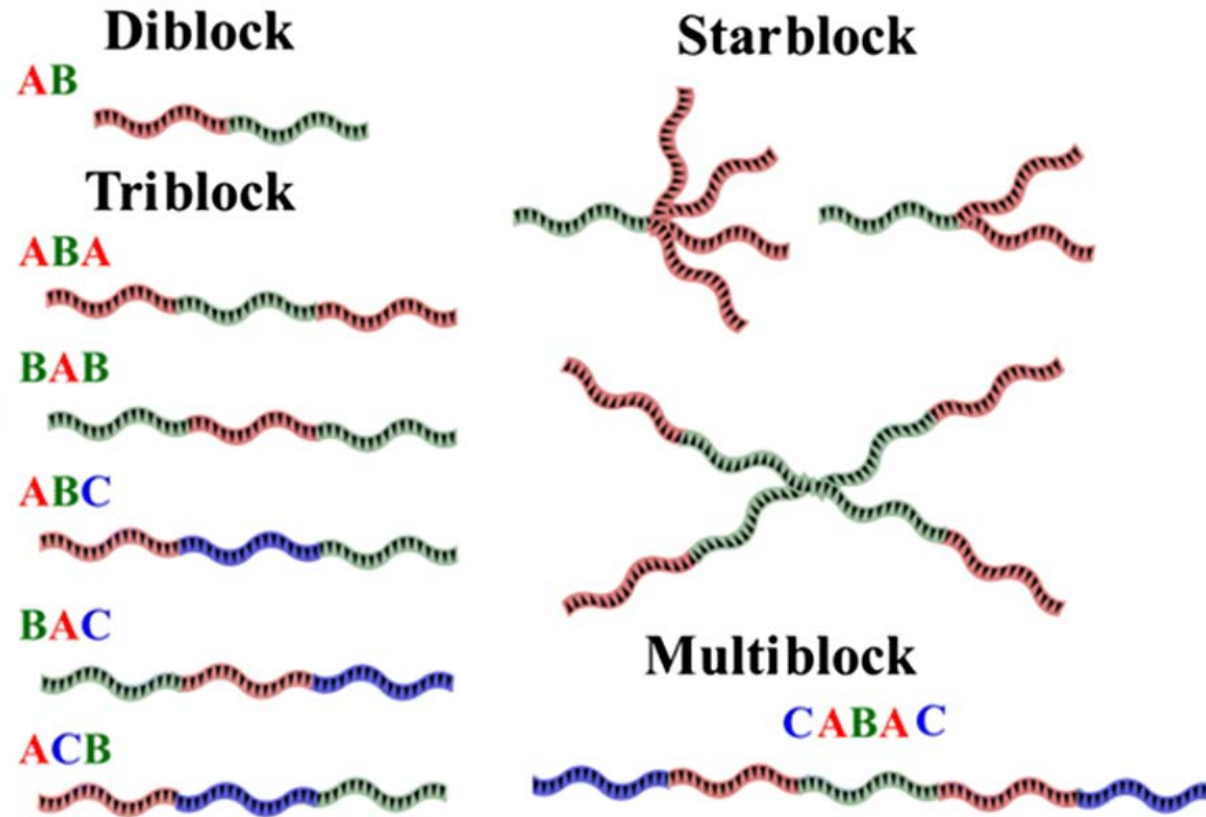


❖ Nomenclature of Polymers



❑ Block co-polymers

In these copolymers, the building blocks of varied monomer compositions are linearly organized.

The blocks are mixes of homo-polymers and copolymers with different compositions.

❑ Example:

Polystyrene-block-polybutadiene-block-polystyrene copolymer having the linear arrangement of monomer blocks of different components such as styrene and butadiene synthesized by ionic polymerization method.

Polymer

Some Linear High Polymers, Their Monomers, and Their Repeat Units

Polymer	Monomer	Repeat Unit
Polyethylene	$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2\text{CH}_2-$
Poly(vinyl chloride)	$\text{CH}_2=\text{CHCl}$	$-\text{CH}_2\text{CHCl}-$
Polyisobutylene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$
Polystyrene ^a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array}$
Polycaprolactam (6-nylon)	$\begin{array}{c} \text{H}-\text{N}(\text{CH}_2)_5\text{C}-\text{OH} \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{O} \end{array}$	$\begin{array}{c} -\text{N}(\text{CH}_2)_5\text{C}- \\ \quad \quad \quad \\ \text{H} \quad \quad \quad \text{O} \end{array}$
Polyisoprene (natural rubber)	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{C}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} -\text{CH}_2\text{CH}=\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$

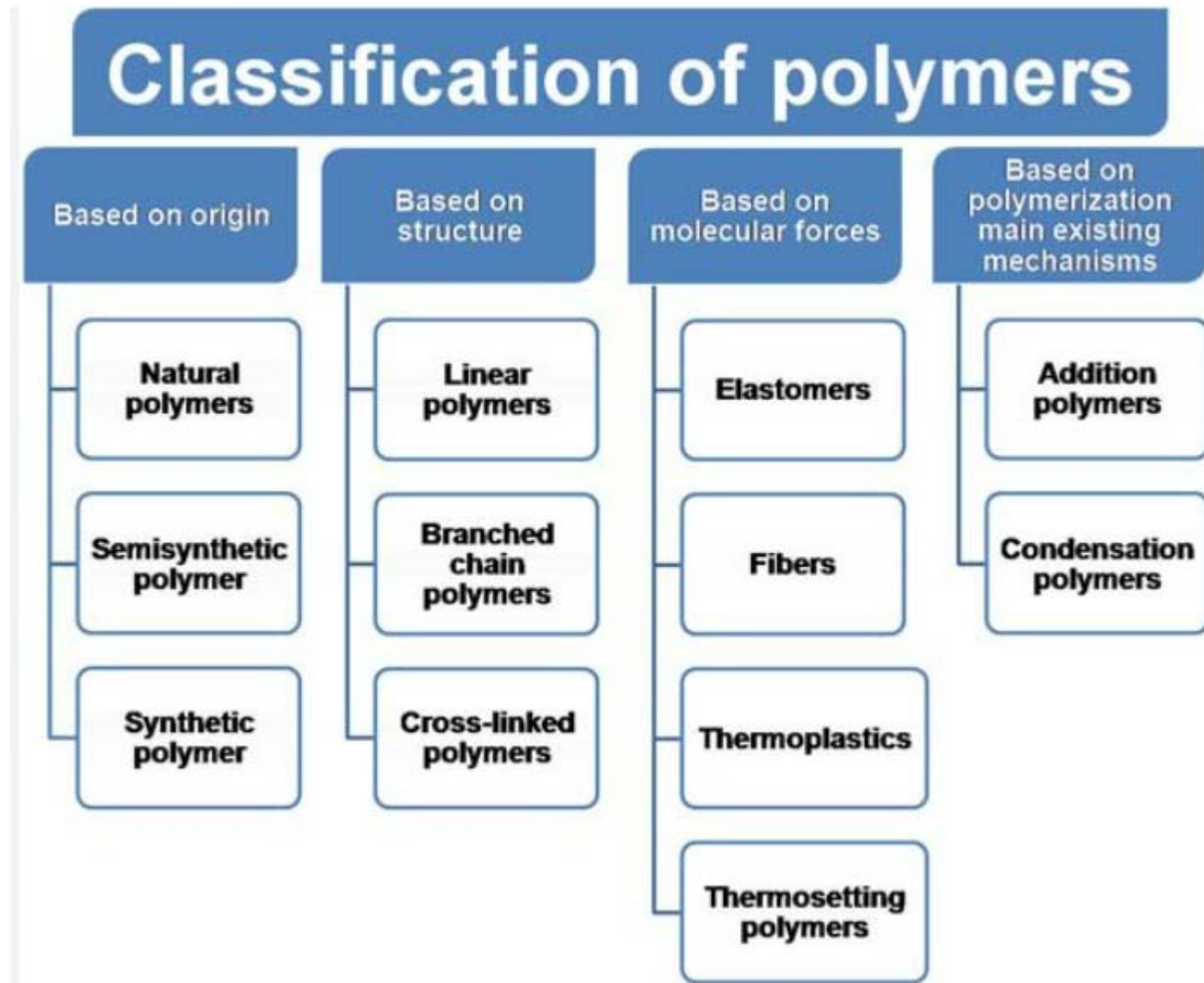
Polymer

❖ Some Commercially important Polymers and Their Dates of introduction

Date	Polymer	Date	Polymer
1930	Styrene-butadiene rubber	1943	Silicones
1936	Poly(vinyl chloride)	1944	Poly(ethylene terephthalate)
1936	Polychloroprene (neoprene)	1947	Epoxies
1936	Poly(methyl methacrylate)	1948	ABS resins
1936	Poly(vinyl acetate)	1955	Polyethylene, linear
1937	Polystyrene	1956	Polyoxymethylene
1939	66-Nylon	1957	Polypropylene
1941	Polytetrafluoroethylene	1957	Polycarbonate
1942	Unsaturated polyesters	1964	Ionomer resins
1943	Polyethylene, branched	1965	Polyimides
1943	Butyl rubber	1970	Thermoplastic elastomers
1943	6-Nylon	1974	Aromatic polyamides

Flory 1953; Mark 1966, 1967, 1977, 198 1; Staudinger 1970; Marvel 1981; Seymour 1982

Polymer



Classification of Polymers

1. Based on Origin

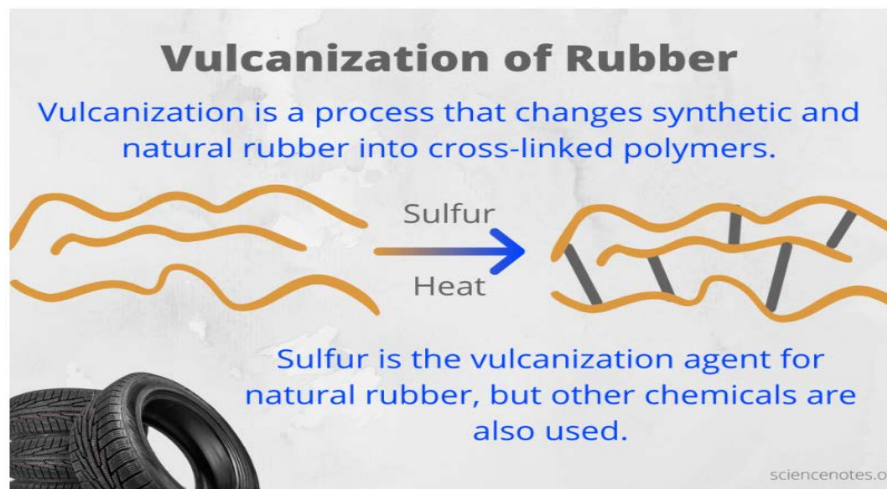
Polymers are categorized as **natural**, **synthetic**, and **semi-synthetic** depending on their source.



