



Pages 5-9

Basic Definitions

Soronomous **Macromolecules**: Large Molecules composed of many repeat units derived from monomers
Macromolecule: Macromol, not molecule of repetitive structure
Oligomer: Low-molecular weight polymer

↳ no clear distinction into field between polymer and oligomer
↳ Generally: Species with MW between several hundreds to several thousands = oligomer
Examples: Plastics, Rubbers, Proteins, Cotton, Silk, wool, Sugars, DNA

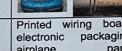
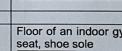
Special Types of Polymers

Poly saccharides: Important polymer materials found in food + living systems
Nano composites: Small amt. Filler/additive mixed with a polymer → small scale applications
Supramolecular Polymers: Self-assembly, bonded with Hydrogen or Metathesis bonds (polymers generally covalent)
↳ Examples: Stimuli-responsive gels which exhibit property change upon application of a stimulus
OLEDs: Highly conjugated electroluminescent polymers → could replace liquid crystal displays (LCDs)
↳ Organic Light Emitting Diodes as they provide ↑ performance & ↓ cost
Color-changing: Change w/ stress, usually visible under UV
Functional Polymers: Usual Attributed properties, but certain functions are selectively enhanced
↳ **Attractive Properties**: Light weight, good mechanical props, toughness, and excellent processability
Kevlar: Structure → very strong! 5x stronger tested @ = weight
↳ ability to spin into fibers very attractive
Ultra high MW PE (UHMWPE): Special Synthesis needed
↳ **Gel-spun**: Forces molecules to align along a direction, greatly strengthens its structure
Polybenzoxazoles: Can create stronger fibers than UHMWPE, but environmentally sensitive
Spiders silk: Highest specific strength known to all materials. can only get close in lab!

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Common Polymer Applications in the Household

Polymer	Application examples	Polymer	Application examples
Thermoplastics Amorphous Polymers		Thermoplastics Amorphous Polymers	
Polystyrene	Cups, styroform packaging,  	Poly(vinyl chloride)	Shoes, hose, toys, raincoat, pipes     
Poly(methyl methacrylate)	Window materials, contact lens, optical fiber, photoframe  	Polycarbonate	Helmet, CD, headlight cover   
Semicrystalline Polymers		Semicrystalline Polymers	
High density polyethylene	Pipe, paper, rope, shampoo container  	Poly(4-fluoroethylene)	Coating of flying pan, lubricating support, 
Low density polyethylene	Plastic bags, film, paper, wire coating  	Polyamides	Bearing, gear, bolt, pipe, fishing rod, fiber, rope, stockings  
Polypropylene	Film, washing liquid container, bumper, food container  	Poly(ethylene terephthalate)	Bottle, films for condenser, magnetic disk   
Polyoxymethylene	Gear, sporting goods  	Poly(lactic acid)	3D printing utensils 

Thermosets		Thermosets	
Epoxy resins	Adhesive, automotive and aerospace parts, composites 	Phenolic resins	Electric devices, decorative panel, composites 
Melamine resins	Decorative coating, food container, electrical devices 	Unsaturated polyester resins	Automotive parts, composites 
Bismaleimide resins	Airplane parts, high temperature application 	Benzoxazine resins	Printed wiring board, electronic packaging, airplane parts 
Elastomers		Elastomers	
Polybutadiene	Automotive tire 	Polyurethane rubber	Floor of an indoor gym, seat, shoe sole 
EP rubber	Radiator hose, window seal, roofing materials 	Silicone rubber	Sealing material, medical flexible tube 
Natural rubber	Automotive tire, support of an engine, rubber band 		

Commercially Used Copolymers

Synthetic Polymers

Polymers to Remember

Recycling Numbers & Associated Polymers

Recycling number	Polymer	Recycling number	Polymer
	Poly(ethylene terephthalate)		Polypropylene
	High density polyethylene		Polystyrene
	Poly(vinyl chloride)		Other
	Low density polyethylene		

