



# 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

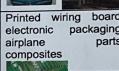
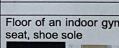
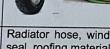
## Special Types of Polymers

**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!

# Pages 10 - 19

## Common Polymer Applications in the Household

Polymer	Application examples	Polymer	Application examples
<b>Thermoplastics</b> Amorphous Polymers		<b>Thermoplastics</b> 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 decorative composites devices, panel, parts. 
Melamine resins	Decorative coating, food container, electrical devices 	Unsaturated polyester resins	Automotive composites, parts. 
Bismaleimide resins	Airplane parts, high temperature application 	Benzoxazine resins	Printed wiring board, electronic packaging, airplane composites 
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		

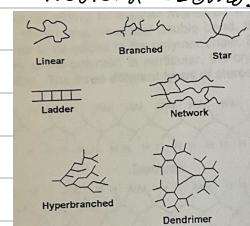
↳ Good to memorize as they are encountered so frequently in everyday life

- Poly + "name of monom" despite polystyrene not reporting styrene's structure.
    - ↳ Common and won't cause too much confusion, but never 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
  - $M_N = \frac{\sum N_x M_x}{\sum N_x}$
  - $M_w = \frac{\sum w_x M_x}{\sum w_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$
  - $M_z = \frac{\sum N_x M_x^3}{\sum N_x M_x^2}$
  - $M_z > M_w > M_N$
  - 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: - A A A A A A A A A -  
B B B B B B B B B B



- Thermo plasti~~s~~c: softens + liquifies upon heating
  - Thermo sets: become permanently solid upon heating

Typically  $\xrightarrow{\text{Cross-linked}}$   $\hookrightarrow$  usually thermally and chemically resistant

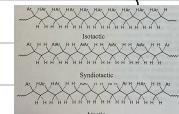
  - Structural Isomers

Linear	Branched	Star

  - cross-link~~ed~~ge: when polymers covalently

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

- After the Polymers are usually amorphous



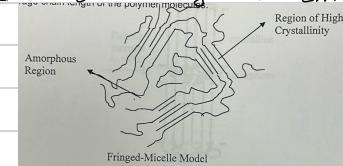
## Pages 20-22

- 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

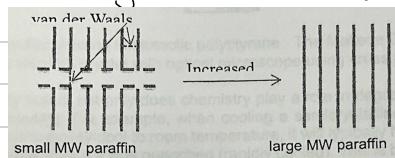


Fringed-Micelle Model

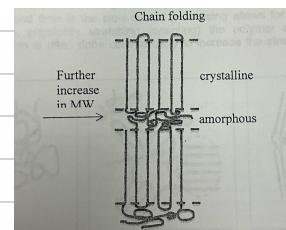
- Chain Folded Model: Molecular chains in a platelet themselves → Folds occurring on the faces of the platelet. Avg Platelet thickness much less than avg. chain length of polymer molecule.

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

- Combining two above models: Amorphous

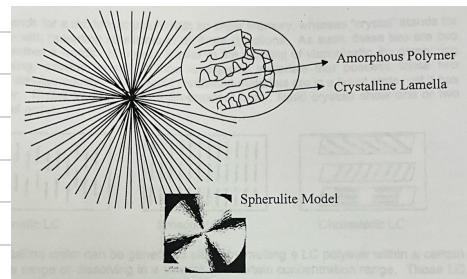


Regions between two cryst. regions, where there is no ordered packing



Further increase in MW

- 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.



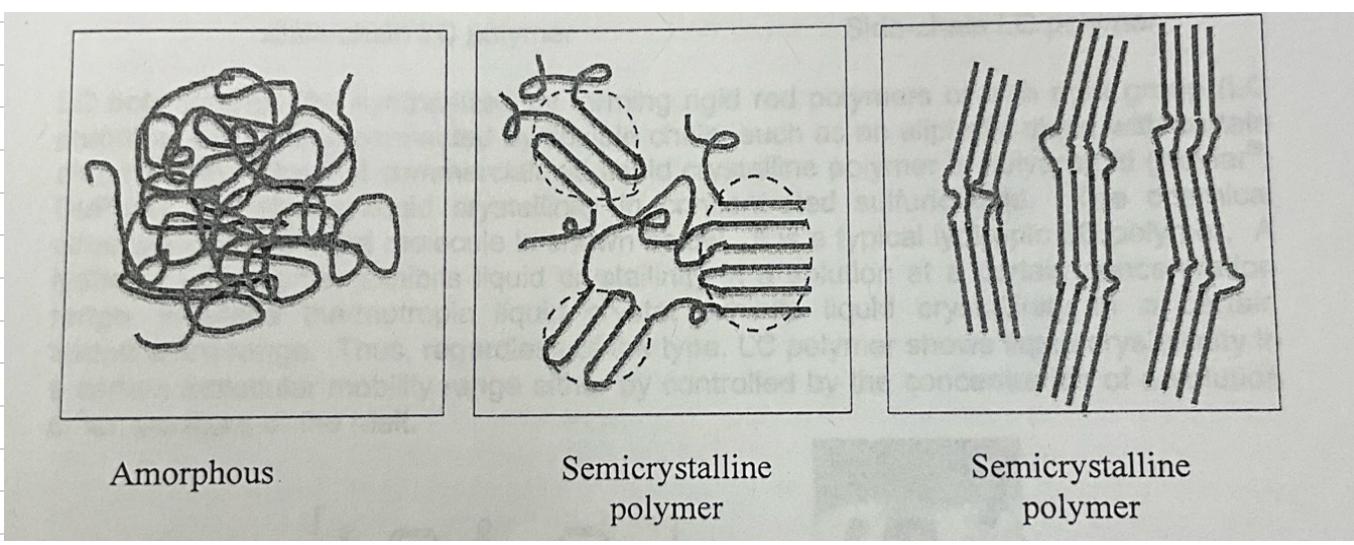
Spherulite Model

• 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



## Pages 23-24

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

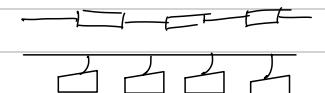
(Thermotropic LC Polymers)

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  $\xrightarrow{\text{curled}}$  LC polymers  
  ||  
  placed in the side chain  $\xrightarrow{\text{curled}}$  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

## Pages 25-26

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( $\gamma$ -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

## Pages 27-30

### Ways to Improve Sustainability

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

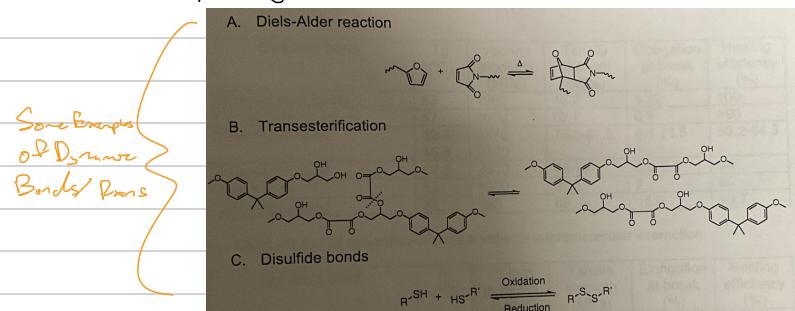
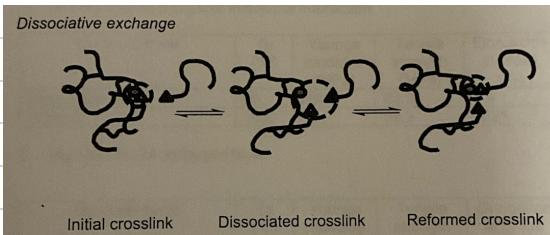
### Reprocessing of Thermoplastics

- Been done for many years, though in modest 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 ed 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 reform depending on temp.
- Bonds formed in Vac temperatures broken during reprocessing under heat  $\rightarrow$  cooled then visible



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  
(PHAs)



✓ Can Decompose quicker than petroleum based polymers

X • Potential contaminants of pesticides and herbicides

✓ Energy efficient synthesis

X • Natural degradation is not efficient, need

✓ Rescues non-renewable fossil fuel

composters which are limited in some places

X • More expensive products than petroleum

### Microplastics water transports readily

- Debris with diameter  $< 5 \text{ mm}$  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.

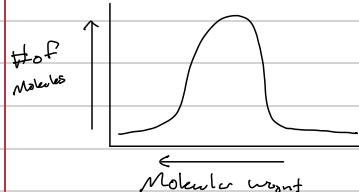
## Pages 32-33

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

## Pages 34-35

### Vapor Pressure

- Used to determine  $M_n$  as well

↳ Experimental Procedure Summarized at bottom of pg. 33

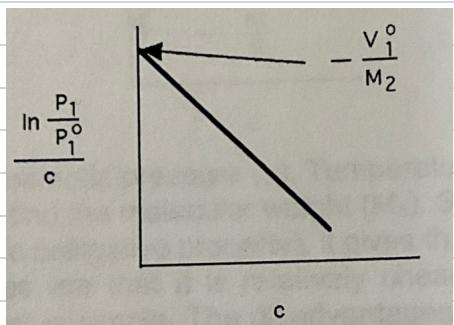
- Condensed vapor on polymer thermocouple creates a temp. increase due to the heat of condensation.

- 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

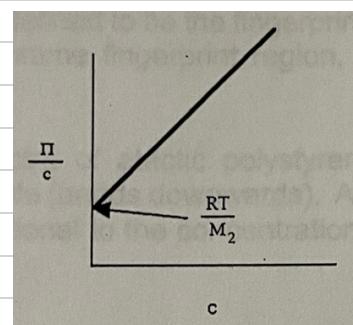
- Chemical Potential Driving Force pushes until hydrostatic pressure is high enough to stop the flow of the solvent (equilibrium)

- Knowing Concentration  $c$ , osmotic pressure  $\Pi$ , 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  $\text{cm}^{-1}$

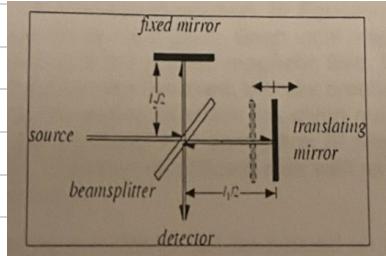
- Foraging of IR bands characteristics of specific types of chemical bonds

↳ Makes IR useful in identifying organic and organometallic molecules

## Pages 36-37

**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)
- $^2\text{H}$  and  $^{13}\text{C}$  have odd # of protons and neutrons -> magnetic dipole moment present
- <sup>1</sup>H and C are heavily studied due to abundance of H and C

$$\nu = 2\pi\omega \cdot B \quad (1) \quad \text{and} \quad B = \mu_0 (1 - \sigma) \quad (2)$$

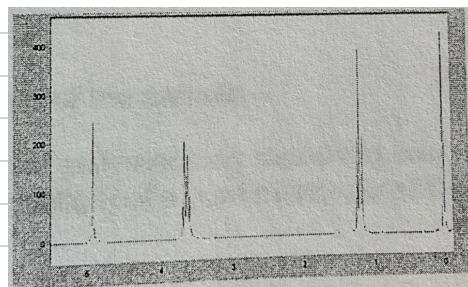
$\nu$ : dipole moment of nucleus,  $B$ : local magnetic field around nucleus,  $\mu_0$ : applied magnetic field,  $\sigma$ : chemical shift factor

- 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.