Natural polymers



Synthetic Polymers



a) Natural Polymers

Found in nature, produced by plants, animals, or microorganisms.

Examples:

- Proteins (e.g., silk, wool, collagen)
- Polysaccharides (e.g., cellulose, starch)
- Natural rubber (polyisoprene)

b) Synthetic Polymers

Man-made polymers synthesized from monomers.

Examples:

- Polyethylene (PE) – packaging
- Polystyrene (PS) – disposable cups
- Nylon, Polyester – textiles

c) Semi-synthetic Polymers

Chemically modified natural polymers.

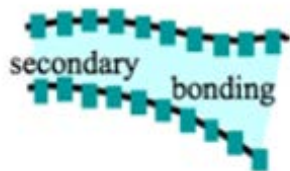
Examples:

- Cellulose acetate – used in films and fibers
- Vulcanized rubber – modified natural rubber

Classification of Polymers

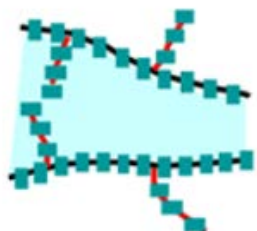
2. Based on Structure

- ❑ **Linear Polymers:** Composed of extended chains aligned in a 'spaghetti-like' morphology, held together by secondary interactions such as van der Waals forces or hydrogen bonding. These weak intermolecular forces permit chain mobility upon heating, rendering linear polymers predominantly **thermoplastic** and reprocessable through melting and re-solidification.

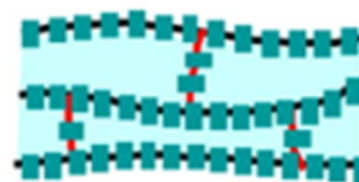


Linear

- ❑ **Branched Polymers:** Structurally similar to linear polymers but feature short side-chain branches along the main backbone. These branches hinder close chain packing, reducing crystallinity and density. Most branched polymers exhibit **thermoplastic** behavior, though highly branched or complex architectures may undergo thermal degradation before melting, exhibiting **thermosetting-like** characteristics.

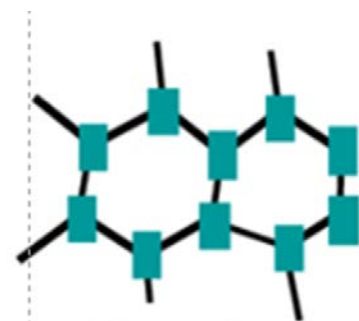


Branched



Cross-Linked

- ❑ **Crosslinked Polymers:** Consist of polymer chains interconnected via covalent bonds, forming a networked, ladder-like structure. These covalent crosslinks restrict molecular mobility and confer thermal rigidity, classifying such materials as **thermosets**, which do not soften upon heating and instead degrade at elevated temperatures.



Network

- ❑ **Networked polymers:** are complex polymers that are heavily linked to form a complex network of three-dimensional linkages. These polymers are nearly impossible to soften when heating without degrading the underlying polymer structure and are thus thermosetting polymers.

Classification of Polymers

2. Based on Structure

Polymers can have different **architectures of the molecular chain**:



a) Linear Polymers

- ☐ Long, straight chains without branching.
- ☐ Properties: high density, strong intermolecular forces.
- ☐ Example: **High-density polyethylene (HDPE), PVC**

b) Branched Polymers

- ☐ Chains with side branches.
- ☐ Properties: lower density, flexible.
- ☐ Example: **Low-density polyethylene (LDPE)**

c) Cross-linked Polymers

- ☐ Chains linked by covalent bonds forming a network.
- ☐ Properties: rigid, thermosetting.
- ☐ Example: **Bakelite, Melamine**

d) Network Polymers

- ☐ Highly cross-linked 3D structure.
- ☐ Example: **Phenol-formaldehyde resin**

Classification of Polymers

3. Based on Molecular Forces



❑ **Elastomers:** Elastomers are polymers with very weak intermolecular forces. These weak forces are enough to hold the polymer chains together, but they allow significant mobility of the chains.

➤ **Key Features:**

Soft and elastic in nature.

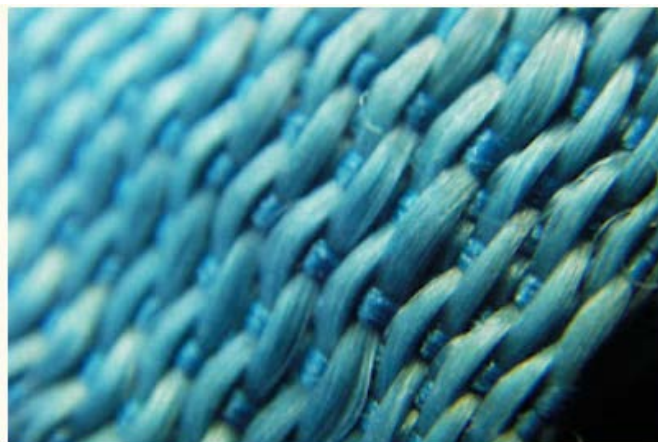
Capable of undergoing large elastic deformation when a force is applied and can return to their original shape when the force is removed.

Weak van der Waals forces between chains provide flexibility, while occasional cross-links prevent permanent deformation.

➤ **Examples:** **Natural Rubber** (polyisoprene), **Synthetic Rubber-** Buna-S (styrene-butadiene rubber), Buna-N (nitrile rubber), Neoprene (polychloroprene)

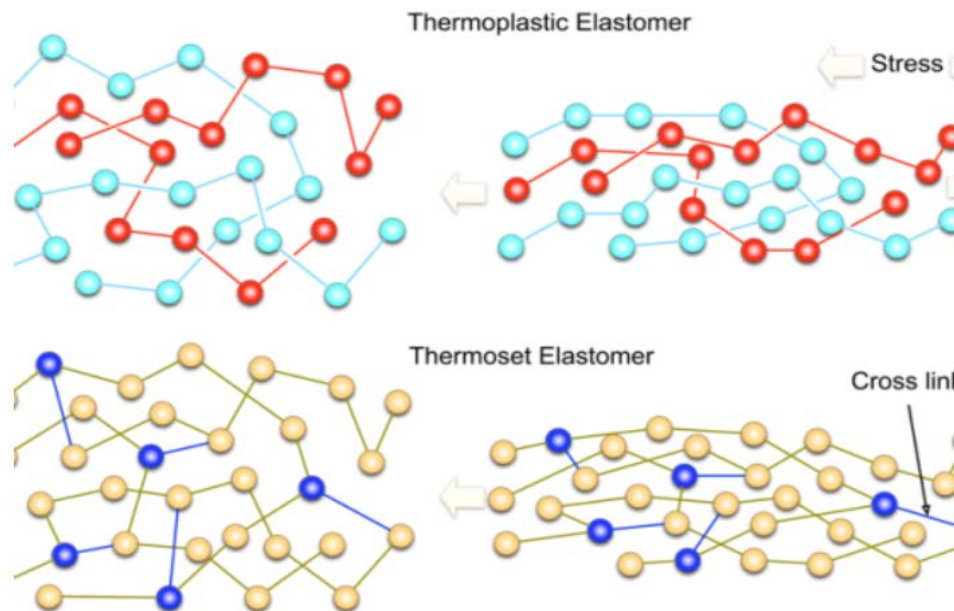
❑ **Fibers:** Fibers are polymers that are thread-like and crystalline in nature, having strong intermolecular forces such as hydrogen bonding or dipole-dipole interactions)

➤ **Examples:** Polyamides (Nylon-6,6, Nylon-6), Polyesters



Classification of Polymers

3. Based on Molecular Forces



❑ **Thermoplastics:** Thermoplastics are polymers in which the intermolecular forces are **intermediate in strength** (stronger than elastomers but weaker than fibers).

➤ **Key Features:**

Can be softened upon heating and hardened upon cooling (reversible process), They can be remolded and recycled, Flexible and tough.

➤ **Examples:**

Polyethylene (PE), LDPE (branched), HDPE (linear), Polyvinyl Chloride (PVC), Polystyrene (PS)

❑ **Thermosets:** Thermosets are polymers where chains are heavily cross-linked through strong covalent bonds, forming an infusible and insoluble rigid network.

➤ **Key Features:**

Once set (hardened), they cannot be remolded. Hard, brittle, and highly heat-resistant. High mechanical strength and chemical resistance.

