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Basic Definitions

Synonomously used, along w/ 'Han Polymer'

Polymer: Large Molecule comprised of many repeat units derived from monomers
Macromolecule: More general, not indicative of repetitive structure
Oligomer: Low-molecular weight polymer
↳ no clear distinction in the 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

Polysaccharides: Important polymeric materials found in food + living systems
Nanocomposites: Small amt. filler/additive mixed with a polymer → Small scale applications
Supramolecular Polymers: Self-assembly, bonded with Hydrogen or Metallic bonds (polymers generally covalent)
↳ Example: Stimuli-responsive gels which exhibit property change upon application of a stimulus
OLEDs: Highly conjugated, electroluminescent polymers → could replace liquid crystal displays (LCDs) as they provide ↑ performance @ ↓ cost
↳ Organic Light Emitting Diodes
Color-changing: Change w/ stress, usually visible under UV
Functional Polymers: Usual Attractive properties, but certain functions are selectively enhanced
↳ Attractive Properties: Light weight, good mechanical props, toughness, and excellent processability
Kevlar: Structure → very strong! 5x stronger to steel @ = 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 strengthening its structure
Polybenzoxazole: Can create stronger fibers than UHMWPE, but environmentally sensitive
Spider's Web: 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		Thermoplastics	
Amorphous Polymers		Amorphous Polymers	
Polystyrene	Cups, packaging, styroform	Poly(vinyl chloride)	Shoes, hose, toys, raincoat, pipes
Poly(methyl methacrylate)	Window materials, contact lens, optical fiber, photoflame	Polycarbonate	Helmet, CD, lens, 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 condensor, magnetic disk
Polyoxymethylene	Gear, sporting goods	Poly(lactic acid)	3D printing wires, utensils

Thermosets Epoxy resins	Adhesive, automotive and aerospace parts, composites	Thermosets 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, composites
Elastomers Polybutadiene	Automotive tire	Elastomers 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

General name of copolymers	Comonomers	Applications
Acrylonitrile-butadiene-styrene rubber (ABS)	$H_2C{=}CH{-}C{\equiv}N$, $H_2C{=}CH{-}C_6H_5$, $H_2C{=}CH{-}CH{=}CH_2$	Pipes, gaskets, high impact containers
Butyl rubber	$H_2C{=}C(CH_3)_2$, $H_2C{=}CH{-}CH{=}CH_2$	Inner tubes
Ethylene-methacrylic acid ionomer (Surlyn)	$H_2C{=}CH_2$, $H_2C{=}C(CH_3)COO^-M^+$, $H_2C{=}C(CH_3)COOH$	Golf ball
Nitrile-butadiene rubber (NBR)	$H_2C{=}CH{-}C{\equiv}N$, $H_2C{=}CH{-}CH{=}CH_2$	Adhesives, hoses
Saran	$H_2C{=}CHCl$, $H_2C{=}CCl_2$	Diffusion resistant films
Styrene-butadiene rubber (SBR)	$H_2C{=}CH{-}C_6H_5$, $H_2C{=}CH{-}CH{=}CH_2$	Tires
Viton	$F_2C{=}CF{-}CF_3$, $H_2C{=}CHF$	Gaskets

Synthetic Polymers

Name	Chemical formula		
Aromatic amide (Kevlar®)	$-NH-C_6H_4-NH-CO-C_6H_4-CO-$	Poly(tetrafluoro-ethylene)	$-CF_2-CF_2-$
Nylon-6	$-NH-CO-(CH_2)_5-$	Polyimide (Kaptone®)	[pyromellitimide]$-C_6H_4-O-C_6H_4-$
Nylon-6,6	$-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-$	Polyisobutylene	$-CH_2-C(CH_3)_2-$
Polyacrylamide	$-CH_2-CH(CONH_2)-$	cis-1,4-Polyisoprene	$-CH_2-C(CH_3){=}CH-CH_2-$ (cis)
Polyacrylonitrile	$-CH_2-CH(C{\equiv}N)-$	trans-1,4-Polyisoprene	$-CH_2-C(CH_3){=}CH-CH_2-$ (trans)
cis-1,4-Polybutadiene	$-CH_2-CH{=}CH-CH_2-$ (cis)	Poly(methyl methacrylate)	$-CH_2-C(CH_3)(COOCH_3)-$
trans-1,4-Polybutadiene	$-CH_2-CH{=}CH-CH_2-$ (trans)	Polypropylene	$-CH_2-CH(CH_3)-$
1,2-Polybutadiene	$-CH_2-CH(CH{=}CH_2)-$	Polyoxymethylene	$-CH_2-O-$
Polycarbonate	$-C_6H_4-C(CH_3)_2-C_6H_4-O-CO-O-$	Polystyrene	$-CH_2-CH(C_6H_5)-$
Poly(dimethyl siloxane)	$-Si(CH_3)_2-O-$	Poly(vinyl acetate)	$-CH_2-CH(OCOCH_3)-$
Polyethylene	$-CH_2-CH_2-$	Poly(vinyl alcohol)	$-CH_2-CH(OH)-$
Poly(ethylene oxide)	$-CH_2-CH_2-O-$	Poly(vinyl chloride)	$-CH_2-CHCl-$
Poly(ethylene terephthalate)	$-CO-C_6H_4-CO-OCH_2CH_2O-$	Poly(vinylidene chloride)	$-CH_2-CCl_2-$