## Pages 38-39

### Nuclear Magnetic Resonance Spectroscopy (NMR) Continued

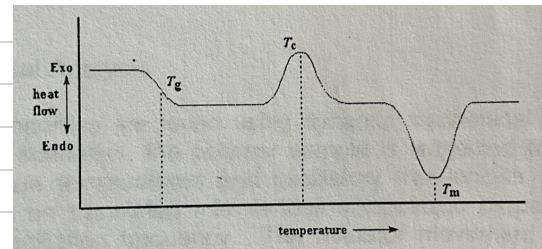
- For  $^1\text{H}$  NMR, relative sizes of peaks are proportional to the # of protons in the same magnetic field environment
- Advantages:** Highly specific and interpretation of chemical shifts is simple
- Disadvantages:** Sensitivity per scan is low, measurement time is long (signal averaging), complex mixtures are difficult to analyze, polymer must be soluble in an appropriate solvent, instrument is expensive to operate and maintain
- Solid sample shows very broad resonance due to dipole-dipole coupling → cannot be studied using ordinary liquid sample NMR spectrometers  
 ↳ well-resolved resonances can now be observed with a special Sample spinner and signal observation angle (magic angle)
- NMR spectrum of ethyl alcohol shown to the right



### Differential Scanning Calorimetry (DSC) Characterization of Therm. Properties

- Studies Thermal Transitions of a Polymer: Melting Temp (if applicable),  $T_g$ , Crystallization Temperature (if applicable), and degree of crystallinity
- Measures heat required to maintain the same temperature against a reference material that doesn't undergo transitions in the desired temp. range
- Full Procedure outlined on Pg. 38
- Melting and Crystallization Temperatures are **First-order** transitions → show peaks
- Glass Transition Temperature is a **Second-order** transition → appears as a slope change  
 ↳ **2nd Order**: No heat involved; only a change in heat capacity
- $T_g$  is determined from the value in the middle of the slope change range
- Can determine percent crystallinity of semicrystalline polymers using DSC  
 ↳ Difficulties compared to other properties but doable still
- Dividing area of curve by heating rate renders area  
 ↳  $\frac{\Delta H}{T_g}$
- Heat given off by polymer upon melting ( $H_f$ ) can be determined if samples' mass is known, and the melting peak is isolated
- $H_c$ , the heat of crystallization, can be found and must be subtracted off to find out how much of polymer was crystalline before experiment. This desired value is called  $H'$

$$H' = H_m - H_c$$

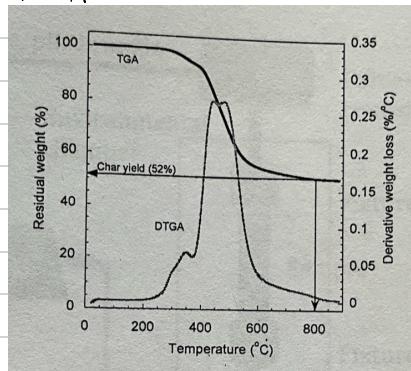


- To find total grams that were crystallized:  $m_c = \frac{H'}{H_m^*}$ ;  $H_m^*$  is latent heat of fusion.
- Percent of Crystallinity can be found as  $\frac{m_c}{m_t} \times 100$  where  $m_t$  is total sample's mass
- Conversion of Polymers monomer can be determined similarly, comparing the heat of reaction (polymerization) of a pure monomer and the heat of reaction of the partially polymerized material.

$$H' = \frac{H_m^*}{H_m^*}; H_m^* \text{ is latent heat}$$

## Thermo gravimetric Analysis (TGA) Characterization of Thermal Properties

- Uses highly accurate quartz balances to measure weight of sample as a function of temperature
- Thermal Decomposition is a unique signature of the chemical structure of a polymer
- Used to study thermal stability and char yield
  - ↳ Char Yield: Residual weight @ a certain temperature  
→ This is useful in studying materials for high temp applications and flame retardants
- Differentiate weight/temp curve → derivative TGA thermogram (DTGA)
  - ↳ much more sensitive about the decomposition process.
- TGA & DTGA for polybenzoxazine, which is designed for advanced composite manufacturing shown to the right.



# Pages 40-41

## Mechanical and Viscoelastic Properties Analysis

### Static Mechanical Properties

- Stress - Strain curves can be found very easily
  - ↳ Mechanical testing machine (Instron) pulls a sample w/ known geometry and records stress & strain
- Stress - Strain curve helps determine important polymeric properties
  - ↳ **Ex Properties:** Modulus, lower/upper yield points, material strength, stress req. to fracture

### Dynamic Mechanical Analysis (DMA)

- Viscoelastic properties found very DMA or a rheometer
- Samples response to forced sinusoidal movement at various temperature  $\rightarrow$  viscoelastic properties
  - ↳ Magnitude of phase lag = degree of viscoelasticity (**purely elastic  $\Rightarrow$  no phase lag**)
  - When phase lag is measured by phase angle,  $0^\circ$  phase angle = pure elastic,  $90^\circ$  angle = pure viscous
  - Allows us to determine storage modulus ( $G'$ ) & loss energy that is recoverable
  - Loss modulus ( $G''$ ): energy that is unrecoverable and lost as heat

$\hookrightarrow G'$  and  $G''$  is sensitive to sample geometry

$\rightarrow \tan \delta$  takes away this sensitivity by taking a ratio  $\hookrightarrow$  shows good reproducibility

$\bullet T_g$  can be found at the peak of the  $G''$  spectrum, though  $\tan \delta$  is also used

$\bullet$  Can also be used to find cross-linked density based on rubber plateau from
 

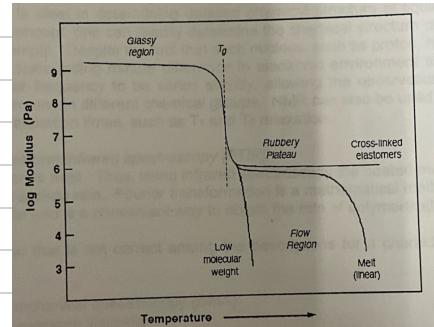
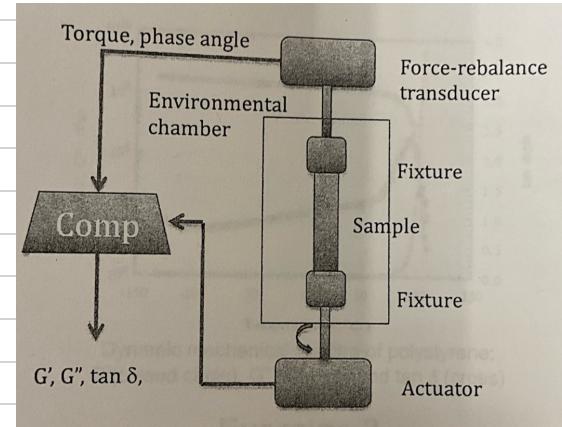
- ↳ Theory developed by Flory
- Rubber plateau modulus used to calculate tensile property

$\bullet$  Region above  $T_g$  is sensitive to temperature

- (i) Thermoplastics:  $G'$  continues to decrease as temperature increases due to molecular flow
- (ii) Cross-linked Polymers: Shows the rubbery plateau with nearly a constant  $G'$  despite temp. increases

$\hookrightarrow$  Consistency of  $G'$  used as a proof that a material is cross-linked

(Image)  $G'$  spectrum of a polymer shows for glassy regions, glass transition region, and rubbery region. Cross-linked material shows a nearly flat rubbery plateau.



# Pages 45-46

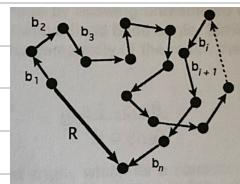
## Single Chain Properties

- Polymers made up of covalent bonds  $\rightarrow$  capable of rotation and creating a large number of possible conformations

- $R$ : end-to-end distance of a chain. Distance between two terminal atoms

$\hookrightarrow$  In a good solvent,  $R$  is large.

$\hookrightarrow$  In a poor solvent, the chain forms a tight ball and  $R$  is usually much smaller, as shown to the right



- To calculate  $R$ , covalent bonds are treated as vectors

$\hookrightarrow$  Vector sum of vectors  $b_i$  along polymer chain make up  $R$ 's calculation

$$R = \sum_{i=1}^n b_i, \text{ where } b_i \text{ is the length of the bond between atoms in the polymer backbone}$$

- Polymers move on fire, so  $R$  is calculated as an average over time  $\langle R \rangle$

- $\langle R^2 \rangle$  is often considered for calculations avoiding regular/300 averages, then  $\langle R^2 \rangle^{1/2}$  is reported

$\hookrightarrow \langle R^2 \rangle$  is the dot product of  $R$  with itself  $\langle R \cdot R \rangle$

$$\langle R^2 \rangle = \sum_{i=1}^n \langle b_i^2 \rangle + 2 \sum_{i=1}^n \sum_{j < i} \langle b_i \cdot b_j \rangle, \text{ where } n \text{ is the # of bonds in the polymer backbone chain}$$

$\hookrightarrow n = 2 \times n - 1$  for PE

$\hookrightarrow \langle b_i^2 \rangle$  is also a dot product so by definition

$$\langle b_i^2 \rangle = b_i \cdot b_i \cdot \cos \theta_{i,j}, \text{ where } \theta_{i,j} \text{ is the angle between the two vectors}$$

## No restrictions in Bond Angle

- When bond angles are unrestricted,  $\langle \cos \theta_{i,j} \rangle = 0$  as  $\cos \theta$  ranges from 1 to -1 (0  $\text{deg}$ )