➤ **Examples:**

Bakelite (Phenol-formaldehyde resin), Melamine-formaldehyde resin, Epoxy resins

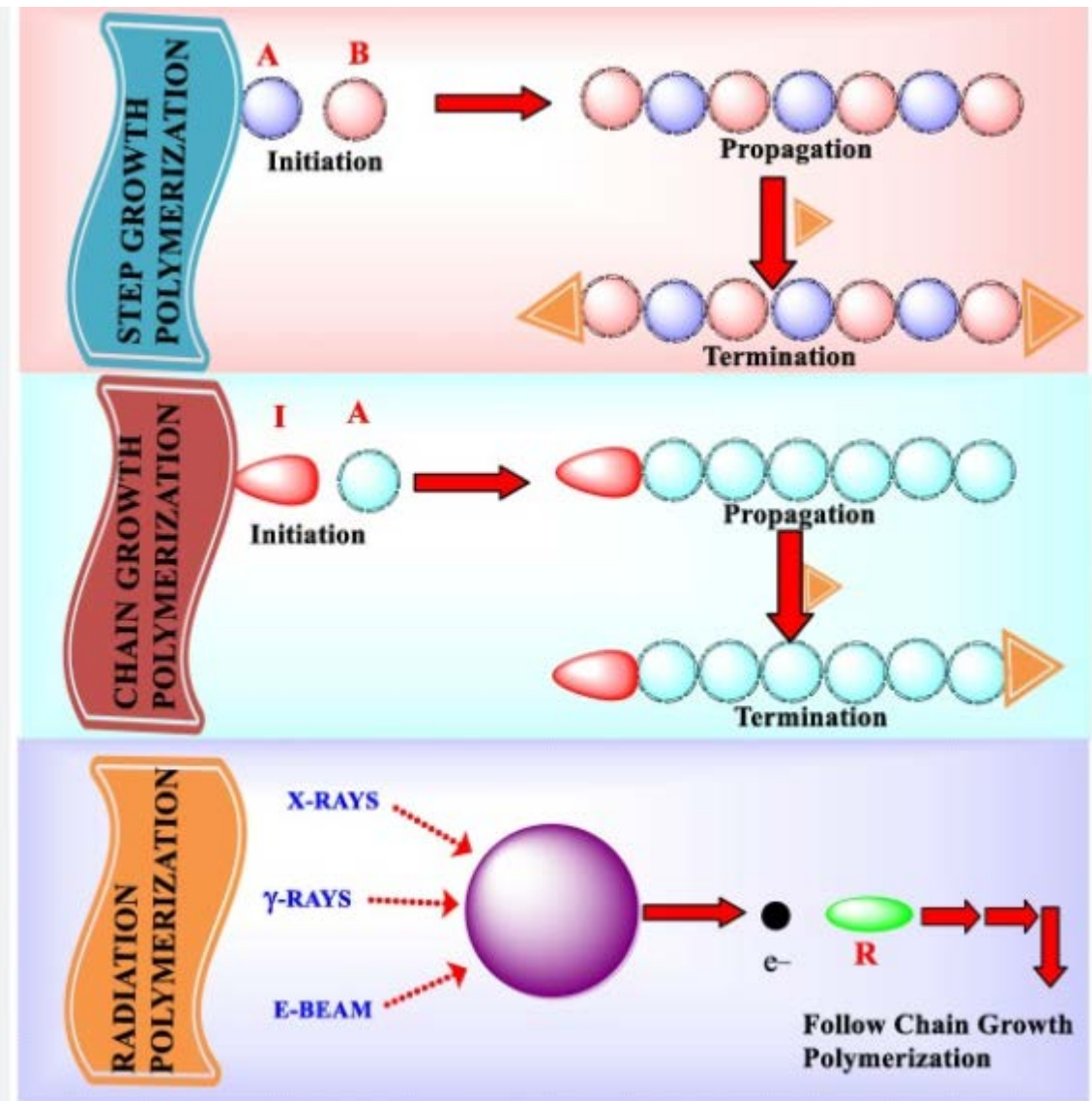


Classification of Polymers

3. Based on Molecular Forces(Comparison Table)

Category	Forces Involved	Characteristics	Examples
Elastomers	Weak van der Waals forces	Soft, elastic, stretchable	Natural rubber, Buna-S
Fibers	Hydrogen bonding/dipole	High tensile strength, crystalline	Nylon-6,6, Polyester
Thermoplastics	Intermediate forces	Re-moldable, flexible	PVC, Polyethylene
Thermosets	Strong covalent cross-links	Hard, brittle, non-remoldable	Bakelite, Melamine resin

Polymerization Processes.



- ❑ The processes of polymerization were divided by Flory (1953) and Carothers (Mark 1940) into two groups known as condensation and addition polymerization or, in more precise terminology step- and chain-reaction polymerization.

Condensation (Step-Reaction) Polymerization: Involves the reaction of polyfunctional monomers, forming large molecules with the elimination of small byproducts (like water); proceeds gradually and often results in polymers with heteroatoms in the backbone.

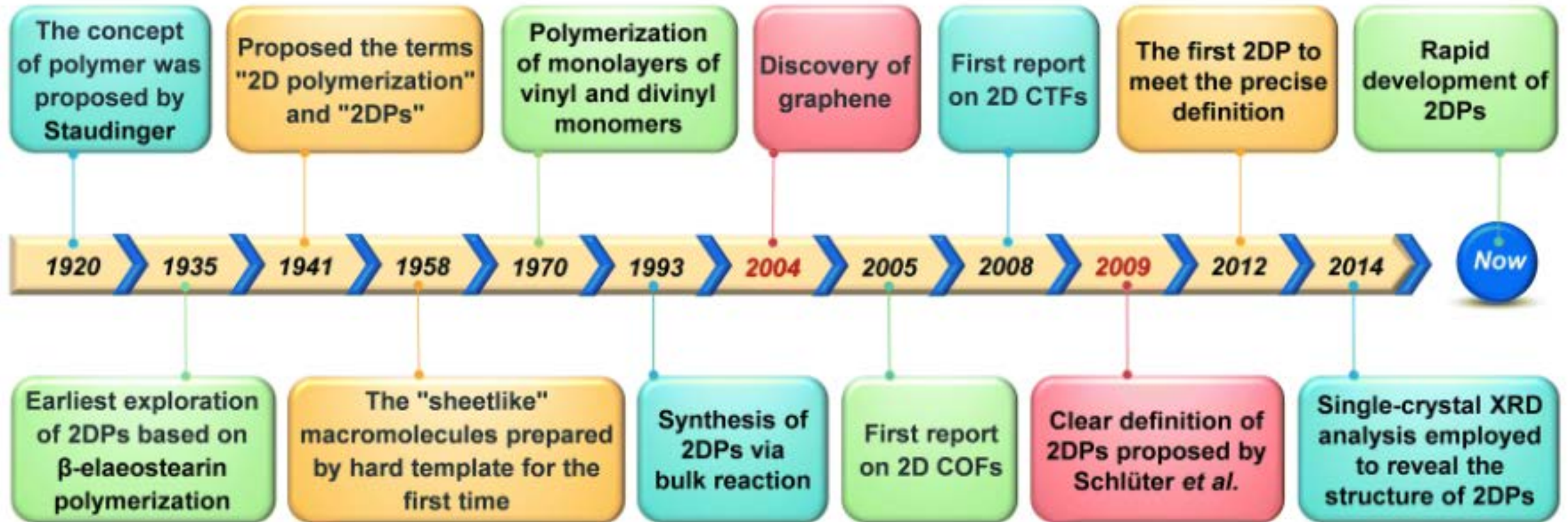
Addition (Chain-Reaction) Polymerization: Involves rapid chain growth initiated by reactive species (e.g., free radicals), where monomers add without byproduct elimination; typically forms homochain polymers with carbon-only backbones.



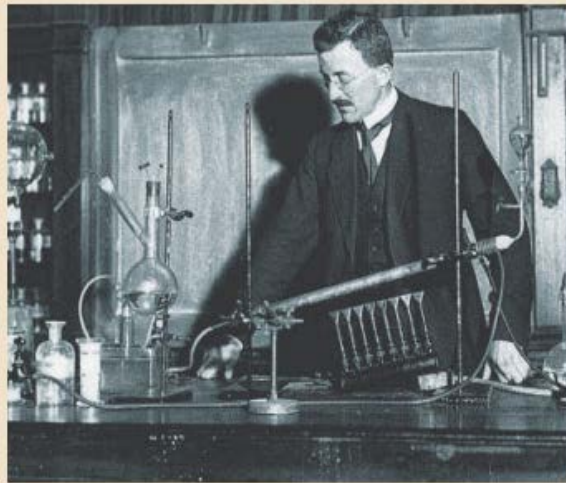
Polymerization Processes.

Chain Polymerization	Step Polymerization
Only growth reaction adds repeating units one at a time to the chain.	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction.	Monomer disappears early in reaction: at $DP \approx 10$, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Long reaction times give high yields but affect molecular weight little.	Long reaction times are essential to obtain high molecular weights.
Reaction mixture contains only monomer, high polymer, and about 10^{-8} part of growing chains.	At any stage all molecular species are present in a calculable distribution.

Short History of The Polymerization Process



Short History of The Polymerization Process



Hermann Staudinger early in his career.



Hermann Staudinger (center) with colleagues in 1935.



Hermann Staudinger House, the home of the Institute for Macromolecular Chemistry.



Hermann Staudinger receiving the Nobel Prize for chemistry from King Gustav Adolf of Sweden.

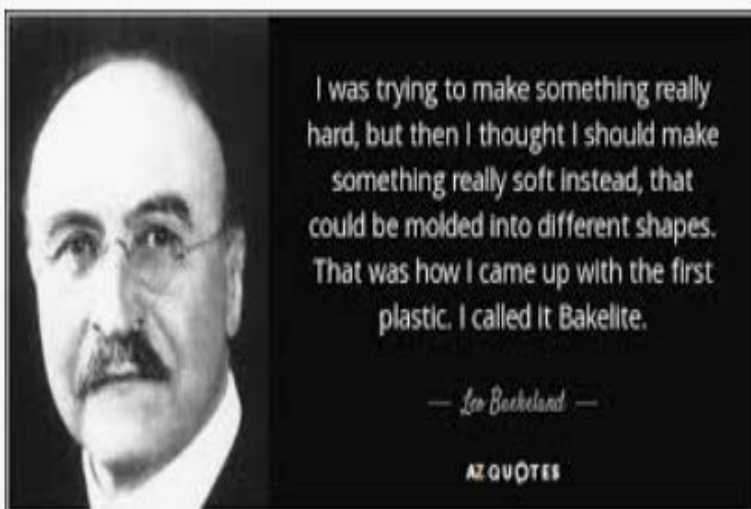
❖ Early Observations (Pre-20th Century)

- ❑ **1839:** *Charles Goodyear* discovered **vulcanization of natural rubber** by heating rubber with sulfur, improving elasticity and durability.
- ❑ **Mid-1800s:** *Hermann Staudinger* proposed that polymers are **long-chain molecules**, challenging the earlier idea that they were aggregates of small molecules.