↳ Good to memorize as they are encountered so frequently in everyday life

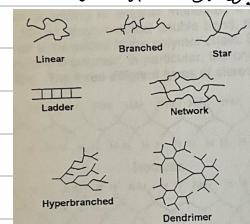
- Poly + "name of monomer" despite polystyrene not reporting styrene's structure.
 - ↳ Common and won't cause too much confusion, but newer polymers vary with polymerization techniques...
 - Molecular Weight : Sum of all atomic weights that comprise the molecule. **Unitless**
 - ↳ Need to use molecular weight distributions to describe larger molecules
 - $M_N = \frac{\sum N_x M_x}{\sum N_x}$
 - $M_w = \frac{\sum w_x M_x}{\sum w_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$
 - $M_z = \frac{\sum N_x M_x^z}{\sum N_x M_x^2}$
 - Polydispersity index measures breadth of distributions of the molecular weights in a polymer

$$PDI = \frac{M_w}{M_N}$$

Always greater than 1

Method	Type	M.W. type	MW range
Colligative properties		Mn	
Boiling point elevation	Absolute	Mn	$< 10^4$
Freezing point depression	Absolute	Mn	$< 10^4$
Vapor pressure lowering	Absolute	Mn	$< 10^4$
Osmotic pressure	Absolute	Mn	$2 \times 10^4 - 10^6$
Terminal group concentration	Absolute	Mn	$< 10^4$
Light scattering	Absolute	Mw	$10^4 - 10^8$
Sedimentation	Absolute	Mw, Mz	$10^2 - 5 \times 10^6$
Intrinsic viscosity	Relative	Mv	$10^3 - 10^8$
Size exclusion chromatography(SEC)	Relative	Mn, Mw, Mz	$10^2 - 10^7$

Graft. - AAAA AAAA AAAA -
B B B B B B B B



- Thermo plastics: softens + liquifies upon heating
 - Thermo sets: become permanently solid upon heating

Typically Cross-linked \rightarrow Usually thermally and chemically resistant

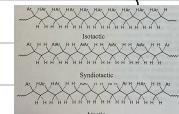
 - Structural Isomers

		
Linear	Branched	Star

 - cross-links: when polymers covalently

- cross-linked: when polymers covalently linked together @ non-end points
- Stereo Isomers:

- After the Polymers are usually amorphous



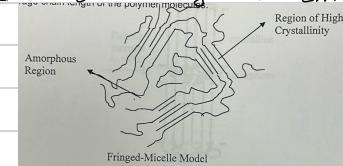
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- Semicrystalline nature of polymers: Crystal Complements lead to crystalline regions dispersed within amorphous material. Misalignment of chains creates these amorphous regions.

↳ Degree of crystallinity can vary from completely amorphous to 95% crystalline

- Fringed-micelle model: small cryst. regions with precise chain alignment embedded in amorphous

*Crossed
micelles* matrix of randomly oriented molecules. As shown to the right. Possible for one polymer chain to pass through several micelles

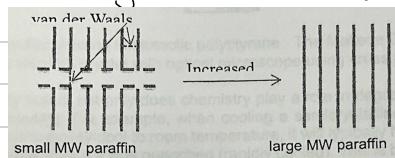


Fringed-Micelle Model

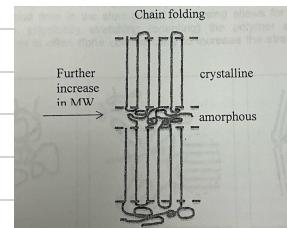
- Chain Folded Model: Molecular chains in a platelet themselves → Folds occurring on the faces of the platelet. Avg Platelet thickness much less than avg. chain length of polymer molecule.

→ As chain length ↑, packing changes. Long-chain molecules develop metastable

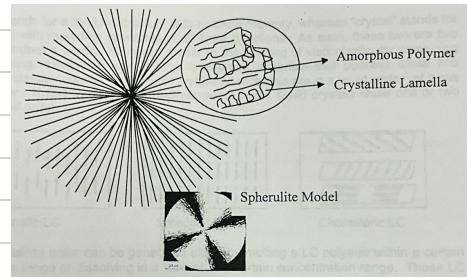
- Combining two above models: Amorphous



Regions between two cryst. regions, where there is no ordered packing



- Spherulite Model: Lamellae (ribbon-like chain-folded crystallites) radiate from the center outward. Separated by an amorphous material. On the right, a single spherulite grows in isotactic polystyrene. Maltese Cross pattern seen by observing crystal with optical microscope using cross polarizer.