$\hookrightarrow$  Second term in above eq goes to 0

$$\langle R^2 \rangle = nb^2 \longrightarrow R = \sqrt{\langle R^2 \rangle} = b\sqrt{n}$$

## Final (Restricted) Bond Angle

$$\langle R^2 \rangle \approx nb^2 \frac{1 + \cos(\pi - \Theta)}{1 - \cos(\pi - \Theta)} = nb^2 \frac{1 - \cos \Theta}{1 + \cos \Theta}, \text{ where } \Theta \text{ is unrestricted bond angle or constant}$$

- For a common polymer backbone consisting of C-C bonds,  $\Theta = 104.28^\circ$  and  $\cos \Theta \approx -\frac{1}{3}$

$$R = \sqrt{\langle R^2 \rangle} = \sqrt{nb^2 \frac{1 + \frac{1}{3}}{1 - \frac{1}{3}}} = \sqrt{2nb^2} = \sqrt{2}(b\sqrt{n}) \quad \text{EZ times larger than unrestricted bond angle}$$

## Barrier for Internal Rotation

- For more accurate calculations, restriction due to angle of rotation must be considered

$\hookrightarrow$  The energy barrier,  $\Delta E$ , for internal rotation is thus considered

$$\langle R^2 \rangle = nb^2 \frac{1 - \cos \Theta}{1 + \cos \Theta} \cdot \frac{2t \exp(-\frac{\Delta E}{kT})}{3 \exp(-\frac{\Delta E}{kT})}, \text{ where } k \text{ is the boltzmann constant \& } T \text{ is the absolute temperature}$$

EK3

## Pages 47-48

### Radius of Gyration

- $R$  is often hard to measure, so radius of gyration  $S$  is often used  
 $\hookrightarrow$  easier to measure as it's measured w/ a light scattering technique
- Mean-square value of the radius of gyration can be related to mean square value of end-to-end distance

$$\langle S^2 \rangle = \frac{1}{6} \langle R^2 \rangle$$

- Average distance from center of gravity to the chain segment  
 $\hookrightarrow$  smaller for polymer in a poor solvent than a good solvent  
 Good solvents  $\Rightarrow$  small and separate polymer chains
- For a polymer with equal molar mass, radius of gyration is different for the polymer with and without branching  
 $\hookrightarrow$   $g$ -factor can be defined and used to evaluate degree of branching

$$g = \frac{\langle S^2 \rangle (\text{branched polymer})}{\langle S^2 \rangle (\text{linear polymer})}$$

### Thermodynamics of Polymer Solutions-Stokes Theory (Flory-Huggins Theory)

- Obtaining thermodynamic functions of polymer solutions? Phase equilibrium, osmotic pressure & other thermodynamic properties can be studied
- Gibbs free energy provides extra energy that can be utilized  $\rightarrow$  appropriate to evaluate energy obtained from mixing a polymer into a solvent

$$G = H - TS = U + PV - TS, \quad G: \text{Gibbs free energy} \quad T: \text{temperature (K)} \quad P: \text{hydrostatic pressure} \quad V: \text{volume} \\ H: \text{enthalpy} \quad S: \text{entropy} \quad U: \text{internal energy}$$

- Flory & Huggins independently calculated  $\Delta S$  from a lattice model analogous to the rigid

$\hookrightarrow$  Open circles = solvent molecules

$\hookrightarrow$  Closed circles = chemical repeat units of a polymer chain

$\rightarrow$  Assumptions made by Flory & Huggins

(i) A polymer solution can be regarded as chemical repeat units of the polymer chain occupying each lattice unit

(ii) The lattice units have equal sizes, and each lattice unit can be occupied either by a solvent molecule or the chemical repeat unit

(iii) Number of neighboring chemical repeat units is called the valence number

(iv) Placement of  $N_1$  polymer chains in  $N_2$  lattice units ( $w(N_1, N_2)$ ) provides the entropy of mixing,  $\Delta S$ , according to the Boltzmann equation shown below

$$\Delta S = k \log [w(N_1, N_2)] \rightarrow \Delta S = -R (\phi_1 \log \phi_1 + \frac{\phi_2}{m_2} \log \frac{\phi_2}{m_2})$$

$R$ : gas constant,  $\phi$ : volume fraction,  $m$ : degree of polymerization; 1: solvent, 2: polymer

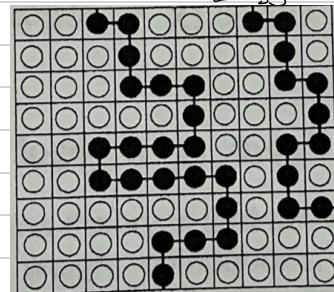
- For polymer blends with the second polymer being the solvent of the first polymer

$$\Delta S = -R (\frac{\phi_1}{m_1} \log \phi_1 + \frac{\phi_2}{m_2} \log \phi_2)$$

- If the solvent-solvent interaction is denoted as  $\varepsilon_{11}$ , solvent-chained repeat unit interactions as  $\varepsilon_{12}$  and chained repeat unit-chained repeat unit interactions as  $\varepsilon_{22}$ , the enthalpy of mixing  $\Delta H$  is

$$\Delta H = \phi_{12} \Delta \varepsilon_{12} \quad \phi_{12} = \# \text{ of contacts between solvent molecules \& the chemical repeat units}$$

$$\Delta \varepsilon_{12} = \phi_{12} (\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12}$$



- The interaction parameter is defined as  $\chi_{12}$

$$\chi_{12} = \frac{z \Delta \varepsilon_{12}}{kT}, \text{ where } z \text{ is the valent number}$$

- Gibbs free energy of mixing  $\Delta G$  ① using interaction parameter and ② for polymer blends

$$\textcircled{1} \quad \Delta G = RT \left( \Phi_1 \log \Phi_1 + \frac{\Phi_2}{m_2} \log \frac{\Phi_2}{m_2} + \chi_{12} \Phi_1 \Phi_2 \right)$$

$$\textcircled{2} \quad \Delta G = RT \left( \frac{\Phi_1}{m_1} \log \Phi_1 + \frac{\Phi_2}{m_2} \log \Phi_2 + \chi_{12} \Phi_1 \Phi_2 \right)$$

- Advantages:**

(i) Equation is quite simple

(ii) m=1 corresponds to small MW compounds and  $m_1, m_2$  can be used to describe polymer blends

- Shortcomings:**

(i) Assumption of lattice units being filled in a bray fashion implies volume of mixing  $\Delta V_{120}$ , which is false

(ii) Fixed lattice size does not allow us to evaluate thermal expansion of the system

(iii) Effect of different size solvent molecules cannot be evaluated

# Pages 49-50

## Solubility Parameter

- Solubility Parameter ( $\delta$ ) first developed by Hildebrand

↳ Purpose was for calculating estimates of free energy of mixing  $\Delta H_{mix}$  for mixtures of liquids expressed in units of  $(\text{cal cm}^{-3})^{1/2}$

- Unit Conversion:** Multiply by 2.045 to convert to 81 units of MPa

- If solubility parameter of a polymer is less than solvent, then the polymer will dissolve well in the solvent

- Solubility parameter of some well-known polymers & solvents are shown to the right (upper table)

- Hildebrand solubility parameter can be estimated by the following equation

using the published table of molar contributions of each quantity

$$\delta = \frac{\sum p^*}{\sum V^*} \quad (\text{lower table})$$

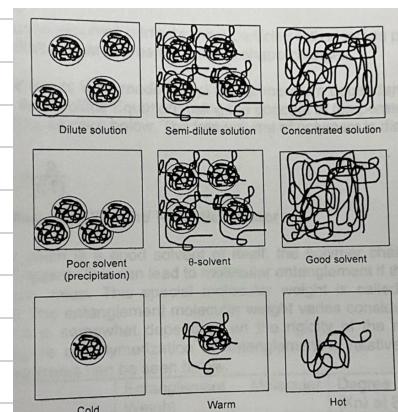
↳ where  $p^*$  is the molar attraction contribution &  $V^*$  is the molar volume contribution

Polymers	$d$ ( $\text{cal cm}^{-3})^{1/2}$	Solubility parameter of common solvents	
		Solvents	$d$ ( $\text{cal cm}^{-3})^{1/2}$
Polytetrafluoroethylene	6.2	n-Hexane	7.2
Polyethylene	8.0	Carbon tetrachloride	8.6
Polypropylene	8.3	Toluene	8.9
Polystyrene	9.0	Chloroform	9.3
Polybutadiene	8.4	Carbon disulfide	10.0
Poly(vinyl chloride)	9.7	Acetonitrile	11.9
Ethyl cellulose	10.3	Dimethylsulfoxide	12.0
Poly(vinyl alcohol)	12.7	Propylene glycol	12.6
Polyacrylonitrile	12.7	Methanol	14.5
Nylon-6,6	13.7	Water	23.4

Group structure	Molar volume contribution, $V^*$ ( $\text{cm}^3/\text{mol}^1$ )	Molar attraction contribution, $F^*$ ( $[\text{cal cm}^{-3}]^{1/2} \text{ mol}^{-1}$ )
-CH <sub>3</sub>	31.8	218
-CH <sub>2</sub> -	16.5	132
>CH-	1.9	23
>C<	-14.8	-97
CeH <sub>3</sub>	41.4	562
CeH <sub>4</sub>	58.5	652
CeH <sub>5</sub>	75.5	735
CH <sub>2</sub> =	29.7	203
-CH=	13.7	113
>C=	-2.4	18
-OCO-	19.6	298
-CO-	10.7	262
-O-	5.1	95
-CI	23.9	264
-CN	23.6	426
-NH <sub>2</sub>	18.6	275
>NH	8.5	143
>N-	-5.0	-3

## Viscosity

- Polymer molecules in dilute solution exist as ball-like structures, with size being determined by the radius of gyration
  - ↳ radius of gyration depends on interaction of polymer molecules w/ the solvent
- Concentration  $\uparrow \rightarrow$  ~~ball-like~~  $\uparrow$  until the polymer and solvent start interacting
  - ↳ structure seen is semi-dilute concentrations.
  - On a conc. sln. the polymer molecules no longer exist as separate balls, instead begin to interact with each other
    - ↳ Think of a polymer chain being a solvent of water chains
- Schematic diagram of the polymer molecules in solution is shown to the right
- Some exceptions for those polymers that show low critical sln temp (LCST)
  - ↳ Such exceptions show opposite trend from those in solvents.  $\downarrow$  ~~some H-bonds form above LCST temp~~
  - These dissolve in cold solvent and precipitate in hot solvent above LCST temp