❖ Foundation of Polymer Science

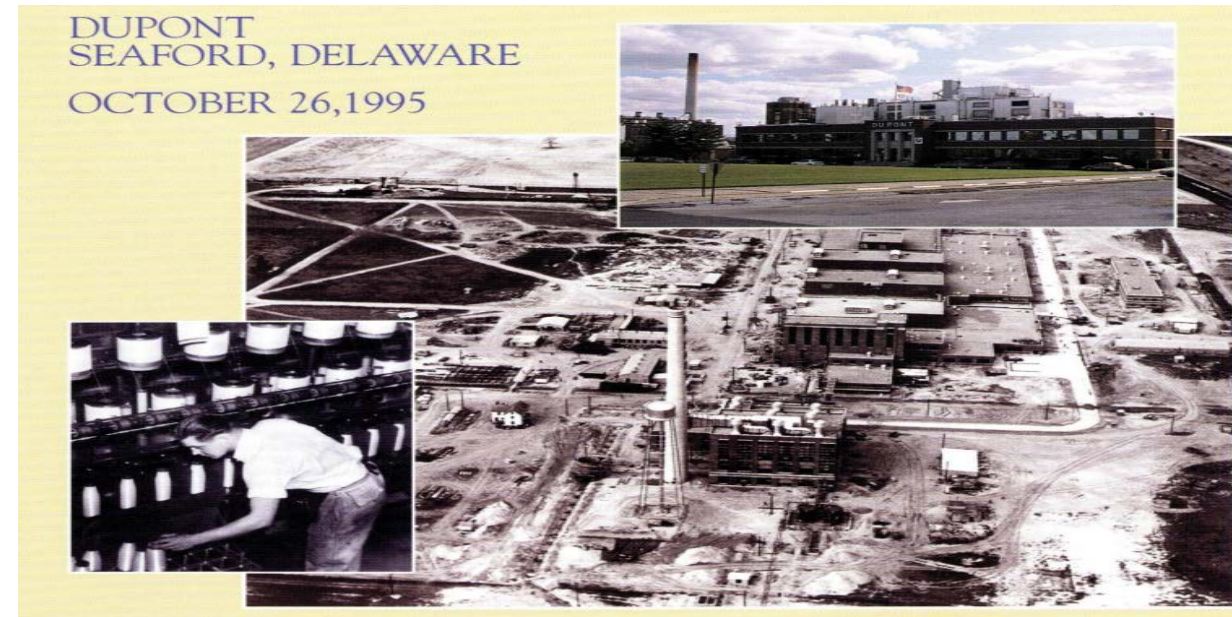
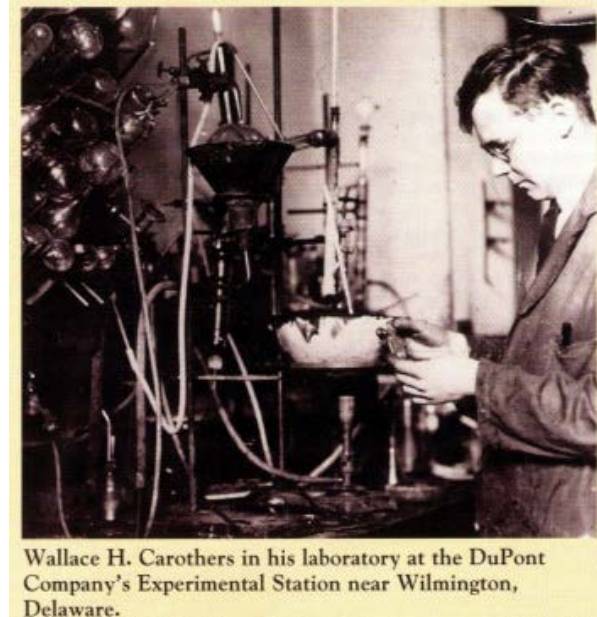
- ❑ **1920:** Staudinger introduced the **macromolecular theory**, proving that polymers are covalently bonded long chains.
(He received the **Nobel Prize** in 1953 for this work.)

Short History of The Polymerization Process



❖ Development of Synthetic Polymers

- ❑ **1907:** *Leo Baekeland* developed **Bakelite**, the first fully synthetic thermosetting polymer.
- ❑ **1920s–1930s:** Discovery of **vinyl polymers** (PVC, polystyrene) and **polyamides** (Nylon).
- ❑ **1935:** *Wallace Carothers* (DuPont) synthesized **Nylon-6,6**, marking the era of fiber-based polymers.



Short History of The Polymerization Process

Karl Ziegler and Giulio Natta

In the early 1950s Ziegler and Natta discovered a new process for synthesizing polymers that made possible a lot of common plastics, including high-density polyethylene and polypropylene.

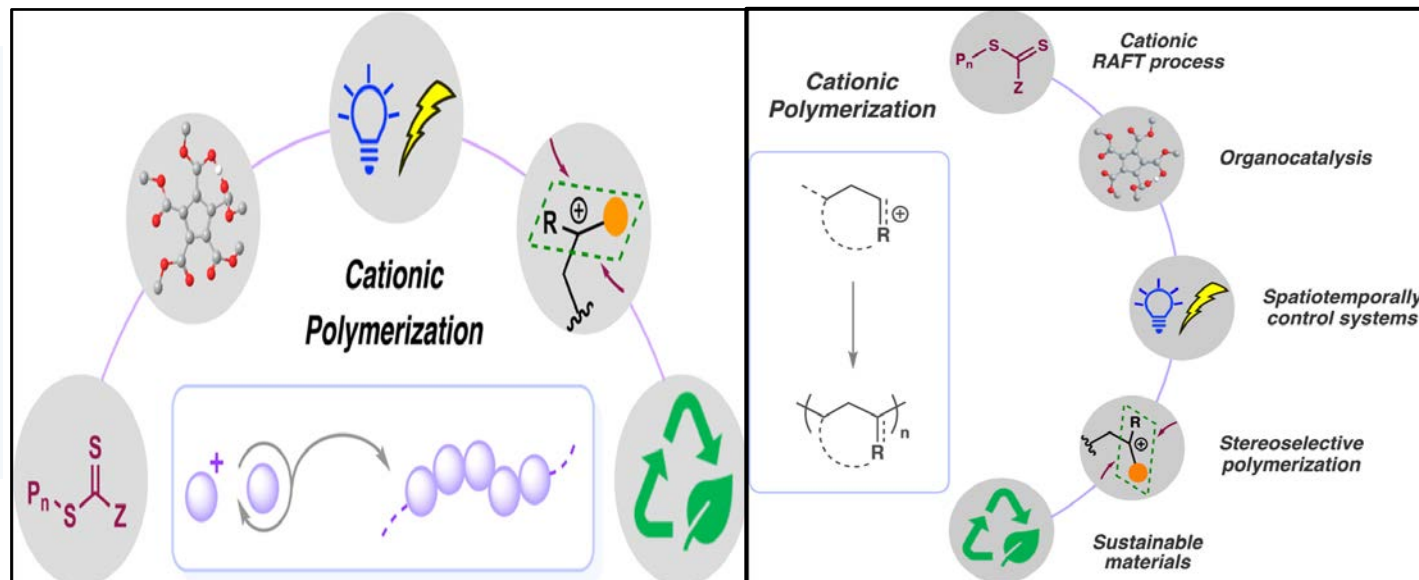
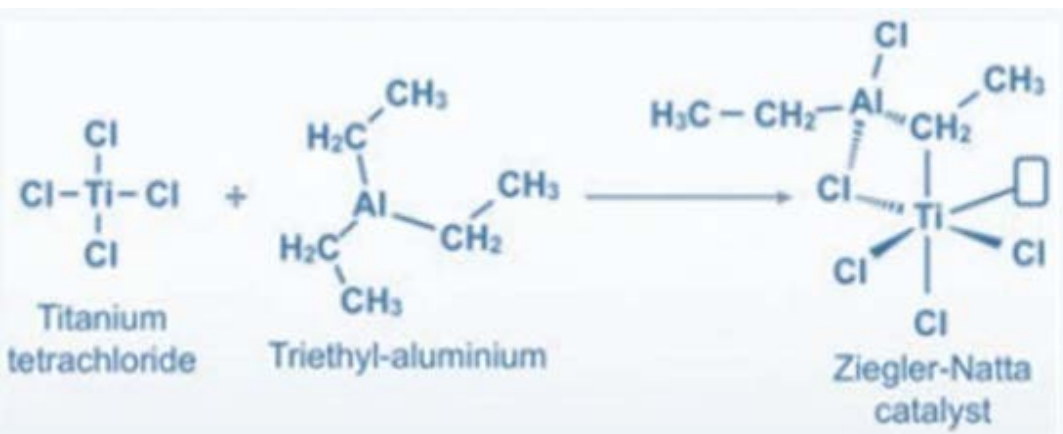
Portrait of Giulio Natta, 1963.
Wikimedia Commons



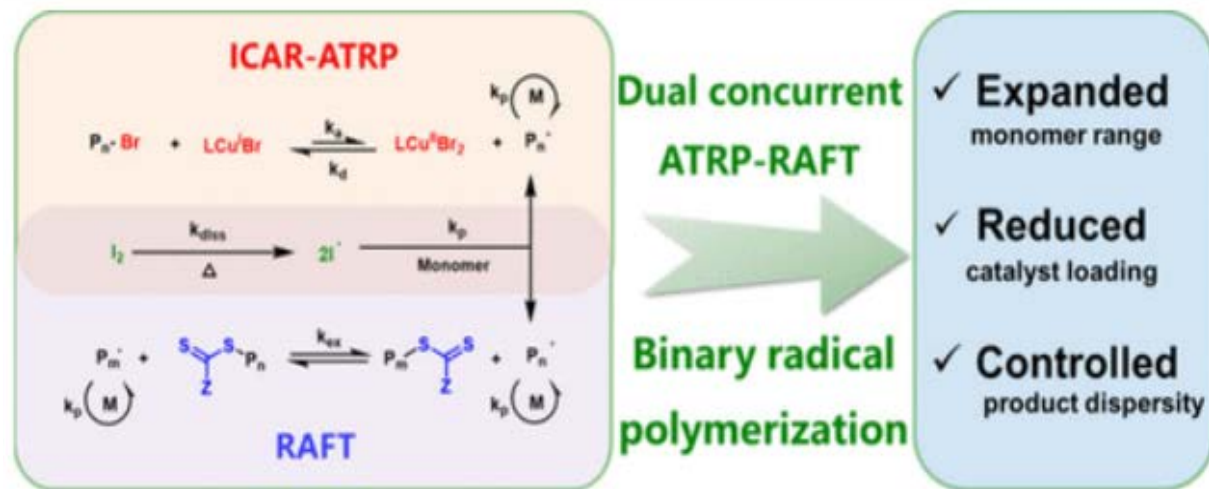
❖ Modern Polymerization Methods

❑ **1950s:** Karl Ziegler and Giulio Natta developed **Ziegler-Natta catalysts** for stereospecific polymerization (e.g., isotactic polypropylene).
(They won **the Nobel Prize** in 1963.)

❑ **1960s–1970s:** Development of **anionic, cationic, and coordination polymerization techniques** for better control.