Polymers to Remember

Polymer	Monomer
$-[O-CO-C_6H_4-CO-O-CH_2-CH_2-O]_n-$ Poly(ethylene terephthalate) (PET)	$HOOC-C_6H_4-COOH$ terephthalic acid; $HOCH_2CH_2OH$ ethylene glycol
$-(CH_2-CH_2)_n-$ Polyethylene (PE)	$H_2C{=}CH_2$ ethylene
$-(CH_2-CHCl)_n-$ Poly(vinyl chloride) (PVC)	$H_2C{=}CHCl$ vinyl chloride
$-(CH_2-CH(CH_3))_n-$ Polypropylene (PP)	$H_2C{=}CH(CH_3)$ propylene
$-(CH_2-CH(C_6H_5))_n-$ Polystyrene (PS)	$H_2C{=}CH(C_6H_5)$ styrene
$-(CH_2-C(CH_3)(COOCH_3))_n-$ Poly(methyl methacrylate) (PMMA)	$H_2C{=}C(CH_3)COOCH_3$ methyl methacrylate
$-[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]_n-$ Nylon-6,6	$HOOC(CH_2)_4COOH$ adipic acid; $H_2N(CH_2)_6NH_2$ hexamethylenediamine
$-(O-C_6H_4-C(CH_3)_2-C_6H_4-O-CO)_n-$ Polycarbonate (PC)	$HO-C_6H_4-C(CH_3)_2-C_6H_4-OH$ bisphenol-A; $Cl-CO-Cl$ phosgen
$-(CH_2-CH{=}CH-CH_2)_n-$ Trans-1,4-polybutadiene	$CH_2{=}CH-CH{=}CH_2$ butadiene
$-(CF_2-CF_2)_n-$ Poly(tetrafluoro ethylene)	$F_2C{=}CF_2$ tetrafluoro ethylene

Recycling Numbers & Associated Polymers

Recycling number	Polymer	Recycling number	Polymer
1	Poly(ethylene terephthalate)	5	Polypropylene
2	High density polyethylene	6	Polystyrene
3	Poly(vinyl chloride)	7	Other
4	Low density polyethylene		

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

- Poly + "name of monomer" despite polystyrene not repeating 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
- $M_N = \frac{\sum N_x M_x}{\sum N_x}$ number avg
- $M_w = \frac{\sum W_x M_x}{\sum W_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$ weight avg
- $M_z = \frac{\sum N_x M_x^3}{\sum N_x M_x^2}$ z-avg

$\} M_z > M_w > M_N$

- Polydispersity index measures breadth of distributions of the molecular weights in a polymers

$PDI = \frac{M_w}{M_N}$ Always greater than 1

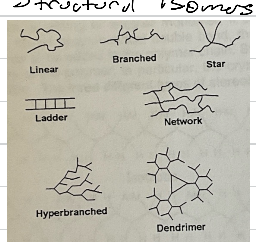
Nature of MW's obtained by different methods

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	$2x10^4 - 10^6$
Terminal group concentration	Absolute	Mn	$< 10^4$
Light scattering	Absolute	Mw	$10^4 - 10^8$
Sedimentation	Absolute	Mw, Mz	$10^2 - 5x10^6$
Intrinsic viscosity	Relative	Mv	$10^3 - 10^8$
Size exclusion chromatography(SEC)	Relative	Mn, Mw, Mz	$10^2 - 10^7$

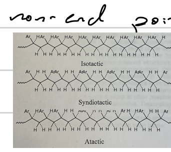
- Thermoplastics: softens & liquifies upon heating
- Thermosets: become permanently solid upon heating

Typically Cross-linked ↗ ↳ usually thermally and chemically resistant

- Structural Isomers



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



- Atactic Polymers are usually amorphous

Graft: -A A A A A A A A A-
B B B B
B B B B
B

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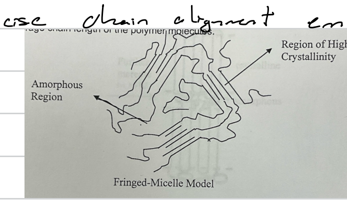
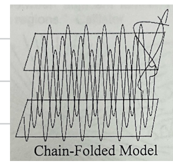
- Semicrystalline nature of polymers: Crystal Complexity leads to crystalline regions dispersed within amorphous material. Misalignment of chains create these amorphous regions.
  - ↳ Degree of crystallinity can vary from completely amorphous to 95% crystalline
- Fringed-micelle model: small cryst. regions with precise chain alignment embedded in amorphous matrix of randomly oriented molecules. As shown to the right. Possible for one polymer chain to pass through several micelles

Called micelles

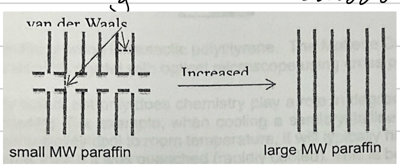


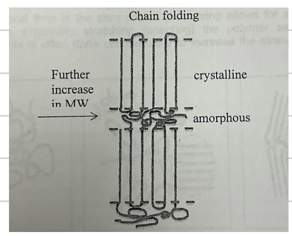
- Chain Folded Model: Molecular chains in a platelet fold back and forth on themselves → Folds occuring on the faces of the platelet. Avg Platelet thickness much less than avg. chain length of polymer molecules.



