaller pK_a = more likely to give up H⁺

Larger pK_a = more likely to take up H⁺

Characteristic pK_a values

- 1. C terminus → 2
- 2. N terminus → 9-10
- 3. charged AA side groups → each has a pK_a

PI → Iso Electric Point

→ pH value at which net charge of peptide is zero

Procedure to find:

1. ID all pK_a of Molecule
2. Find 2 Most central pK_a's
3. PI is avg of those 2

1° Structure = Amino Acid sequence

Key Point: Proteins have specific structure/ Properties b/c they have very specific Amino Acid sequences

2° Structure = short range interactions

• IMF between AA can lead to local ordering

1. α -Helix → H-bonding between "N-H" & "C=O"
(AA_n) (AA_{n-3,4})

Stability Factors:

- 1. Steric Bulk of R-Groups
↳ Less Bulky = More Favorable
- 2. Charge state of R Groups
↳ Like charges = unfavorable
- 3. Rigidity of AA
↳ Not too flexible or rigid

2. B-Sheet → H-Bonding between 2 AA far from each other
↳ Same factors effect stability

Key Points:

- IMF happen spontaneously
- More likely to appear when R groups don't interfere

3° - Long Range Interactions

- 1. Hydrogen Bonding
- 2. Hydrophobic Interactions
- 3. Salt Bridge
- 4. Di-Sulfide Bridges

Proteins as Nano-Devices



P = Protein
L = Ligand

PL = Protein-Ligand Complex

$$K_d = \frac{[\text{P}][\text{L}]}{[\text{PL}]}$$

$$\Theta = \frac{[\text{L}]}{[\text{L}] + K_d}$$

w/ cooperativity → where binding

PROMOTES further binding

Enzymes

1. Enzymes bind to substrate via tailoring IMF

2. IMF must STABILIZE intermediate

3. pH can destabilize wrong substrate can destabilize

Binding Site

* Calculating Energy of DNA Hybridization

* See End of LN 20

- Add Gibbs Free energy of terminal base pairs
- Add up Gibbs of every nearest neighbor sequence

Advantages of DNA as Material

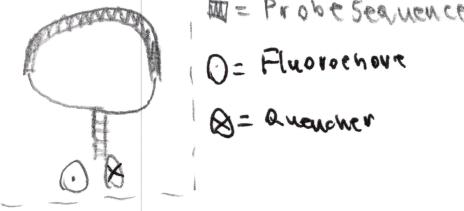
- Bio Compatability
- Highly Programmable
- Molecularly Pure

Anti-Sense Gene Therapy

- Selectively destroy RNA that code for diseased proteins

DNA-Based Sensor

- Has to target specific nucleic acid sequence
- High specificity
- Has to have on/off ratio



- When Target absent, Stem closed, F Fluorescence quenched
- Loop on top opens up F Fluorescence not Quenched

DNA Chips used for Multiplexed Arrays

DNA NanoTechnology

- single stranded = highly flexible
- double stranded = rigid

* Build several motifs that allow for 2D or 3D Bending

DNA tiles must have:

- rigid sections → repeatable shape
- "sticky" ends → that allow for tiling

Key Hypothesis: Most stable structure will maximize # of duplex DNA connections between particles

91d-42 430pm * Cinnage H 638

To 45' above H 638
Cinnage H 638 0.37g/m³
Cinnage H 638 0.37g/m³

water level H 638 to 639.3 calculated

2018 9 22 3 (AMM 2)

10000 JSS reading 76.2m

calibration reading 76.2m

10000 JSS reading 76.2m
calibration reading 76.2m

calibration reading 76.2m

calibration reading 76.2m