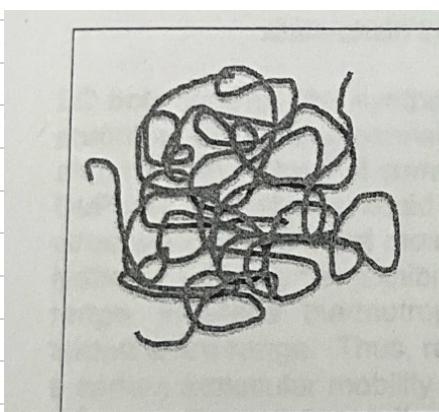


• Cooling a semi-crystalline polymer from melt → slow cooling = more crystallinity (as opposed to quenching)

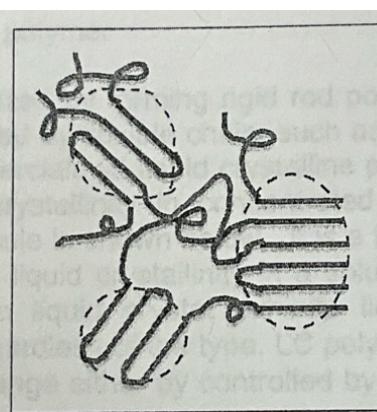
↳ due to excess thermal energy + time allows for stable crystal formations

• Physically stretching, or orienting, the polymer can induce crystallization.

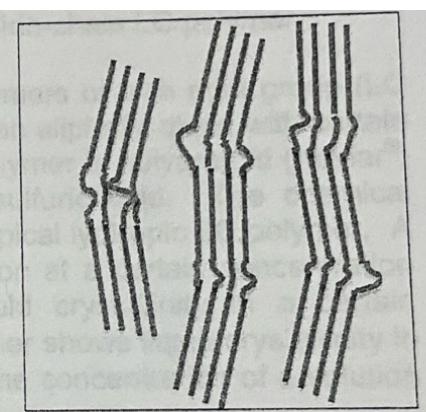
↳ often done commercially to ↑ strength of product



Amorphous



Semicrystalline polymer



Semicrystalline polymer

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Liquid: Random Structure with no order memory

Crystal: A structure with repeating structures in all 3 directions

> Opposite end opposing ends

Liquid Crystalline: Molecules in liquid states yet it has some order.

↳ show one or two dimensional order



→ Generated by melting an LC polymer within a certain range

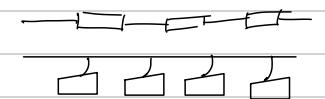
(Thermotropic LC Polymers)

Regardless of type LC polymer shows liquid crystallinity in a certain molecular mobility range.

→ Generated by dissolving in a solvent & a certain conc. range (Lyotropic LC Polymers)

Cholesteric LC is used for computer/TV monitors w/ switches on/off with an electric field

{ LC chromophores placed in the main chain of polymer → LC polymers
 ||
 placed in the side chain → side-chain LC polymers



→ Can be synthesized by forming rigid rod polymers or with rigid group

Connected by flexible chains
Sustaining aliphatic chain with certain chain length

Thermotropic Polymers often show multiple LC transitions

↳ Crystal-to-smectic, smectic-to-nematic, nematic-to-isotropic transitions can often be observed in a single differential scanning calorimetric (DSC) thermogram

LC polymer advantages

• lower viscosity in LC state compared to non-LC state

• Ease of molecular orientation for ↑ mechanical strength

↳ Used to manufacture Kevlar fiber for bullet-proof jackets

It has been difficult to use 'green' polymers as it was more expensive than petroleum-based alternatives

Bio-polymers

↳ Biomaterials study / Focus on tree specifically

→ polynucleotides (DNA/RNA), polysaccharides (cellulose, chitin, starch, etc.), and polyproteins (collagen, glutens, etc.)