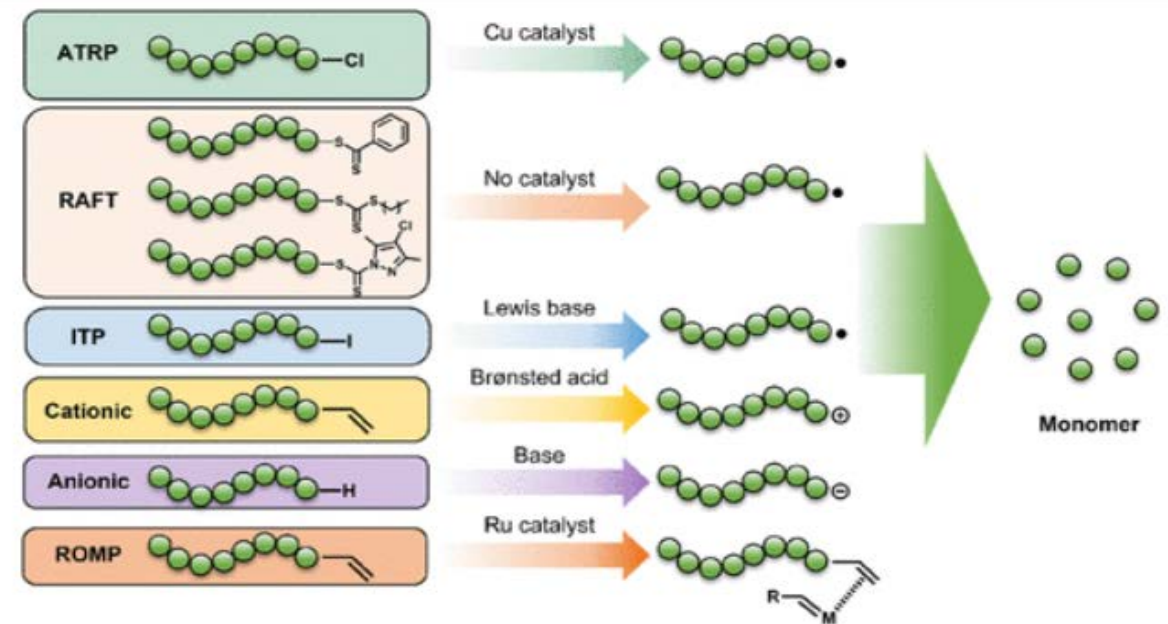
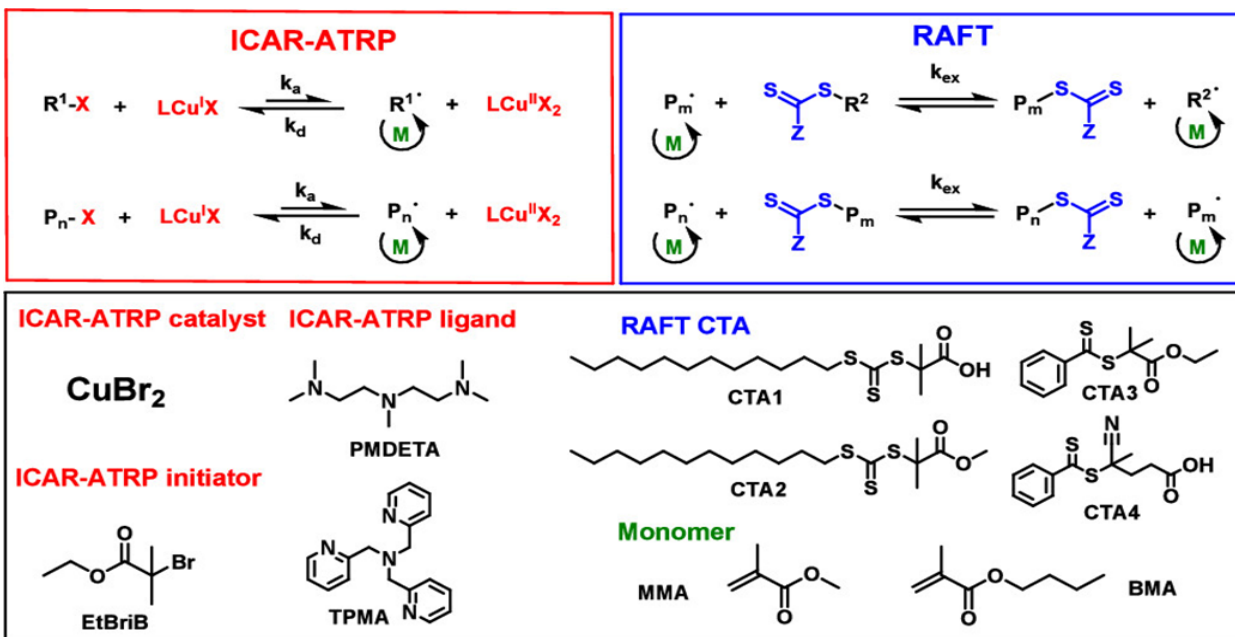


Short History of The Polymerization Process

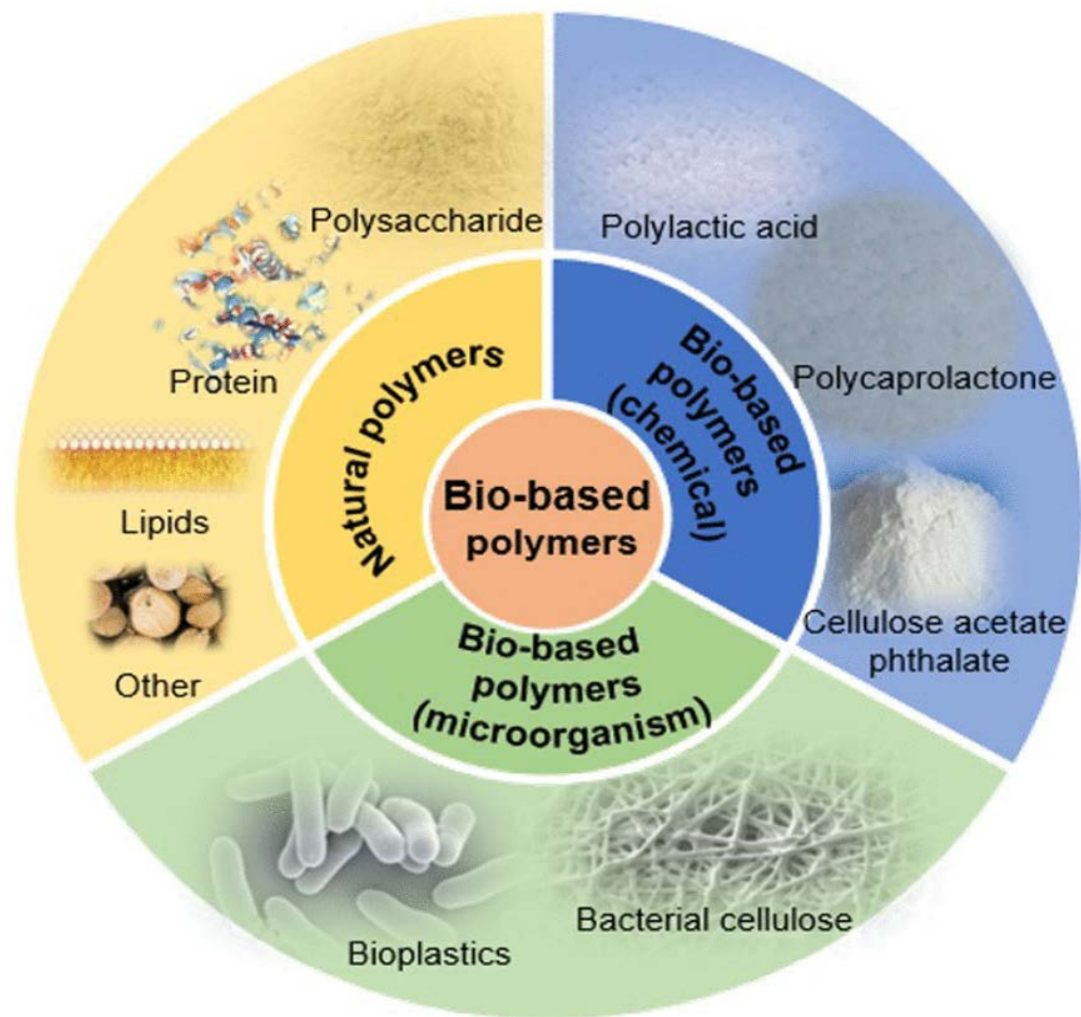


❖ **Late 20th Century:**

- ❑ **Living polymerization** (e.g., ATRP, RAFT) allowed controlled molecular weight and architecture.
- ❑ **Metallocene catalysts** for precise polyolefin production.



Short History of The Polymerization Process

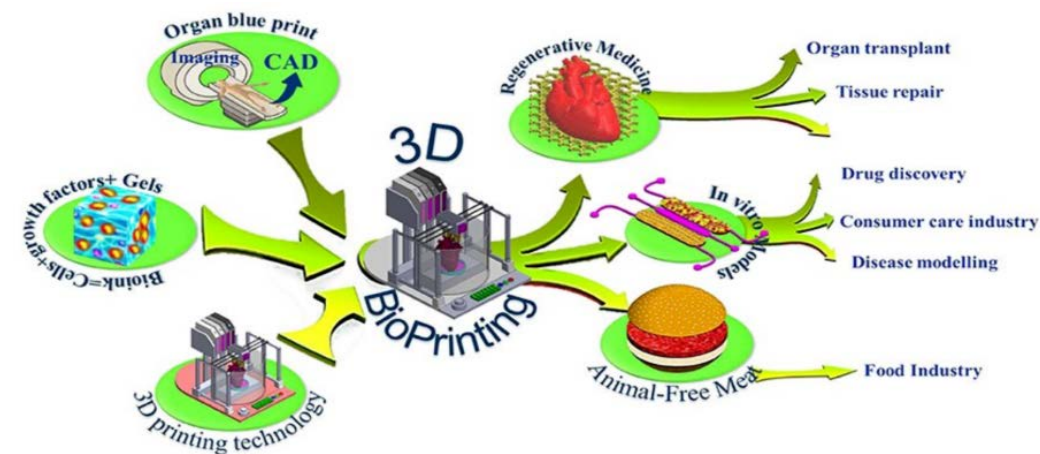


❖ 21st Century & Beyond

❑ Biodegradable polymers

➤ Bio-based stimuli-responsive materials, mainly carbohydrate polymers, are extensively explored for biomedical applications. This review outlines their types, response mechanisms, and advantages/limitations, with a focus on drug delivery and anticounterfeiting systems, highlighting both benefits and challenges in these applications.