- Solvent receives resistance when it moves through polymer balls
  - ↳ Difficult to flow is viscosity  $\eta$
- Viscosity = more difficult to be expressed in terms of  $\eta_0$ , the viscosity of the solvent
 
$$\eta = \eta_0(1 + aC + bC^2 + \dots)$$

where  $\lim \frac{\eta - \eta_0}{\eta_0 C} = a$
- $a$  relates to the property of individual polymer chains, and  $b$  relates to polymer-solvent interaction. Above eq extrapolated to  $C=0$  to obtain  $\rightarrow$  higher tens can be ignored

# Pages 53-54

## Glass Transition Temperature

- Occurs in both amorphous & semi-crystalline polymers

↳ If specific volume measured, there is a change as shown to the right

- As temp increases, slope changes at the glass transition Temp

$T_g$  (glass transition temp): the temperature at which the amorphous polymer or the amorphous component of a semi-crystalline polymer undergoes a change from glass  $\rightarrow$  rubber state

↳ Material Softens considerably

- Pure amorphous polymer doesn't show any further transitions past  $T_g$

- Semi-crystalline Polymers exhibit a melting temperature  $T_m$  past  $T_g$

- Properties that change across  $T_g$ : thermal expansion coeff, heat capacity, refractive index, diffusion coeff, dielectric constant, modulus

↳  $T_g$  can thus be observed by many methods: Dilatometry, DSC & DMA commonly (convenient)

- Increased volume above  $T_g$  due to ↑ specific volume polymer chains can freely move  $\rightarrow$  This space is called free volume

↳ The space where the molecular chain itself occupies is called occupied volume

$$\text{Fraction of Free Volume: } f = f_g + \alpha_f(T - T_g) - \beta_f P \quad f_g: \text{frac. of free volume at } T_g \quad \beta_f: \text{volume expansion coeff. of free volume}$$

$\alpha_f$ : CTE of free volume  $P$ : Hydrostatic Pressure

↳  $f_g \approx 0.025$  from experimental results

$\nwarrow$  CTE = coeff. of Thermal Expansion

- Polymers are often mixed together, but we still want to predict the  $T_g$  of the blend

$$\text{Fox Equation: } \frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad T_g: \text{tg. to } T_g \text{ of blend}$$

$T_{g1}, T_{g2}$  are respective glass transition temps

\* This only applies for thermodynamically miscible polymers (homogeneous blend w/ negligible phase separation)

- A more accurate equation for polymer blends due to consideration of respective CTEs is

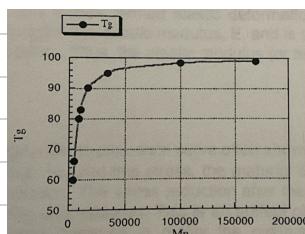
$$\text{Gordon-Taylor Eq: } T_g = \frac{T_{g1} + (K T_{g2} - T_{g1}) \phi_2}{1 + (K - 1) \phi_2} \quad K = \frac{\partial \phi_2}{\partial a} \quad \phi: \text{volume fraction of each polymer}$$

- Glass Transition temp of polymer increases as Backbone rigidity increases

↳ common polymers  $T_g$  shown to the right

- Higher  $T_g$  values corresponds to higher  $M_n$  values

↳  $T_g$  has strong molecular weight dependence as shown to the right



Polymer	$T_g$ (°C)	Polymer	$T_g$ (°C)
Polyethylene	-125	Nitrocellulose	53
Polydimethylsiloxane	-123	Nylon-66	50
Polybutadiene	-90	Nylon-6	50
Polyisobutylene	-70, -60	Poly(ethylene terephthalate)	69
Polyoxymethylene	-50 (-85)	Poly(vinyl alcohol)	85
Poly(1-pentene)	-40, -24	Poly(vinyl chloride)	87
Poly(vinylidene fluoride)	-35	Poly(styrene)	100
Poly(1-butene)	-25	Poly(methyl methacrylate)	105 (isotactic) 105 (syndiotactic)
Poly(vinyl fluoride)	-20, 73	Polyacrylonitrile	104
Polypropylene	-18, -10	Poly(vinyl formal)	105
Poly(vinylidene chloride)	-17	Intracycl cellulose	105
Poly(methyl acrylate)	3	POLycarbonate)	150
Poly(vinyl acetate)	29	Poly( $\alpha$ -methyl styrene)	167
Poly(chlorotrifluoroethylene)	45		

## Melting Temperature

- Used to characterize semi-crystalline solid (polymers)

↳ does not pertain to amorphous polymers

- Marks the transformation of a solid material to a highly random viscous liquid

$\text{↳ "Solid" refers to a material having aligned molecular chains and ordered structure}$

- Can use equations to predict  $T_m$  based on thermodynamic parameters and molecular weight

↳ Not discussed in this class; outside of course scope (P.)

- There tends to be a correlation between melting and glass transition temperatures of polymers

$$\text{Boor-Berman Rule: } T_g \approx \frac{1}{2} T_m \text{ for symmetric molecules}$$

$$T_g \approx \frac{2}{3} T_m \text{ for asymmetric molecules}$$

## Pages 51-52

### Viscosity Contd.

- $\eta^*$  is called the intrinsic viscosity  $[\eta]$ . The intrinsic viscosity of a polymer is given by expressed by

$$[\eta] = KM \text{ where } a \text{ and } K \text{ are constts (0.02 < } a < 0.8) \text{ and } M \text{ is viscosity average molecular weight (Mv)}$$

Mark-Houwink-Sakurada Equations

- Relative viscosity is given by ratio of solution & solvent viscosity:  $\eta_r = \frac{\eta}{\eta_0}$

- For very dilute suspensions of particles, w/ no particle-particle interactions, Einstein proposed

$$\eta = \eta_0 (1 + \frac{2}{3} \phi)$$
 with prefactor  $\phi$  for particles and  $\phi$  packing fraction

- Using temperature dependent free volume fraction  $f(T)$ , temperature dependence of viscosity is given by

$$\log \eta = \log A + \frac{B}{f(T)} \quad \text{Doos Little Equation} \quad f(T) \text{ discussed later}$$

### Entanglement Molecular Weight/ Reptation Theory

- Polymer chain good solvent itself  $\rightarrow$  chains are more more stretched & elongated

$\hookrightarrow$  leads to entanglement above a certain molecular weight called the entanglement molecular weight

- Entanglement MW comes from polymer

to polymer and is solvent dependent  
on molecular structure rigidity

$\hookrightarrow$  Degree of Polymerization  $\propto$  Entanglement  
is relatively constant (shown to right)

Polymer	Entanglement Molecular Weight	Degree of Polymerization (Xn) at Entanglement MW
polyethylene	4,000	140
cis-1,4-polybutadiene	7,000	130
cis-1,4-polyisoprene	14,000	210
polyisobutylene	17,000	300
polydimethylsiloxane	29,000	390
polystyrene	35,000	340

- Below entanglement MW & constant T, viscosity is linearly proportional to weight average MW ( $M_w$ )

- At entanglement MW, there's also viscosity increase due to extra chain entanglements.

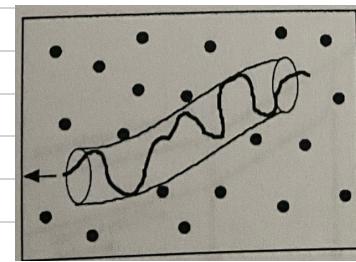
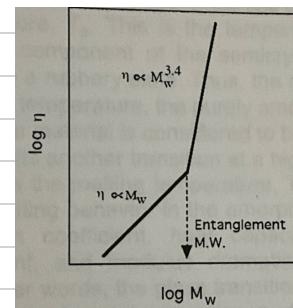
- Above entanglement MW viscosity  $\propto M_w^{3/4}$

$\hookrightarrow$  relationship on right (left: mag)

- Do Gennes Reptation model (right - magenta)

shows polymer reptating through a tube

$\hookrightarrow$  black dots indicate entanglement points



Polymer chains move toward direction of tube, but cannot in transverse direction due to entanglement

### Thermal Properties of Polymers

- Aggregation state of a material changes by varying the temperature & pressure of the material

- Evaporation, melting, freezing are all phase transitions

- Solids & liquids generally incompressible  $\rightarrow$  only need to consider temp effects

- N-th order transition: Gibbs free energy differential ( $\Delta G$ ) = 0 for discrete but n-ths discrete.

$\hookrightarrow$  melting & evaporation discrete w/ respect to specific volume  $\hookrightarrow$  1st order transition

- Tg accompanies disordering in thermal expansion coeff. & heat capacity  $\hookrightarrow$  Tg is 2nd order

Recent understandings suggest Tg is not a thermal transition but instead due to reduction in motion of large segments of chains

- Various physical and mechanical properties of polymers change at phase transition points

## Pages 55-56

### Mechanical Properties of Polymers

- Mechanical Properties of Polymers are more sensitive to parameters like temperature and strain rate  $\leftarrow$  unlike metals and ceramics materials
- Usually measured by recording load ( $P$ ) and elongation ( $\Delta l$ ), calculated from stress ( $\sigma$ ) and strain ( $\epsilon$ )
- Engineering stress** is the load divided by the original cross-sectional area
- The stress is when the load is divided by the actual cross-sectional area at any given time, t
- Strain is defined as the elongation divided by the original length

$$\sigma = \frac{P}{A} \text{ and } \epsilon = \frac{\Delta l}{l_0}$$

- Polymer first deforms linearly up to proportional limit  $\sigma_y$
- $\hookrightarrow$  Completely recoverable deformation so this is elastic deformation
- Stiffness from a tensile test is the elastic modulus ( $E$ ) which is the slope of the initial linear region

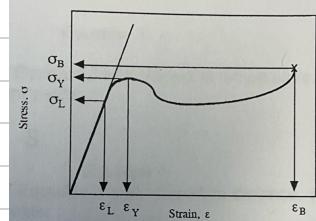
$$E = \frac{\sigma}{\epsilon} = \frac{\text{stress}}{\text{strain}}, E = \text{Elastic or Tensile or Young's Modulus} \quad (\text{all to same quantity just diff name})$$

- Maximum after linear region is yield strength ( $\sigma_y$ )
- $\hookrightarrow$  Material deforms permanently beyond  $\sigma_y$  (plastic deformation experienced)
- Stress reduces after yield stress due to 'cold drawing' or 'necking' phenomena
- Effect of using engineering stress as cross-sectional area decreases (contracted) upon drawing
- Neck deforms to gauge length  $\rightarrow$  Stress remains relatively constant
- Polymer chains begin to align  $\rightarrow$  ultimate strength increases
- Necking phenomenon is used to draw fibers to make originally spun fibers even stronger
- Material eventually fractures at the ultimate strength ( $\sigma_B$ )