↳ Many others synthesized from naturally occurring monomers

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Class	Polymer	Class	Polymer
Animal base polysaccharides		Lipids	
	Chitin/chitosan		Acetoglycerides / waxes / surfactants
	Hyaluronic acid		Emulsan
Bacterial base polysaccharides		Polyphenols	
	Cellulose		Humic acid
	Curd lan		Lignin
	Dextran		Tannin
	Gellan	Proteins	
	Levan		Collagen / gelatin
	Polygalactosamine		Elastin
	Xanthan gum		Poly(amino acid)
Fungal polysaccharides			Silk
	Elsinan		Soy, wheat gluten, casein
	Pullulan		Serum albumin
	Yeast glucans		
Plant base polysaccharides			
	Agar		
	Alginate		
	Carrageenan	Others	
	Cellulose		DNA/RNA
	Guar gum etc.		Natural rubber
	Pectin		Poly(γ -glutamic acid)
	Starch		Shellac
	Konjac		

↳ Recent Progress: Attempts to produce new polymers from bio-based monomers such as poly(lactic acid) but do not naturally exist

Consider the rough representation

Representative Properties

Polymer	Melting point (°C)	Elongation at break at R.T (%)	Tensile strength (MPa)	Flexural modulus (GPa)
Poly(lactic acid)	165	5	50	—
Thermoplastic starch resin	150	272	12	0.24

Explaining the 12 Green Chem Principles

- Prevention**
It is better to prevent waste than to treat or clean up waste after it has been created.
- Atom Economy**
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Less Hazardous Chemical Syntheses**
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- Designing Safer Chemicals**
Chemical products should be designed to effect their desired function while minimizing their toxicity.
- Safer Solvents and Auxiliaries**
The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- Design for Energy Efficiency**
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- Use of Renewable Feedstocks**
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- Reduce Derivatives**
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- Catalysis**
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- Design for Degradation**
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- Real-time analysis for Pollution Prevention**
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- Inherently Safer Chemistry for Accident Prevention**
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Twelve Principles of Green Chemistry

- Prvention
- (vii) Use of Renewable Feedstocks
- Atom Economy
- (viii) Reduce Derivatives
- (ix) Less Hazardous Chemical Syntheses
- (x) Catalysts
- Designing safer chemicals
- (xi) Design for degradation
- Super solvents and Auxiliaries
- (xii) Real-time analysis for pollution prevention
- Design for Energy Efficiency
- (xiii) Inherently Safer Chemicals for Accident Prevention

Explained in detail
to the right

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Ways to Improve Sustainability

- Use Naturally renewable resources
- Reuse already produced materials
 - ↳ these plastics are the obvious choice \rightarrow reprocessing

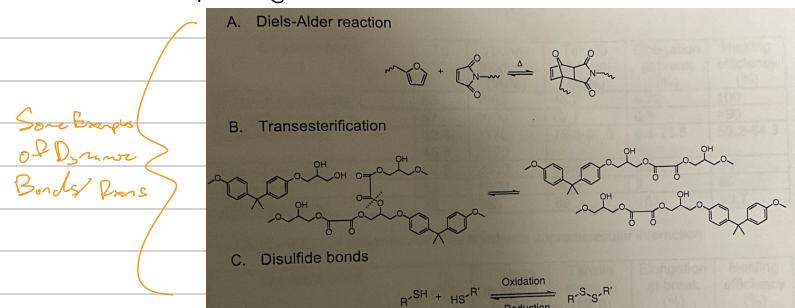
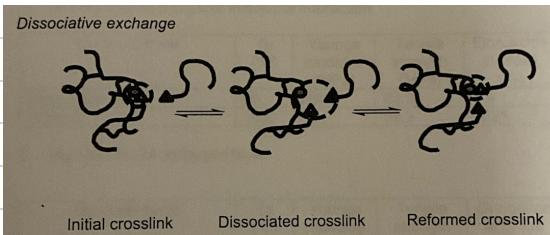
Reprocessing of Thermoplastics