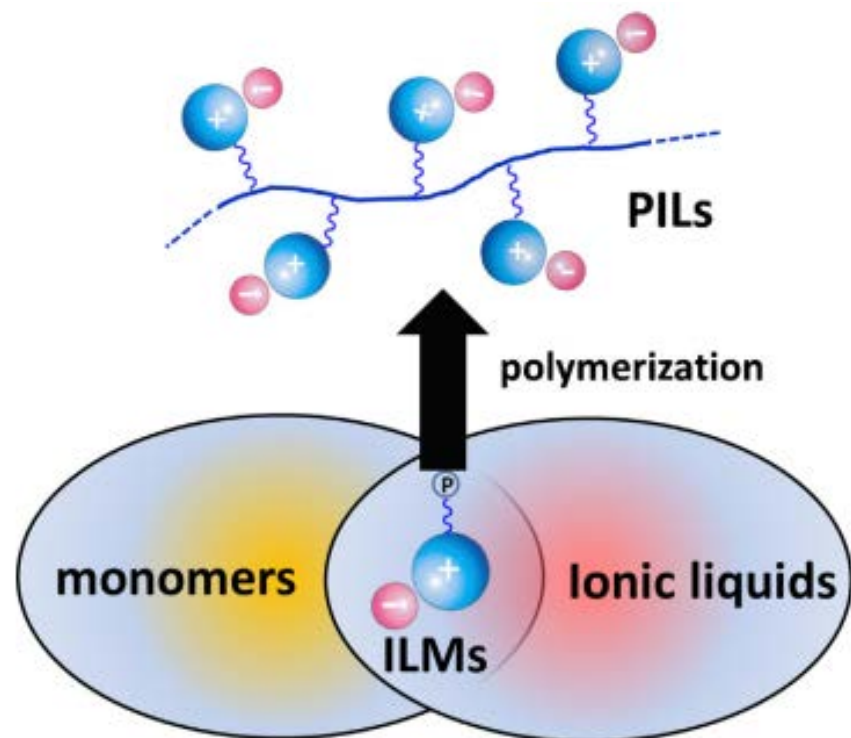
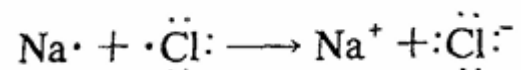
❑ **Advanced polymerization** for nanomaterials, biomedical applications, and 3D printing.



MOLECULAR FORCES AND CHEMICAL BONDING IN POLYMERS

- ❖ The bonding between atoms is explained by quantum mechanics, where valence electrons those in the outer shells participate in chemical reactions and form primary bonds.

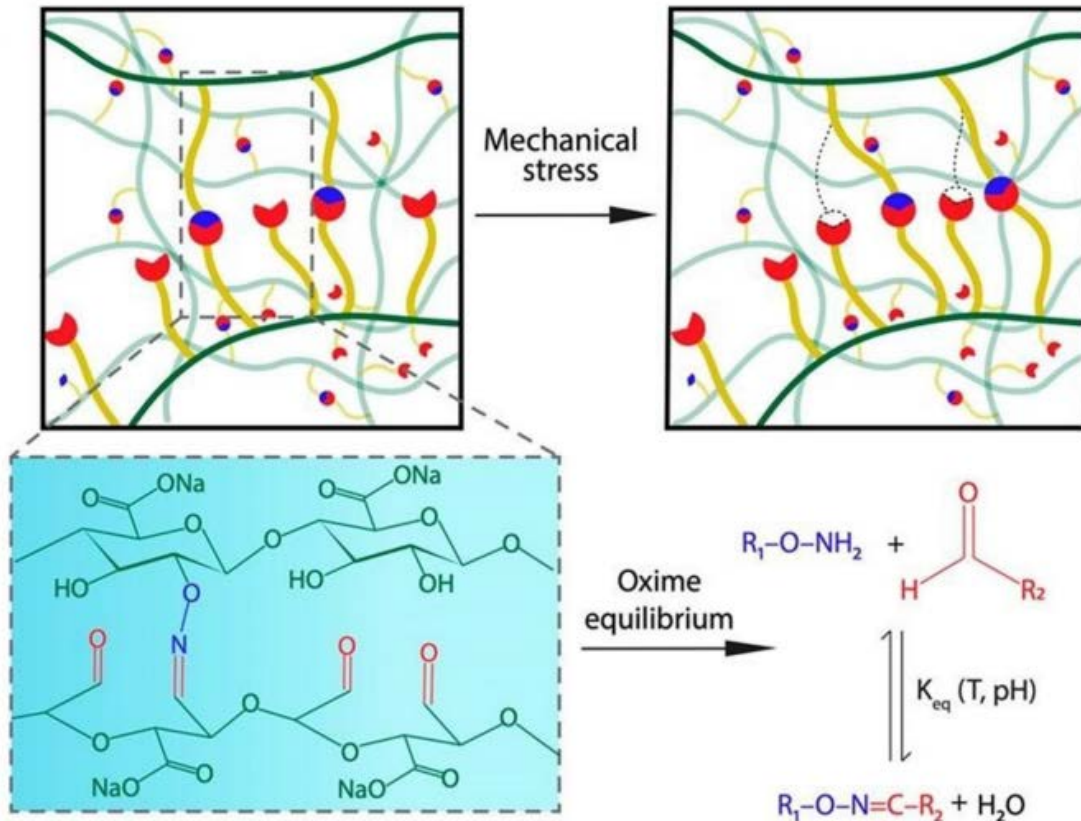
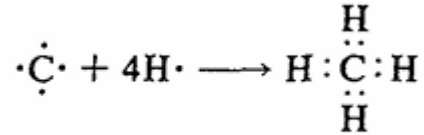
Primary Bonds



- ❑ **Ionic bond** :The most stable electronic configuration for most atoms (except hydrogen) important in polymers is a complete outer shell of eight electrons, called an octet In inorganic systems this structure may be obtained by the donation of an electron by one atom to another to form an Ionic bond.
- ❑ **Nature**: Ionic bonds form between positively and negatively charged groups, typically between metal cations and acidic or basic functional groups (e.g., -COO^- , -SO_3^-).
- ❑ **Occurrence**: In ionomers, which are polymers containing a small fraction of ionic groups dispersed along the chain (e.g., Surlyn®, a copolymer of ethylene and methacrylic acid neutralized with metal ions).
- ❑ **Applications**: Used in ion-conducting membranes, drug delivery, smart hydrogels, and electroactive materials.

MOLECULAR FORCES AND CHEMICAL BONDING IN POLYMERS

❖ Primary Bonds



❑ **Covalent Bond:** These bonds are formed when one or more pairs of valence electrons are shared between two atoms, again resulting in stable electronic shells. The covalent bond is the predominant bond in polymers

❑ **General Reversible Covalent Reactions:** Involve the formation or breakage of covalent bonds with different reactants and products (e.g., $\text{A} + \text{B} \rightleftharpoons \text{C}$ or $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$). Examples include Diels-Alder reactions, imine formation, and sulfhydryl oxidation. These reactions often require different conditions for forward and reverse directions.

❑ **Dynamic Reversible Covalent Reactions:** Involve the exchange of components between molecules without altering bond types (e.g., $\text{A1} + \text{B1} \rightleftharpoons \text{A2} + \text{B2}$). Examples include ester exchange, disulfide-thiol exchange, and $\text{C}=\text{C}/\text{C}=\text{N}$ exchange. These reactions typically proceed under the same stimulus in both directions.

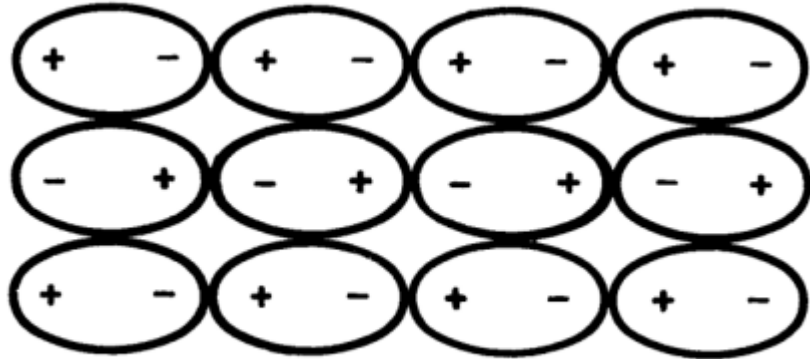
MOLECULAR FORCES AND CHEMICAL BONDING IN POLYMERS