$\rightarrow$  Strains of corresponding stresses are commonly reported in literature

- Poisson's Ratio** ( $\nu$ ) is the amount of decreased width divided by amount of increased length upon stretching ( $\nu = \frac{\Delta d}{\Delta L}$ )
- Poisson's ratio for an ideal rubber is 0.5

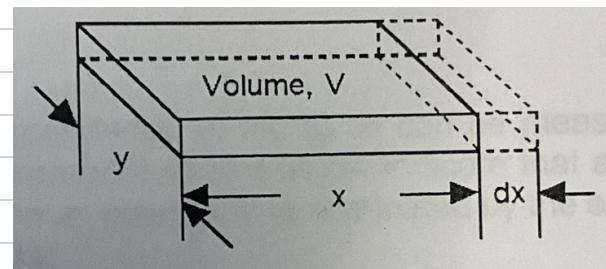
- Toughness is defined as the area under the stress-strain curve. Toughness =  $\int_{\epsilon_L}^{\epsilon_B} \sigma d\epsilon$
- Strong Polymer = High stress at Break ( $\sigma_B$ )
- Ductile Material = High Strain at Break ( $\epsilon_B$ )
- Brittle Material = High Tensile Modulus ( $B$ )
- Tough Material = Large area under stress-strain curve



### Rubber Elasticity Theory

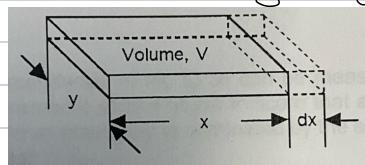
- Characterized by very large deformation and extremely low modulus.
- $\hookrightarrow$  Exhibited in lightly cross-linked rubbers (elastomers)  $\leftarrow$  can deform many times that of their original length
- Cross-linked rubber can maintain elastic (recoverable) deformation at very large strains
- $\hookrightarrow$  as described by the rubber elasticity theory
- Model to the right:

  - $\rightarrow V$ : Volume of the rubber
  - $\rightarrow dx$  is amount/distance rubber is stretched
  - $\rightarrow$  Stretched @ stress  $F$ , temp  $T$ , pressure  $P$



## Pages 57-58

### Rubber Elasticity Theory (Equations) (Continued)



• Increment of internal Energy of rubber:  $dU = TdS - PdV + Fdx$  (1)

$\hookrightarrow S$  is entropy

• Using  $F = U - TS$ , Helmholtz free energy  $dF$  is:

$$dF = dU - TdS - SdT \quad (2)$$

• Plugging Equation (1) into (2) yields:  $dF = TdS - PdV + Fdx - TdS - SdT$

$$\therefore dF = -PdV + Fdx - SdT \quad (3)$$

• Partial Differentiation of  $S$  with respect to temp yields:  $\left(\frac{\partial F}{\partial T}\right)_{V,x} = -S$   $\leftarrow$  Keep volume ( $V$ ) and distance ( $x$ ) constant (4)

• Partial Differentiation of  $S$  with respect to distance yields:  $\left(\frac{\partial F}{\partial x}\right)_{V,T} = f$   $\leftarrow$  Keep volume & temp constant (5)

• Partial Differentiation of  $F = U - TS$  w/ const  $V & T$  yields:  $\left(\frac{\partial F}{\partial x}\right)_{V,T} = \left(\frac{\partial U}{\partial x}\right)_{V,T} - T\left(\frac{\partial S}{\partial x}\right)_{V,T}$  (6)

• Plug (5) into (6) to get:  $f = \left(\frac{\partial U}{\partial x}\right)_{V,T} - T\left(\frac{\partial S}{\partial x}\right)_{V,T}$

• Force & temperature measured @ constant volume  $\Rightarrow$  energy & entropy terms can be independently evaluated  
 $\hookrightarrow$  Not proportional due to thermal expansion so  
 Pleng et al have shown, with  $\varepsilon = \frac{x-x_0}{x_0}$ , that:  $\left(\frac{\partial F}{\partial T}\right)_{V,x} \approx \left(\frac{\partial F}{\partial T}\right)_{P,\varepsilon}$

• Actual measurements indicate that energy  $\approx 0$  @  $T=0$  and force in an elastomer is dominated by the entropy term as:  $f \approx -T\left(\frac{\partial S}{\partial x}\right)_{V,T}$

• Differentiating (4) by  $x$  and (5) by  $T$  yields

$$\frac{\partial^2 F}{\partial x \partial T} = -\left(\frac{\partial S}{\partial x}\right)_{V,T} \text{ and } \frac{\partial^2 F}{\partial x \partial T} = \left(\frac{\partial f}{\partial T}\right)_{V,x} \therefore -\left(\frac{\partial S}{\partial x}\right)_{V,T} = \left(\frac{\partial f}{\partial T}\right)_{V,x}$$

• Thus the final relationship for force is:  $f = -T\left(\frac{\partial S}{\partial x}\right)_{V,T} = T\left(\frac{\partial f}{\partial T}\right)_{V,x}$

$\hookrightarrow$  stretch  $\rightarrow$  polymer chains align  $\rightarrow$  reduced disorder

$\hookrightarrow$  Indicates that entropy decreases upon stretching  $\bullet$  Importantly, force & modulus increase with temp

### Viscoelastic Properties of Polymers

- Materials deform under stress and elasto (ideal) materials completely recover shape after stress is released
- Ideal Viscous materials flow irreversibly at a certain deformation rate, which is proportional to the applied stress (Newtonian)
- Many Polymers show properties that lie between ideal elasto and ideal viscous behavior  
 $\hookrightarrow$  Polymer will flow as though it were a viscous material when shear stress is applied, but will also try to recover the deformation when the applied stress is eliminated

1) Stress Relaxation  $\Leftarrow$  First of two quantities used to characterize viscoelastic properties of polymers

- Polymer under constant strain over time  $\rightarrow$  stress in material will relax  $\Leftarrow$  res. 1st of stress relaxation
- $\hookrightarrow$  Like a rubber band stretched  $\rightarrow$  spring, then relax

• Maxwell model shows spring and dashpot in series with each other demonstrating property of stress relaxation

$\hookrightarrow$  addition exists in the stress of the spring and dashpot and thus total stress in system is:  $\sigma_{\text{Total}} = \sigma_1 + \sigma_2$

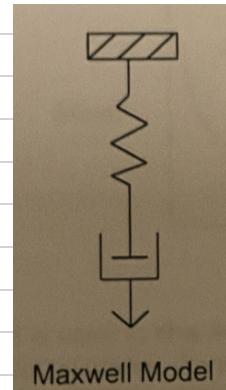
• Thus we have  $\sigma_1 = E\varepsilon_1$  and  $\sigma_2 = \eta \frac{d\varepsilon_2}{dt}$

$$\hookrightarrow \frac{d\varepsilon_{\text{Total}}}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} \therefore \frac{d\varepsilon_{\text{Total}}}{dt} = \frac{1}{E} \left( \frac{d\sigma}{dt} \right) + \frac{1}{\eta} \sigma$$

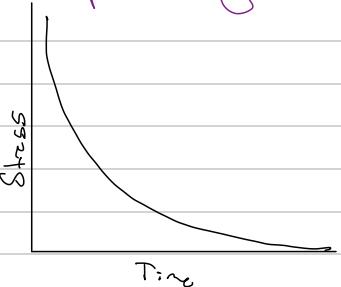
• Total strain does not change with time so we solve:  $\sigma(t) = \sigma_0 e^{-\frac{t}{\tau}}$

$\hookrightarrow$  where  $\sigma_0$  is initial applied stress, and  $\tau$  is a constant

such that  $\tau = \eta/E$



Exponential Decay



Maxwell Model

# Pages 59-60

## Viscoelastic Properties of Polymers (Continued)

2) Creep  $\leftarrow$  Second of two quantities used to characterize viscoelastic properties of polymers

- Characterizes how the strain of a polymer responds over time to a constant applied stress

$\hookrightarrow$  Plastic hanger has pulled by a heavy coat over time

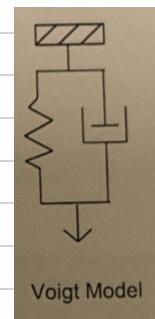
• Voigt Model has spring and dashpot in parallel with each other and the stress is additive for each element

$\hookrightarrow$  Different to the additive strain for Maxwell model

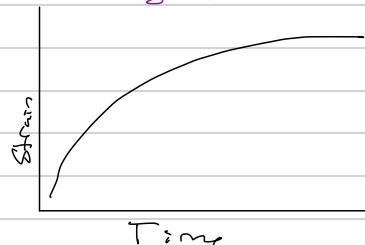
• Total stress of system is constant over time ( $\sigma_0$ )

• Creep eq derived similar to manner on previous page

$$\epsilon(t) = \frac{\sigma_0}{E} \left( 1 - e^{-\frac{t}{\tau}} \right)$$



Logarithmic Graphs



- Usual Stress vs Time plots show purely elastic response of the material represented by vertical line, retarded/delayed response of terminal, and also permanent strain given by graph asymptotic to a non-zero value
- Specimen should be loaded with a stress at time  $t_1$  and load removed at  $t_2$
- $\hookrightarrow$  Thus the **4-element Model** and is used to describe the more complex situation by combining the Maxwell and Voigt models in a series manner

## Oscillatory Deformations

- Stress - Strain relationships also apply to oscillatory deformations as well

$\hookrightarrow$  Can gather much more information using this technique

- Material is twisted in an oscillatory function at a given frequency ( $\omega$ )

$\hookrightarrow$  Subjected usually to a particular strain  $\rightarrow$  Stress response measured with respect to the strain for each cycle

- Perfectly elastic materials will have the stress and strain curve perfectly in phase without other

• Purely viscous materials will have curves  $90^\circ$  out of phase

• Viscoelastic materials respond to sinusoidal strain in between elastic solid and viscous liquid

$\hookrightarrow$  Corresponds to a phase shift ( $\delta$ ) somewhere in between  $0^\circ$  and  $90^\circ$  for each polymer

- Stress can be resolved into two components to aid in data collection.