- Been done for many years, though in different amounts
- Difficult as it's hard to produce recycled materials that are as good quality as the original
- Additives given to many polymers, which we lack \rightarrow the recycled waste
 - ↳ If monomers can be recovered from the other polymerized products properties can be reproduced
- Even in ideal recycled conditions, still bad due to energy costs and random chain scission
- Polymers which can degrade via a unzipping mechanism favored \rightarrow produces monomer products
 - ↳ Such as: polyisobutylene and polymethylmethacrylate

Microbials look at to selectively consume certain polymers

Vitamins

- Ludwik Leibler came up with a producible recyclable thermosetting polymer
- Uses dynamic bonds as part of the main chain of cross-linked networks
 - ↳ Dynamic bonds are broken and reformed depending on temp.
- Bonds formed in vac temperatures broken during reprocessing under heat \rightarrow cooled then usable



Examples of Properties of Materials with Dynamic Bonds found on pp. 29

Biodegradable Polymers

(!) Bio-polymers: Found in nature, contain chemical groups which bacteria decompose

(!) Synthetic Biodegradable: Designed to accelerate bacterial decomposition

- Major of Biodegradable polymers degrade aerobically and cannot dissolve w/o oxygen!

↳ Polyhydroxyalcohols can degrade either aerobically or non-aerobically



- ✓ Can Decompose quicker than petroleum based polymers
- ✓ Energy efficient synthesis
- ✓ Rescues non-renewable fossil fuel

- ✗ Potential contaminants of pesticides and herbicides
- ✗ Natural degradation is not efficient, need Composters which are limited in some places
- ✗ More expensive products than petroleum

Microplastics water transports readily

- Debris with diameter < 5 mm and micromotes
- Can be found anywhere from water from plate decomposers to wind, dust and table salts
- Can be produced via chain scission by UV radiation, mechanical grinding (tires), and microbial ingestion

Def: Microbials = microorganisms like bacteria, protozoa, fungi, algae, etc.

Exercise 1

Including Oligomers

1. (A) Colligative Property Measurements only useful for small MW polymers, but of limited value for large MW polymers.

✓(B) I Agree

2. (A) Poly(Methyl Methacrylate)
 (B) Phenolic Resin
 (C) Unsaturated polyester
 (D) Poly(Ethylene-co-propylene)
 (E) Syndiotactic polystyrene
 (F) Atactic Polystyrene
 (G) Epoxy resin
 (H) Polymethylsiloxane

Thermoplastic

Thermoset

Thermoset

Thermoplastic

Thermoplastic

Thermoplastic

Thermoset

Thermoplastic

30°C 20,000

40°C 30,000

30°C 60,000

$$M_N = \frac{\sum N_x M_x}{\sum N_x}$$

$$M_z = \frac{\sum N_x M_x^2}{\sum N_x M_x^2}$$

$$M_w = \frac{\sum W_x M_x}{\sum W_x}$$

$$PDI = \frac{M_w}{M_N}$$

$$W_x = N_x M_x$$

$$\boxed{M_z = 50,000}$$

4. (A) = alternating copolymer → C, B
 (B) = Random copolymer → C
 (C) = X-Y Di-block copolymer → A
 (D) = X-Y g-p-t copolymer → A

5. (A) Cross-linked
Chains covalently bonded
to or another to create a
network. Crossed Loops
must exist



(B) Long Chain branching
Long chains leave
main chain of polymer
structure

Chains so long can't
be distinguished from
main chain

(C) Syndiotactic Polymer
Polymers main chain has
Red groups which alternate
So iSOP is trans diene



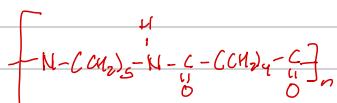
This can crystallize

6. (A) Main chain LC: Chromophores placed in main chain can form stronger polymers
 Side-chain LC: Chromophores placed along side chains of PP transomers
 (B) LC molecules less viscous than isotropic ones as molecules more
together creating less friction
 (C) Thermotropic ~~Forms~~ under temp conditions. Lyotropic Forms under Concentration
'Shows LC state'