❖ Different types of dynamic covalent reactions

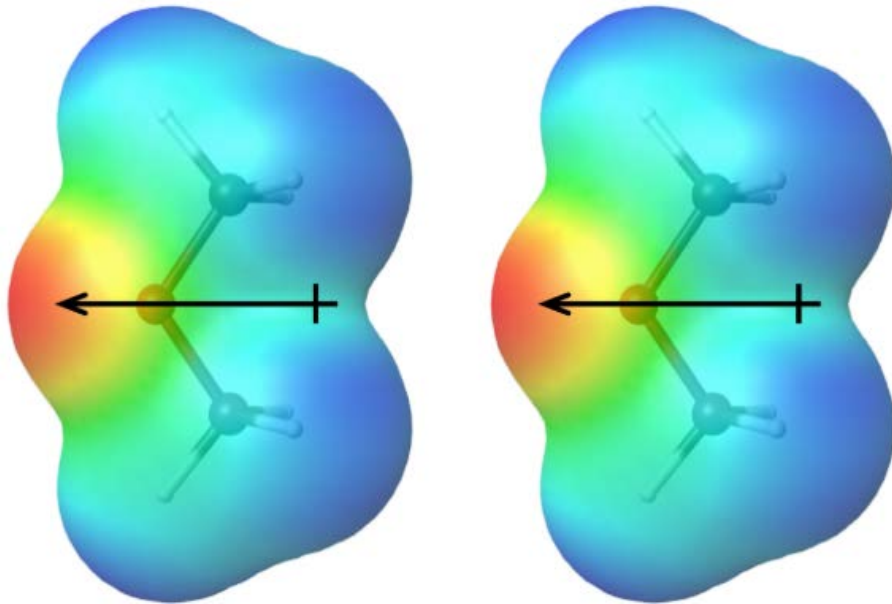
Reaction types	Reaction conditions	Reaction equation
Schiff base reaction	Acid or base catalysis, suitable pH	$R^1-NH_2 + R^2-C(=O)H \rightleftharpoons R^1-N=CH-R^2 + H_2O$ $R^1-CH=N-NH_2 + R^2-C(=O)H \rightleftharpoons R^1-CH=N-CH(R^2)-R^2 + H_2O$ $R^1-C(=O)-NH-NH_2 + R^2-C(=O)H \rightleftharpoons R^1-C(=O)-NH-CH(R^2)-R^2 + H_2O$ $R^1-O-NH_2 + R^2-C(=O)H \rightleftharpoons R^1-O-N=CH-R^2 + H_2O$
Double bond exchange reaction	Low polar organic solvents (e.g. chloroform, dichloromethane) Transition metal catalyst	$R^1-CH=CH-R^2 + R^3-CH=CH-R^4 \rightleftharpoons R^1-CH=CH-R^4 + R^3-CH=CH-R^2$ $R^1-CH=CH-R^2 + R^3-CH=CH-R^4 \xrightarrow{\text{Transition metal catalyst}} R^1-CH=CH-R^4 + R^3-CH=CH-R^2$
Knoevenagel reaction	Weak base catalysis or Lewis acid catalyst	$R^1-C(=O)R^2 + R^3-CH_2-CH_3 \rightleftharpoons R^1-C(=O)C(R^3)=CH-R^2 + H_2$
DA reaction	Forward reaction: low temperature Reverse reaction: high temperature	$R^1-CH=CH-R^2 + R^3-CH=CH-R^4 \rightleftharpoons R^1-CH_2-CH(R^3)-CH(R^4)-CH_2-R^2$
Disulfide exchange reaction	Room temperature or moderate temperature	$R^1-S-S-R^2 + R^3-S-S-R^4 \rightleftharpoons R^1-S-S-R^4 + R^3-S-S-R^2$
Thiol-Michael addition reaction	Alkali or nucleophile as catalyst, neutral pH	$R^1-SH + R^2-CH=CH-R^3 \rightleftharpoons R^1-S-CH_2-CH(R^2)-CH_2-R^3$
Thiol-thioester exchange reaction	Neutral medium (e.g. aqueous phase)	$R^1-C(=O)-S-CH_2-CH_2-CH_2-OOH + SH-R^2 \rightleftharpoons R^1-C(=O)-S-CH_2-CH_2-CH_2-SH + CH_2=CH_2 + H_2O$
Transesterification reaction	Catalysis under acidic conditions	$R^1-C(=O)-OR^2 + R^3-OH \rightleftharpoons R^1-C(=O)-OR^3 + R^2-OH$ $R^1-C(=O)-OR^2 + R^3-C(=O)-OR^4 \rightleftharpoons R^1-C(=O)-OR^4 + R^3-C(=O)-OR^2$
Boronic ester exchange reaction	Room temperature	$R^1-B(OH)_2 + R^2-CH_2-CH_2-CH_2-OH \rightleftharpoons R^1-B(OCH_2-CH_2-CH_2-OH)_2 + H_2O$ $R^1-B(OH)_2 + R^2-CH_2-CH_2-CH_2-OH \rightleftharpoons R^1-B(OCH_2-CH_2-CH_2-OH)_2 + H_2O$
Siloxane equilibration	Acid or base catalyst	$R^1-Si(R^2)_2-O-Si(R^3)_2-R^4 + R^5-Si(R^6)_2-O-Si(R^7)_2-R^8 \rightleftharpoons R^1-Si(R^2)_2-O-Si(R^3)_2-R^8 + R^5-Si(R^6)_2-O-Si(R^7)_2-R^4$
Diselenide metathesis reaction	Visible light	$R^1-Se-Se-R^2 + R^3-Se-Se-R^4 \xrightarrow{\text{Visible Light}} 2 R^1-Se-Se-R^4$

MOLECULAR FORCES AND CHEMICAL BONDING IN POLYMERS

❖ Secondary-Bond Forces



Dipole–dipole interaction between polar molecules.



❖ Dipole-dipole bonds

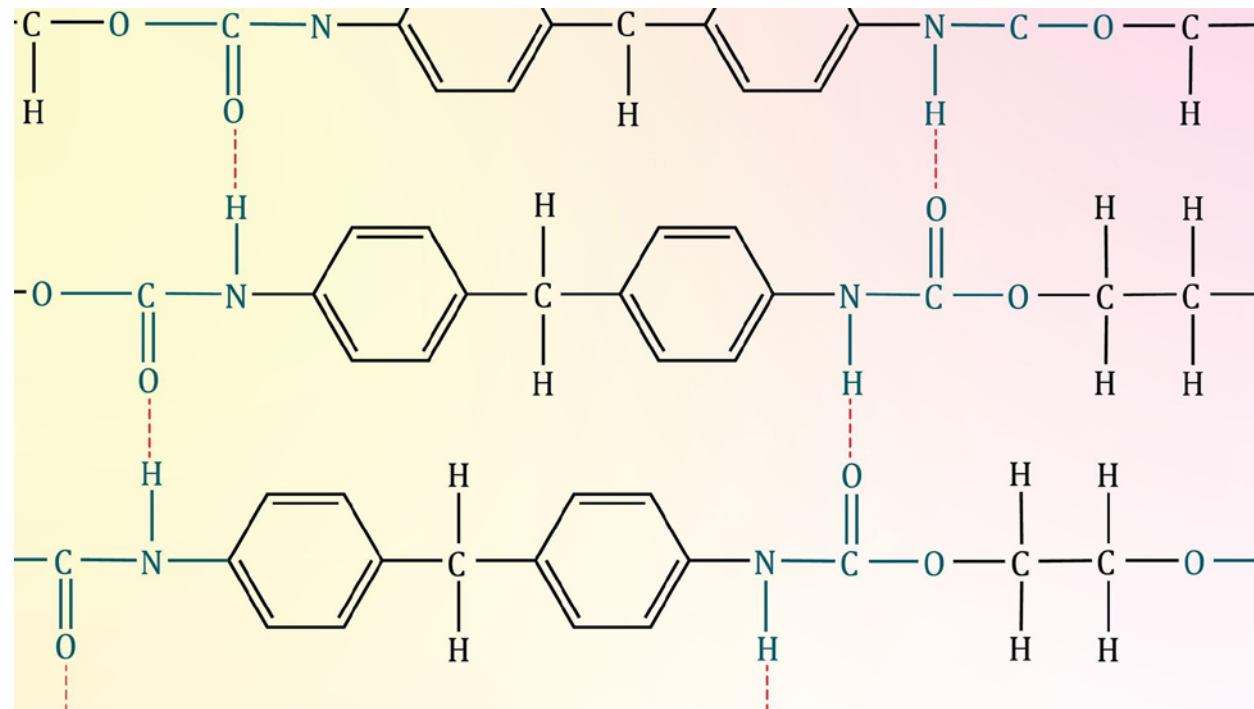
❑ **Nature of Dipole–Dipole Interactions:** Dipole–dipole interactions occur between polar groups in polymer chains where permanent dipoles align such that partial positive and negative charges attract. These are intermolecular forces, weaker than covalent bonds but stronger than dispersion (van der Waals) forces.

❑ **Role in Polymers:** Polymers with polar functional groups such as carbonyls, nitriles, esters, or amides exhibit significant dipole–dipole bonding. These interactions influence melting points, solubility, crystallinity, and mechanical properties.

❑ **Effect on Properties:** These interactions enhance interchain cohesion, leading to higher tensile strength, reduced solubility in nonpolar solvents, and increased glass transition temperatures (T_g).

MOLECULAR FORCES AND CHEMICAL BONDING IN POLYMERS

❖ Secondary-Bond Forces

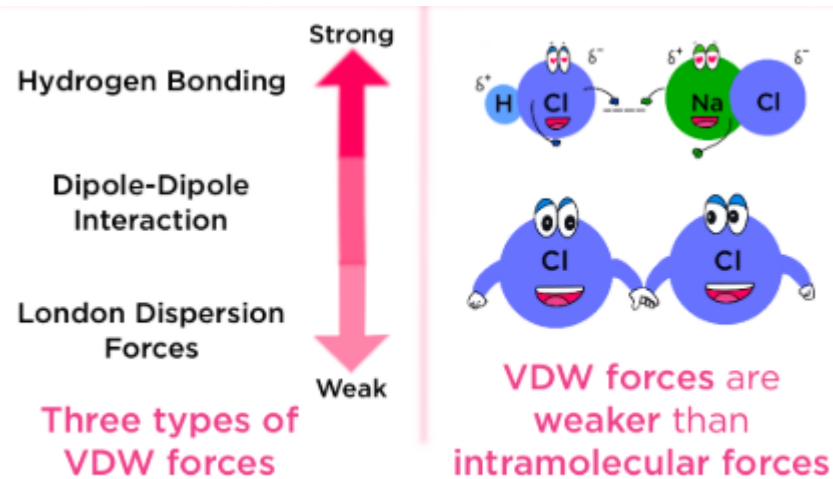


❑ **Hydrogen Bonds:** Hydrogen bonding involves a hydrogen atom interacting with two atoms, typically between a proton donor ($-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{CONH}_2$) and an electronegative acceptor (O, N, or halogens). Though often viewed as electrostatic, it may have partial covalent character. This bond plays a crucial role in polar molecule association (e.g., water, alcohols) and significantly influences the structure and properties of polymers like nylon, cellulose, and proteins, making it essential in biological and synthetic systems.

❑ Importance in Polymers:

- Crucial for the structure and properties of polar polymers (e.g., nylon, cellulose, proteins).
- Provides intermolecular cohesion, enhancing mechanical strength, crystallinity, and thermal stability.