(i) In-phase with strain (elastic) ( $G'$ )

(ii) Out-of-phase with strain (viscous) ( $G''$ )

- Can then develop two parameters to characterize a polymer

1) Dynamic Storage Modulus ( $G'$ )

• Energy stored in the material

• Also described as amount of

recoverable energy from elastic deformation

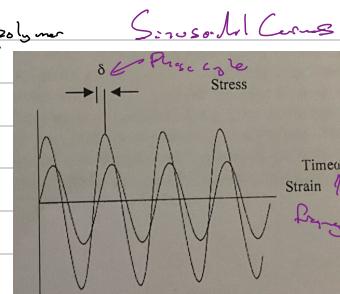
2) Dynamic Loss Modulus ( $G''$ )

• Relates to the irreversible energy

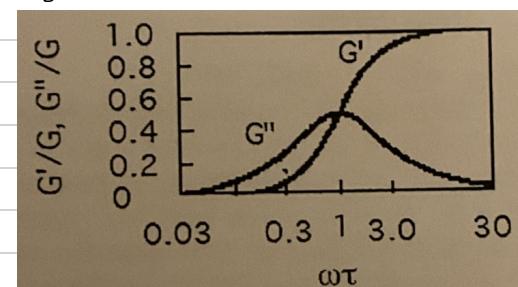
loss due to molecular friction (heat)

$G' = \left| \frac{\sigma'}{\gamma} \right|$   $\Rightarrow$  Stress in phase with the strain  $\gamma$

$G'' = \left| \frac{\sigma''}{\gamma} \right|$   $\Rightarrow$  Stress out of phase with the strain  $\gamma$



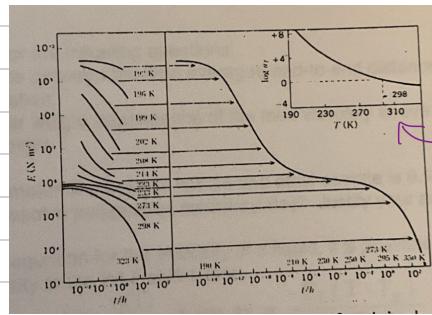
- $G'$  and  $G''$  are both dependent on temperature and frequency with which exponents being indicated
- Loss tangent  $\tan \delta$  measures ratio of energy dissipated to energy stored per cycle as  $\tan \delta = \frac{G''}{G'}$
- When  $G'$  and  $G''$  are plotted as a function of  $\omega t$ ,  $G''$  takes a maximum at  $\omega t = 1$
- At a low frequency such that  $\omega t \approx 0$ ,  $G'/G'' = 0$  and the material flows as a viscous material
- At a high frequency such that  $\omega t \rightarrow \infty$ , the material acts as an elastic solid i.e.



# Pages 61-62

## Time Temperature Superposition Principle

- Often desired to predict a property over a prolonged period of time  
 ↳ testing time is unfortunately very limited
- Time-Temperature superposition principle allows such properties to be predicted without actually performing long-term experiments
  - Properties that take a long time to show at room temp can show much quicker at elevated temp
- Testing may short-term properties at various temperatures, curves can be shifted by a certain value ( $\alpha_T$ ) from reference temperature
  - Gives a "Master Curve" describing how material will behave at extended periods of time at said reference temperature
- Polyisobutylene example can be seen to the right
- Stress relaxation behaviors at various temperatures of Polyisobutylene and their master curve shown. The inset shows the temperature dependence of the shift factor  $\log(\alpha_T)$
- Master curve based on time-temperature superposition principle drawn by calculating the shift factor using the Williams-Landel-Ferry (WLF) equation.



Discussed Insert

- Equation:  $\log_{10}\alpha_T = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})}$  where  $C_1$  and  $C_2$  are experimentally determined quantities that give global meaning to polymer systems
- (i)  $C_1$  value is related to fractional free volume of the polymer at the reference temperature  
 → (ii)  $C_2$  can be used to find the thermal expansion coefficient of the polymer  
 → Note: If  $T_{ref} = T_g$  then  $C_1 = 12.44$  and  $C_2 = 51.6$
- Time-temperature superposition principle only applies to thermorheologically simple materials.  
 ↳ This is not true for semicrystalline polymers, multiphase polymers, and composites!

## Pages 64-66

- Two main methods used to describe the synthesis of polymers (addition, and step polymerizations)

### Step Polymerization

- Monomers with more than one reactive site polymerize

↳ sometimes referred to as condensation reactions as  $H_2O$  or  $HCl$  are often released as byproducts

- Monomers with more than 2 reactive sites  $\Rightarrow$  cross-links are formed (thermoset)

↳ linkages of two worlds form thermoplastics

- Characteristics common to all step polymerizations

(i) Growth by the loss of at least one monomer

(ii) Rapid loss of monomer species (first  $n$  produces  $n$  others)

(iii) Driving force of the reaction is the removal of condensation product

(iv) Molar mass increases slowly throughout

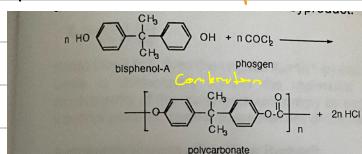
(v) Ends remain active

(vi) At any stage, a range of molecular species are present

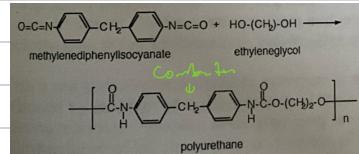
(vii) No initiator is necessary

- Polycondensation rxn of Polycarbonate

Example (HCl is byproduct)



- Step polymerization involves no products is released in formation of Polyurethane



### Crooks Theory

- Can be used to determine number average molecular weight & degree of polymerization

$$X_{av} = \frac{N}{n} \sum \frac{N_i}{n_i} = \text{number average degree of polymerization}, N = \text{number of molecules present initially}$$

- If p% of reactant reacts, then  $X_{av} = \frac{1}{1-p}$   $X_{av} \rightarrow \infty$  as  $p \rightarrow 1$

- Number average degree of polymerization \* molecular weight of the repeat unit =  $M_n$

- To obtain a useful polymer ( $X_{av}=200$  example), rxn must go to 98%, compute

$\rightarrow$  Not as simple for addition reactions

- This applies only for 1:1 stoichiometry

$\rightarrow$  Define reactant ratio  $= \frac{M_n}{N_p}$  for non-stoichiometric reactions  $\leftarrow$  always less than 1

$$\text{Therefore we have } X_{av} = \frac{1+n}{1+n-2np} \quad \text{Note that except } \frac{1}{1-p} \text{ is obtained for } p=1.$$

### Addition Polymerization (Free Radical)

also called chain-growth polymerization

- One monomer unit is added onto to growing polymer chain one at a time

- Propagating species can be a free radical, cation or cation

$\hookrightarrow$  commercial polymers that undergo this are polystyrene, PVC, PMMA, and many others

- Characteristics common to all polymerizations

(i) Growth by addition of monomer only at the end of one chain

(ii) Some monomer ends at the end of one chain

(iii) Driving force of the reaction is conversion of 1 double bond to 2 single bonds

(iv) Molecular mass of backbone increases rapidly

(v) Polymer chain is not reactive after termination

(vi) React mixture contains only monomer, low polymer and a very small amount of growing chains

(vii) Initiator is required

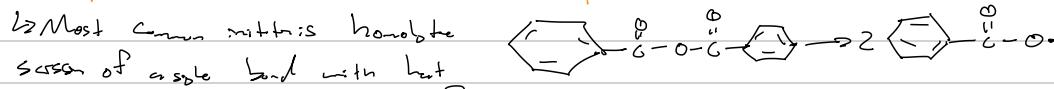
# Pages 67-68

## Addition Polymerization (Continued)

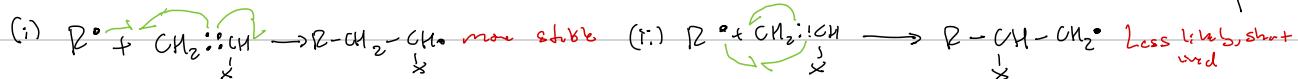
### Initiation

- First step rxn is initiation of a polymer chain
  - Free radical must be formed with initiator

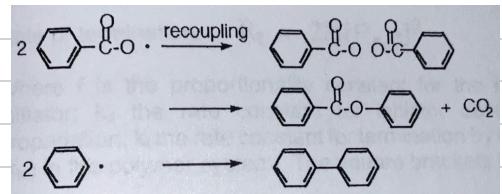
Free radicals are much less reactive than a closed carbon or carbon  $\rightarrow$  easiest to work with as some polymerizations do not react with impurities and terminate the reaction



- Initiator molecule, I, under goes first-order decomposition with rate  $k_{d}$ :  $I \xrightarrow{k_d} 2R\cdot$
- Free radical or the initiator is reactive and attacks monomer w/ a double bond. Two possibilities:



- Not every initiator starts a new polymer chain
  - can recombine, or have side reactions with one another that produce stable compounds not capable of initiating polymer chains as seen to the right



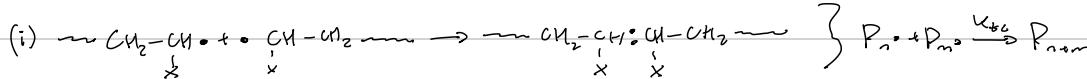
### Propagation

- Next step, monomers M are added on one end or free to the growing polymer chain ( $\text{P}_n\cdot$ ) to form a reactive polymer with one more monomer ( $\text{P}_{n+1}\cdot$ )



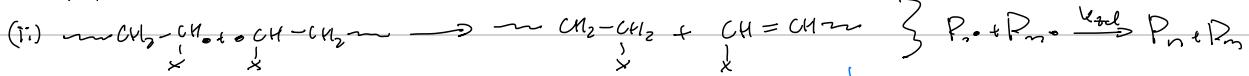
### Termination

- Free radical rxn is terminal when the free radicals are consumed



$\hookrightarrow$  molecular weight will increase dramatically

- Disproportionation involves a hydrogen atom being extracted by the free radical as



$\hookrightarrow$  Disproportionation large MW increase

- D.P. of polymer terminates different pathways

$\hookrightarrow$  PMMA tends to terminate by disproportionation due to steric hindrance

### Kinetics of Free Radical Polymerization

Notes: use steady state assumption  $R_i = R_t$

$$\begin{cases} \text{Initiation: } R_i = 2fK_d[I] \\ \text{Propagation: } k_p[M][P_n\cdot] \\ \text{Termination: } 2K_t[P_n\cdot]^2 \end{cases}$$