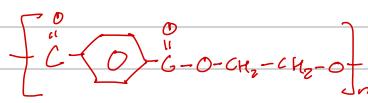
7. M_n tells us the tensile strength
 M_w tells us the viscosity
 M_z tells us precipitation

- A = Absolute Z →
 B = Relative Z →
 (A) Chromotropes D. Terni Group Conc. A
 (B) Osmotic Pressure A. E. Intrinsic Viscosity B
 (C) Light Scattering A. Intrinsic Viscosity B. Size
 Exclu Chromo. (SBC) no 12

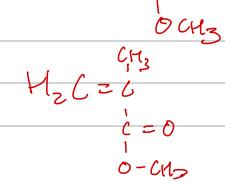
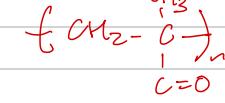
8. (A) Nylon-6,6



(B) PBT poly(Butylene terephthalate)



C. Poly Methyl Methacrylate



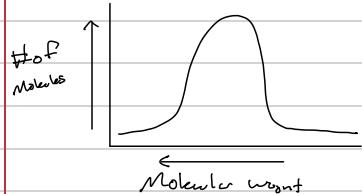
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Key Points for Analysis:

- (i) Pure Sample
- (ii) Optimize signal-to-noise ratio

Size Exclusion Chromatography (SEC)

- Also Known As: Gel permeation chromatography (GPC)
- Most widely used technique for characterizing MW and MW distribution
- Pump Polymer solution through column of packed porous polystyrene gel
 - Gels must be compatible with solvent, and cannot interact w/ the polymer
- Solvent goes through, with larger ones passing through quickly and small going through slowly as they are "caught"
 - The generated curve can be analyzed to solve for M_w , M_n , and M_z



Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry

- Abbrev. MALDI-TOF MS
- Used to determine absolute MW of polymers
- Result interpretation straightforward as unfragmented molecules can be determined
- Only works well for samples with PDI < 1.2
 - ↳ usually used to analyze collected SEC samples as they already have low PDIs

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Vapor Pressure

- Used to determine M_n as well

↳ Experimental Procedure Summarized at bottom of pg. 33

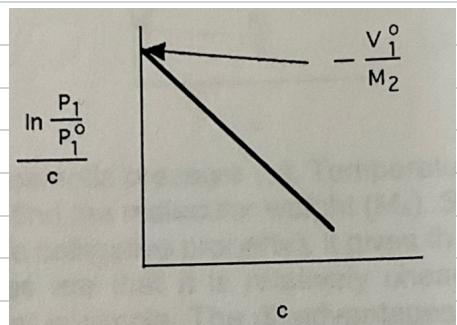
- Condensed vapor on polymer thermocouple creates a temp. increase due to the heat of condensation.

- Vapor pressure lowering is directly related to the temperature increase

↳ Relationship allows Molecular weight to be found

- In the Plot to the Right, P_1^0 is the vapor pressure of the pure solvent, c is the concentration, V_1^0 is the molar volume of the solvent, and M_2 is the number average molecular weight (M_n)

$$\Rightarrow V_1^0 = \frac{\text{mass}}{\text{density}} \Leftarrow \text{of the solvent}$$



- Advantages: Gives a direct number average molecular weight value

- Disadvantages: Molar volume must be calculated or density of polymer must be measured.

Limited to polymers with molecular weights less than 20,000 g/mol

Osmotic Pressure

Polymer solution

- Solvent separated by pure solvent via a semi-permeable membrane

↳ Membrane permeable by solvent, but not to polymer

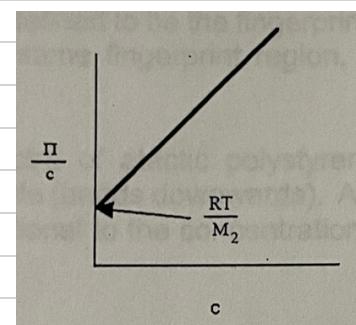
- Chemical Potential Driving Force pushes until hydrostatic pressure is high enough to stop the flow of the solvent (equilibrium)

- Knowing Concentration c , osmotic pressure Π , Temperature T , and gas constant R , the intercept can be used to find M_n