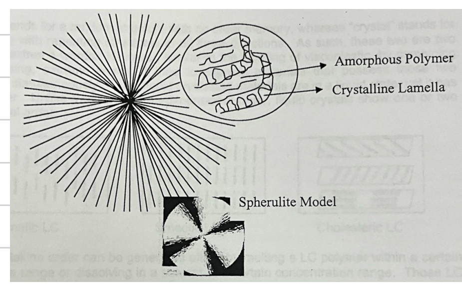
→ As chain length ↑, packing changes. Long-chain molecules develop instability

- Combining two above models: Amorphous Regions between two cryst. regions, where there is no ordered packing

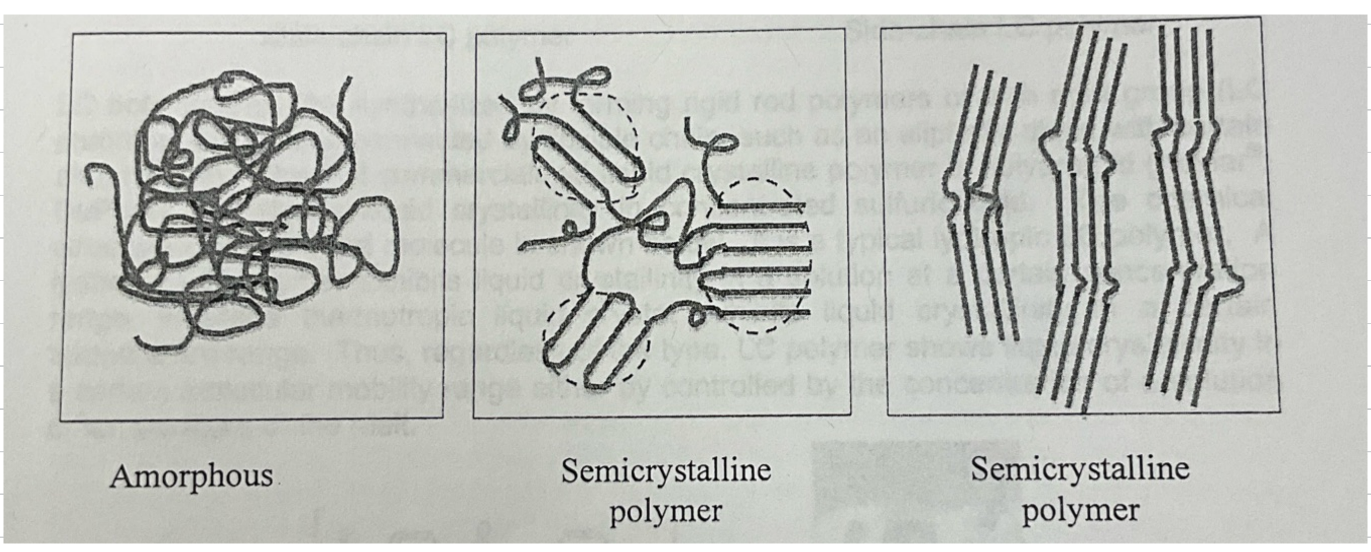




- Spherulite Model: Lamellae (ribbon-like chain-folded crystallites) radiate from the center outward. Separated by an amorphous material. On the right, a single spherulite grows in isotactic polystyrene. Maltese Cross pattern seen by observing crystal with optical microscope using cross polarizer.



- 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 formation
- Physically stretching, or orienting, the polymer can induce crystallization.
  - ↳ Often done commercially to ↑ strength of product



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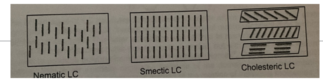
Liquid: Random structure with no order memory

Crystal: A structure with repeating structures in all 3 directions

> Opposite and opposing words

Liquid Crystalline: Materials in a liquid state, yet it has some order.



↳ show one or two dimensional order

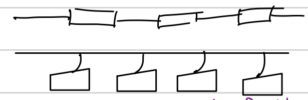
→ Generated by melting an LC polymer within a certain range (thermotropic LC Polymers)

→ Generated by dissolving in a solvent @ a certain conc. range (lyotropic LC Polymers)

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

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

{ LC chromophores placed in the main chain of polymer $\xrightarrow{\text{called}}$ LC polymers
{ 〃 placed in the side chain $\xrightarrow{\text{called}}$ side-chain LC polymers



→ Can be synthesized by forming rigid rod polymers or with rigid group ← Connected by flexible chains such as an alliphatic 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 colorimetric (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

Biopolymers ← Biomaterials study/focus on this specifically

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

↳ Many others synthesized from naturally occurring monomers