- $f$  is proportionality constant for the initiation offing of the decomposed initiator
- $K_d$  and  $k_p$  are rate constants of initiator & propagation, respectively
- $K_t$  is rate constant of termination, slow  $k_t = k_{t1}k_{t2}k_{t3}$

$$\text{Steady-State: } 2fK_d[I] = 2K_t[P_n\cdot]^2 \text{ so } [P_n\cdot] = \left( \frac{fK_d[I]}{K_t} \right)^{1/2} \Rightarrow R_p = k_p \left( \frac{fK_d}{K_t} \right)^{1/2} [I]^{1/2} [M] = K [I]^{1/2} [M]$$

$\hookrightarrow$  where  $K$  is the combination of all the constants in the last expression

- Rate of propagation constant  $\Rightarrow$  depends on both concentration of initiator and monomer

### Kinetic Chain Length

$$\bar{n} = \frac{R_p}{R_i} = \frac{k_p[M]}{2(fK_d)k_t[I]^{1/2}}$$

and  $\bar{x}_n = \bar{n}$  for disproportionation  
 $\bar{x}_n = 2\bar{n}$  for condensation

- To get MW, add weight/mol units to (degree of polymerization times mol. wt unit mol. - mol. wt)

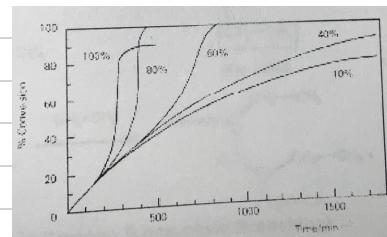
$$\begin{cases} \text{Increase } [M] \Rightarrow R_p \uparrow, \bar{x}_n \uparrow \\ \text{Increase } [I] \Rightarrow R_p \uparrow, \bar{x}_n \downarrow \end{cases}$$

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## Autoacceleration

- The  $R_p$  expression is valid at the start of the run, but  $R_p$  tends to dramatically sharply increase upon + the extent of reaction increases  
 ↳ Called the Trommsdorff - Norrish effect (or autoacceleration, gel effect, or Norrish effect)
- Follows the following molecular steps, and an example can be seen below as well

- As the content of large polymer molecules increases with reaction time and the polymer solution eventually gels, the viscosity of the solution dramatically increases.
- The mobility of the polymer chain radicals nearly halts and hence  $k_t$  is reduced substantially due to the low diffusion rates of the polymer free radicals in such viscous media. In the meantime, the initiator molecules continue to split. Thus, the steady-state condition no longer holds.
- The small monomer molecules can easily diffuse to the polymer free radicals as well as the usual initiator free radicals.  
 Thus, from the overall rate equation, a reduction in  $k_t$  increases both  $R_p$  and  $X_n$ .



Autoacceleration  
Benzoyl peroxide-initiated polymerization of PMMA in benzene @ 50°C

## Chain Transfer in Free Radical Polymerization

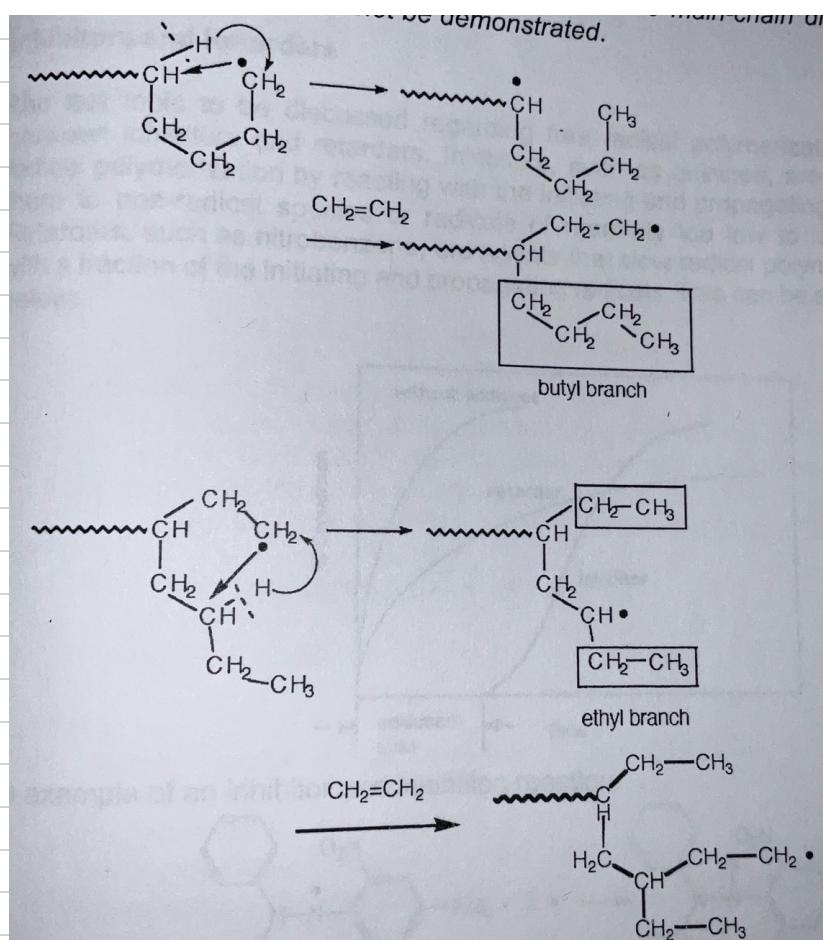
- Chain transfer occurs when one polymer chain is terminated but a new growing chain is initiated.  
 ↳ Net free radical concentration does not change → different from a termination reaction in which all free radicals are consumed

- Types of chain transfer: Intramolecular charge transfer, and intermolecular charge transfer  
**Intramolecular Chain Transfer (Backbiting/Short-chain branching)**

- Growing polymer chain can transfer a free radical within its own polymer chain by forming a quasi branched ring
- Thermodynamic stability of the 6-membered ring leads to this type of Backbiting
- Results in short-chain branching like ethyl and butyl groups being formed

↳ commonly found in polyethylene, as seen below

Note that addition of the monomer unit after the free radical transfer is extremely important to verify the closure of the mono-chain structure. Without the mono-chain structure along the existence of short chains cannot be demonstrated.

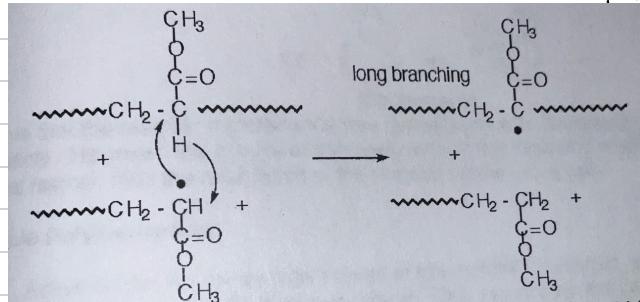


## Pages 71-72

### Chain Transfer in Free Radical Polymerization

#### Intramolecular Charge Transfer (Long-chain Branching)

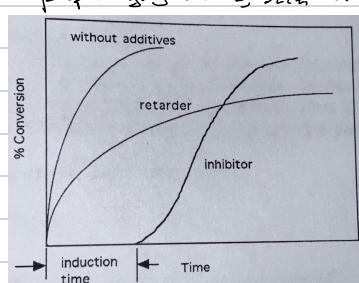
- The type of transfer is b/w two different polymer chains, in which one active chain reacts with a terminal chain.
- The radical is simply switched from one chain to the other as seen below.
- Intramolecular chain transfer b/w two polymer chains can be a cause of long chain branching.



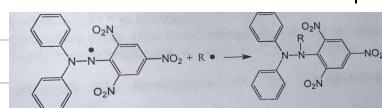
A long chain grows from the newly formed free radical into the middle of the chain to the extent that destruction of the non-chain is difficult due to the similar length of all the chains from the branch point.

### Inhibitors and Retarders

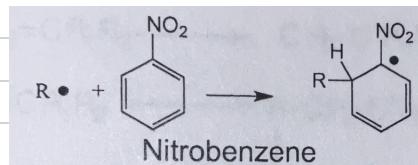
- Inhibitors (like quinones) are agents that prevent radical polymerization by reacting with the radicals and propagating radicals.
- ↳ Converts them to non-radical species or radicals of low reactivity too low to undergo propagation.
- Retarders (like nitrobenzene) are agents that slow radical polymerization by reacting with a fraction of the initiating and prop. radicals, seen below:



#### Inhibitor & Inhibition Example

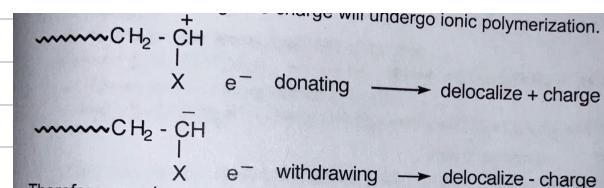


#### Retarder & Retarder Example



### Ionic Polymerization

- Active centers are anions instead of a free radical.
- More monomer specific than free radical.
- ↳ only monomers that can sufficiently stabilize positive or negative charge will undergo ionic polymerization.
- Most monomers cannot be polymerized by ionic polymerization.
- Characteristics of ionic polymerization:
  - Low polymerization is faster than free radical polymerization (generally).
  - $[M^+] = \text{concentration of propagating chain is higher}$
  - $[M^+], [M^-] = 10^4 - 10^6 [M_0]$
  - Counter ion of opposite charge.
  - Degree of association influences rate and stoichiometry of propagation  $\Rightarrow$  polarity of solvent ability to solvate counterion similarly affects it.
  - Termination cannot occur between two growing chains (coupling).
  - Active centers are of the same charge and the same charge repel each other so coupling cannot take place.