- Reacts M_n as this method is sensitive to H of molecules, which is a colligative Property

- Advantages: Relatively cheap, gives absolute molecular weight, and measurement is simple

- Disadvantages: Takes a long time to reach equilibrium and the semi-permeable membrane is rarely available



Infrared Spectroscopy

- A technique used to identify the chemical composition of polymers

- IR Light ranges from 2.5-50 mm, 4000-200 cm⁻¹

↳ Has enough energy to excite molecular vibrations to higher levels

- Molecules which are always moving, absorb IR radiation when their vibrations are at the same frequency as the incident light

- Stretching: Change in bond length between two atoms

↳ Designated symmetric or asymmetric (asymmetric takes more energy)

- Bending: Change in bond angles of atoms in a molecule

↳ Requires less energy than stretching motions

- Molecules only absorb IR light if they can change their dipole moment

↳ Molecules like N_2 and H_2 do not absorb IR

- Groups of atoms have absorption bands @ or near the same wavenumber, regardless of the rest of the molecule structure
↳ These functional groups drastically improve recognizability

- Wavenumber: Common unit for IR, defined as reciprocal of wavelength with units cm^{-1}

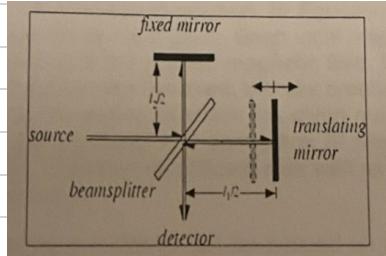
- Foraging of IR bands characteristics of specific types of chemical bonds

↳ Makes IR useful in identifying organic and organometallic molecules

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IR Spectroscopy Combined w/ Raman to analyze chemical structure

- Traditionally use either a narrow slit or grating to select specific frequency radiators.
- ↳ Leads to the loss of tremendous of the energy source!!
- FT-IR doesn't use dispersions -> higher energy throughput (FT-IR = Fourier Transform)
- Acquisition Advantages:** FT-IR's energy transport advantage
- Interferometer usage -> higher frequency accuracy
- Compton's Advantage:** FT-IR's frequency accuracy advantage
- Many data points are collected to obtain unique information
- Fallgut's advantage: Multiplex advantage of FT-IR
- Computer is necessary for FT-IR, but is not an intrinsic advantage!



Micelson Interferometer

- Inverse Fourier transform applied to convert time-domain interferogram to a frequency-domain single beam IR spectrum.

$$\text{Transmittance: } T = \frac{I}{I_0} \quad \text{or} \quad \text{Absorbance Spectrum: } A = -\log T = \log \left(\frac{I_0}{I} \right)$$

- Absorbance intensity is linearly proportional to the concentration of the sample as per Beer-Lambert law

$$A = abc; a: \text{extinction coeff}, b: \text{Sample thickness}, c: \text{Concentration}$$

Nuclear Magnetic Resonance Spectroscopy (NMR)

- Studies properties of nuclear spin in a magnetic field
 - ↳ extremely versatile and powerful probe of atomic scale structure
- Useful in determining information on local environment of nuclei (molecular shapes, degrees, and conformations)
- ^2H and ^{13}C have odd # of protons and neutrons -> magnetic dipole moment present
- ¹H and C are heavily studied due to abundance of H and C

$$\nu = 2\pi\omega \cdot B \quad (1) \quad \text{and} \quad B = H_0(1-\sigma) \quad (2)$$

ν : dipole moment of nucleus, B : local magnetic field around nucleus, H_0 : applied magnetic field, σ : chemical shift factor

- Process described in depth on page 37
- Different functional groups provide a different electromagnetic environment -> Unique chemical shift
- ↳ Makes NMR useful for chemical identification and determining higher scale structure (tautomers and conformers)
- Peak splitting can be noted on NMR spectra -> gives information on # of neighbors a given nucleus contacts
- Splitting follows the "N plus one" rule -> # of peaks seen for each type of hydrogen is equal to the # of hydrogens on adjacent nuclei (N) plus one.

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Nuclear Magnetic Resonance Spectroscopy (NMR) Continued