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## Lewis Polymerization (continued)

### Cationic Polymerization

(i) Initiators: Creation of  $\text{P}^+$  active centers: Monomer + electrophiles,  $\text{P}^+$

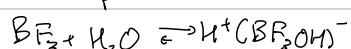
a) Proton acids,  $\text{H}_2\text{SO}_4$  + Protonic acids,  $\text{HClO}_4$  involve addition of  $\text{H}^+$  to monomer

b) Hydrogen halide acids,  $\text{HCl}$  → not suitable because  $\text{Cl}^-$  recombines

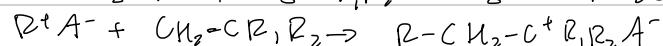
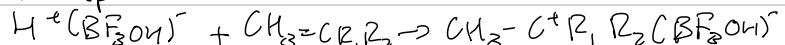
c) Lewis acids + co-catalyst: strong acids and organohalides

↳ Buon trifluoride:  $\text{BF}_3$ ; Aluminum chloride:  $\text{AlCl}_3$ ; Tin tetrachloride,  $\text{SnCl}_4$

#### First Step:



#### Second Step:



initiator

deactivating  $\text{P}^+$

consumes  $\text{A}^-$

### (ii) Propagators

- Similar to free radical. Used for many stereospecific polymers

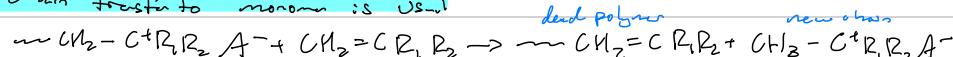
- Predominantly Head-to-Tail

### (iii) Termination

a) Unimolecular rearrangement of ion pair

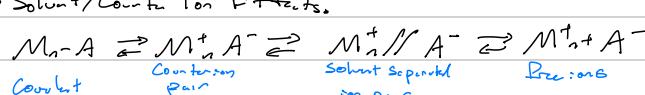


b) Chain transfer to monomer is usual



↳ chain transfer to coupling impurities,  $\text{H}_2\text{O}$ , polymer (branched) are all common

- Kinetics? Specific to actual monomer, solvent, initiators...
- Solvent/Counterion effect?  $\text{PPR}_2\text{A}^-$



- Very polar solvents (chlorobromomethane) separate ions and large, bulky counterions ( $\text{SbCl}_6^-$ ) weakly associated - fast

**General Practical Considerations:**  
Side reactions are many, and likely.  
Sub-zero temperatures are often necessary for high molecular weight polymers  
If water is co-catalyst, it must be stoichiometric  
 $\text{H}_2\text{O}$  is good charge transfer agent  
Rigorously dried, purified  
Rapid; complete conversion in seconds  
Problem: heat transfer  
non-steady state conditions!

**Only Commercially Noteworthy Example:**  
Synthesis of butyl rubber by copolymerization of isobutylene with small amount of isoprene at  $-30^\circ\text{C}$  using Lewis acid initiator ( $\text{AlCl}_3$ ) in chlorinated solvents such as dichloromethane.

## Anionic Polymerization

- Absence of an inherent termination process

→ Ion pair rearrangement involves cleavage of a hydride ion,  $\text{H}^-$  ... highly unfavorable

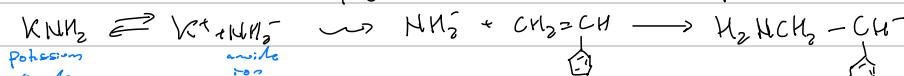
→ Alkal: metal counter ions,  $\text{O}^-$  however tends to recombine with active group centers to form a dead polymer

- No tendency to create an unstable polymer without chain transfer

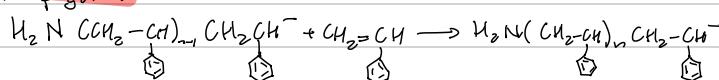
• Lewis Polymerization: Polymer chain that primarily rotates than active centers and grows as long as there is monomer present

↳ Example: Polymerization of styrene in liquid ammonia (one of the first examples of anionic polymerization)

(i) Initiators: Follows Stevens polymerization in liquid ammonia example



### (ii) Propagators



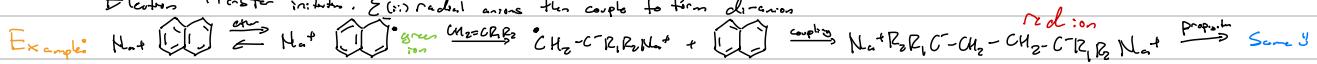
### (iii) Chain Transfer



↳ very reactive

- Organolithium compounds: Butyl lithium used with non-polar hydrocarbon solvents w/ low  $\text{Cs}$  contents -- living Polymerization

- Electron transfer initiators: Involves deprotonation of a single electron to form metal anions



## Molecular Weight Distributions

- Without Termination  $\rightarrow$  Poisson Distributions

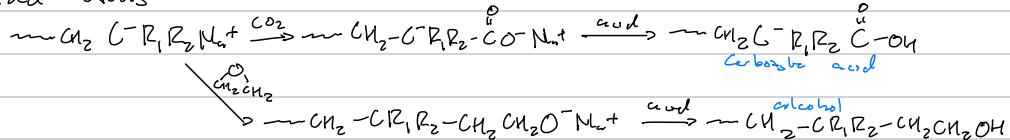
$$\frac{M_w}{M_n} = 1 + \frac{1}{\sigma_n^2}, \text{ as } \sigma_n \rightarrow \infty, PDI \rightarrow 1$$

## Termination of the Propagation Lanes

- Add Alcohols



- Add Acids



## Solvent/Counterion Effects

- $\text{M}^+$  Counter ions are small in A<sup>-</sup>
  - $\rightarrow$  tight bond
  - $\rightarrow$  Propagation  $\text{LO}^2-\text{LO}^2$  times slow than cations
  - $\rightarrow$  Using polar solvents help solvate counterions more
  - If propagation is slow compared with K<sub>12</sub> broad molecular weight distribution results
- Practical Considerations
  - $\rightarrow$  High Reactivity
  - $\rightarrow$  Low Concentration of reactive species
    - Purify, Dryness, inert gases ( $\text{He}, \text{Ar}, \text{CO}_2, \text{O}_2$  and vinyl group chains)
    - Disp. Difficulties: Very narrow PDI, block copolymers of defined length

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## Polymerization by Photo, High Energy Radiation, and Electrons

- Polymerisation doesn't have to depend on chemical initiators  $\Rightarrow$  can take place as long as carbon bonds can be cleaved and active species can be created by other energy sources
    - $\hookrightarrow$  Active species can be made using photons, electrons and other high energies such as  $\gamma$ -rays can be utilized as effective initiators

## A. Photopolymerization and Photo-crosslinking

- UV light (typically) or visible light can be used to initiate monomers for:
    - { Photopolymerization e.g. Acrylamide or  $[CH_2=CH(CO)NH_2]$
    - { Photocrosslinking e.g. Poly(vinyl) cyanoacrylate

A distinct of Photopolymerization in comparison to chemical initiated free radical polymerization

- (i) No contamination by transition metal c.s.c photoinitiator is not added)
  - (ii) Polymerization can be fast (matter of seconds)

- Shallow depth of UV front penetration may be a problem if a bulk polymerisation is desired (UV light cannot penetrate as it degrades the material).

is not a significant limitation; if  $\alpha$  cont. is to be polarized

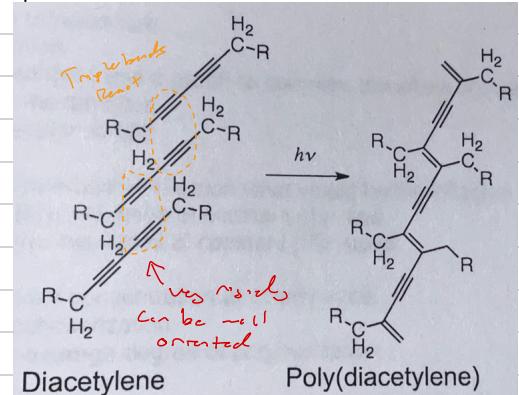
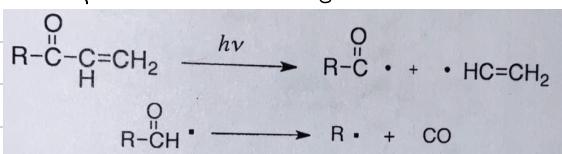
- Visible light can penetrate deeper  $\rightarrow$  able to polymerize thicker films (awkward, expensive and slow)
- # of photo-curable monomers limited because of lack of ideal UV absorption for photo-calc.

↳ Can add a photo sensitizer to allow poor polars to have UV cleavage → can be polarized

• UV light can also be used polymerize certain molecules directly in the solid state (crystalline state)

- Solid-state polymerization of a diacoflate monomer is shown here -  
 $\xrightarrow{\text{With little molecular movement}}$   
 accompanies from the monomer to poly structures

## Exercises of Photoyses



## B. Polymerization by High Energy Radiation

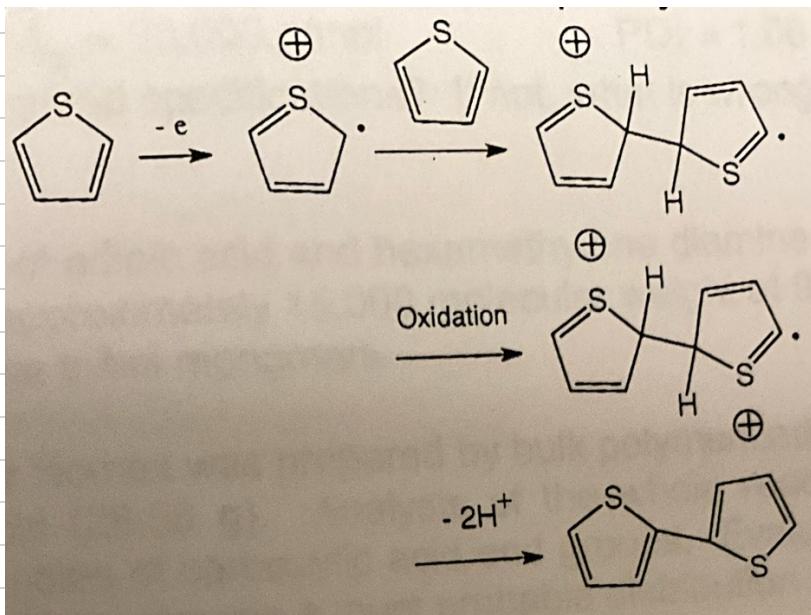
- Almost all forms of living polymerization use living monomers, and  $\gamma$ -ray is often used
  - Initiator is more complicated than classical initiators and is unnecessary when a solvent coexists with the radicals also generates initiating radicals and ions from both the monomer and solvent
  - Advantages:
    - { Homogeneous polymerization throughout the sample
    - Avoidance of contamination by the initiator

## Electrochemical Polymerization

Thiophene

- Potential applied across a solution containing a certain monomer  $\rightarrow$  initiating group formed  $\rightarrow$  propagates to form polymer
- Polymerized material generates freely and homogeneously formed (p-hydroxyl free) coats metal electrode  
 $\hookrightarrow$  Method is ideally suited to prepare coating for corrosion protectors where pit hole is often the starting locus of the corrosion
- The method of polymerization is not appropriate for bulk quantity polymers as the thickness of the film plausibly increases causing efficiency of techniques to be reduced quickly

Example: Initial steps of the electropolymerization of thiophene



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**Pages 84-85**

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