MOLECULAR FORCES AND CHEMICAL BONDING IN POLYMERS



Van der Waals forces:

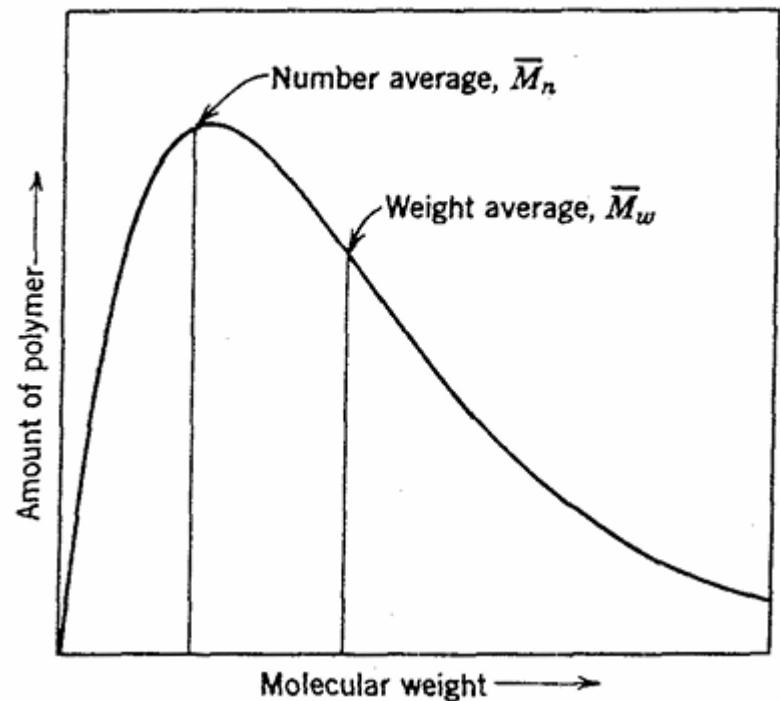
Nature: Van der Waals forces are dispersion forces caused by temporary dipoles formed due to electron movement. These induce complementary dipoles in adjacent molecules, resulting in weak attraction.

Significance in Polymers: These are the primary intermolecular forces in nonpolar polymers (e.g., polyethylene, polystyrene). Although individually weak, the cumulative effect across long chains contributes significantly to the cohesion and physical stability of polymer materials.

Effects on Polymer Properties: Glass transition temperature (T_g) and melting temperature (T_m) are influenced by the strength of these interactions. They affect mechanical properties, such as tensile strength and elasticity, especially in amorphous polymers.

MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS

- ❖ **Distribution of molecular weights in a typical polymer** □ A polymer's molecular weight is the sum of the atomic weights of individual atoms that comprise a molecule. It indicates the average length of the bulk resin's polymer chains. All polymer molecules of a particular grade do not all have the exact same molecular weight. There is a range or distribution of molecular weights. There are two important but different ways to calculate the molecular weight. The most important one is called the number-average molecular weight



The number average molecular weight

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

where “i” is the number of polymer molecules, and “ N_i ” is the number of molecules that have the molecular weight “ M_i ”.

MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS

❖ Distribution of molecular weights in a typical polymer

The weight average molecular weight

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

where “i” is the number of polymer molecules, and “N_i” is the number of molecules that have the molecular weight “M_i”.

❑ **Polydispersity Index (PDI):** is a key parameter that describes the molecular weight distribution of a polymer sample. It indicates how uniform (or varied) the chain lengths are in a given polymer.

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

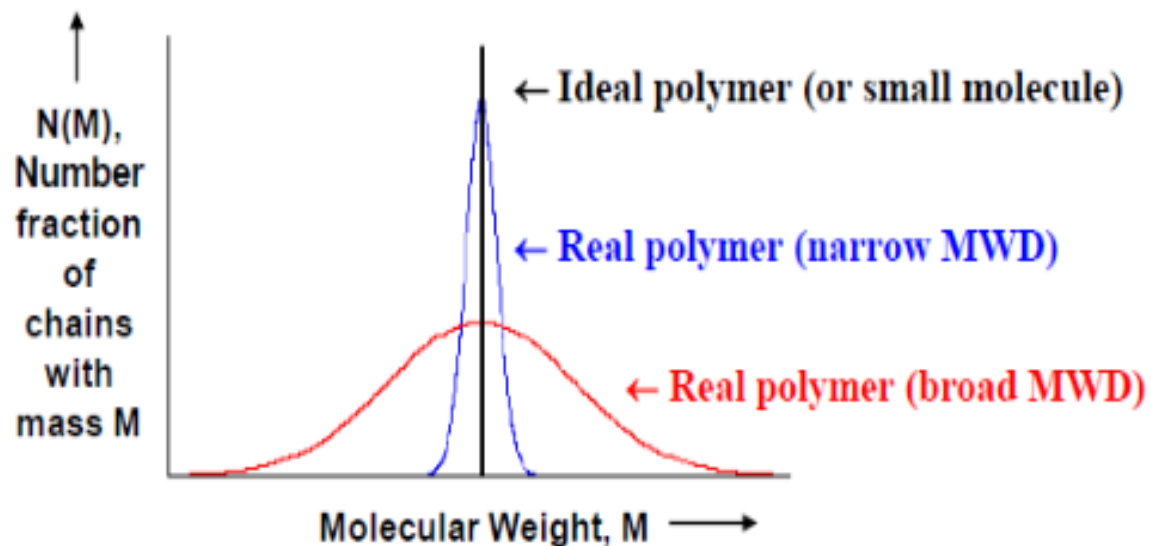
Interpretation: PDI = 1: All polymer chains have the same molecular weight (ideal, monodisperse system — typically only in synthetic uniform polymers or natural biopolymers like proteins).

PDI > 1: Real polymers are polydisperse; a higher value indicates a broader range of chain lengths.

Measurement Methods: Gel Permeation Chromatography (GPC) is the most common technique for determining PDI by separating polymer chains by size.

MOLECULAR WEIGHT DISTRIBUTION IN POLYMERS

❖ Distribution of molecular weights in a typical polymer



Polymer	Range
Hypothetical monodisperse polymer	1.000
Actual "monodisperse" "living" polymers	1.01–1.05
Addition polymer, termination by coupling	1.5
Addition polymer, termination by disproportionation, or condensation polymer	2.0
High conversion vinyl polymers	2–5
Polymers made with autoacceleration	5–10
Addition polymers prepared by coordination polymerization	8–30
Branched polymers	20–50

Section 7

Introduction to Properties Of Polymers

Properties Of Polymers

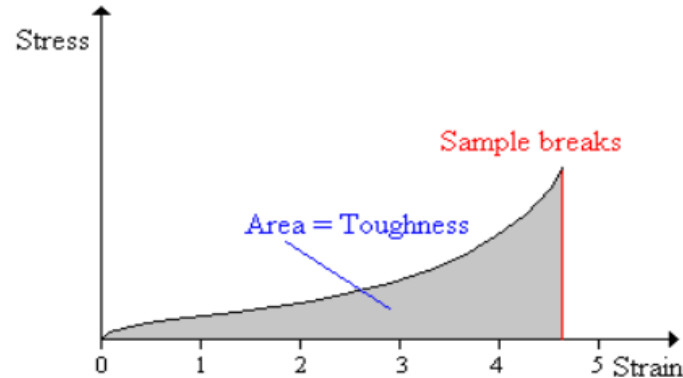


Topics to be discussed

1. Mechanical Properties
2. Thermal Properties
3. Electrical Properties
4. Optical Properties
5. Chemical Properties

Properties Of Polymers

1. Mechanical Properties

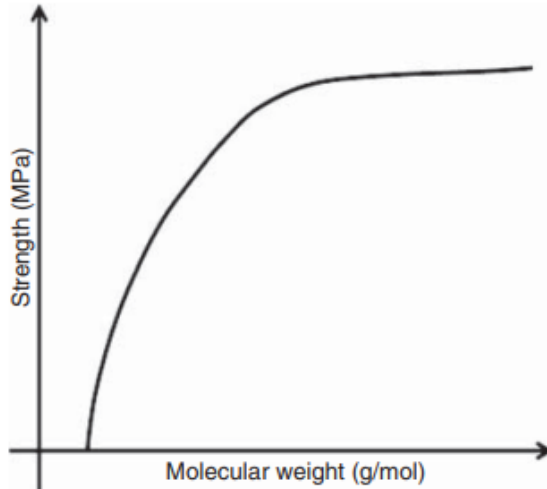


- ❑ **Strength and Elasticity:** Polymers exhibit a wide range of mechanical behaviors from rigid plastics to flexible elastomers.
- ❑ **Viscoelasticity:** They show both viscous and elastic responses, meaning they can deform and recover partially under stress.
- ❑ **Tensile Strength:** Depends on molecular weight, crystallinity, and crosslinking. Crystalline polymers and highly crosslinked polymers are generally stronger.
- ❑ **Rubber Elasticity:** Crosslinked elastomers display reversible deformation due to entropy-driven chain retraction.

Properties Of Polymers

1. Mechanical Properties of Polymers

Understanding the fundamental mechanical properties of a material such as tensile extensibility, flexural behavior, hardness, and fatigue response is critical for determining its suitability for specific applications.



Variation of tensile strength with molecular weight of the polymer

$$\sigma = \sigma_{\infty} - \frac{A}{M}$$

σ_{∞} is the tensile strength of the polymer with molecular weight of infinity. A is some constant, and M is the molecular weight.

1.1 Strength: Strength is the stress needed to break a sample and includes tensile, compressive, flexural, torsional, and impact types. Polymer strength generally increases in the order: **linear** < **branched** < **crosslinked** < **network**.

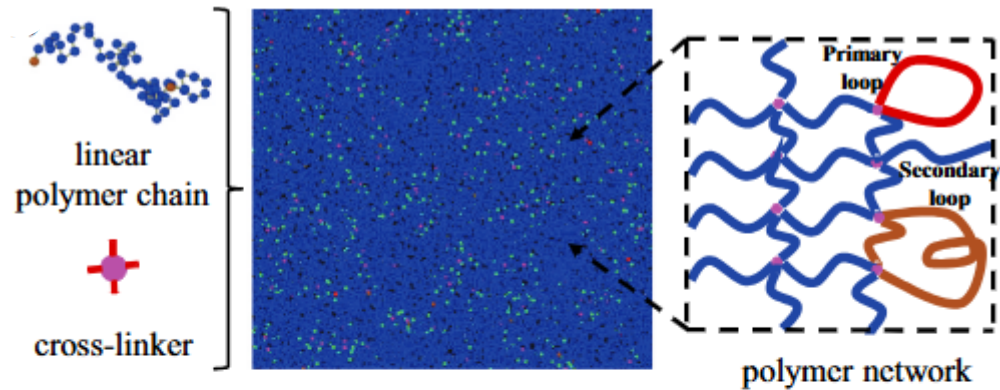
❑ Factors Affecting the Strength of Polymers

1.1.1 Molecular Weight

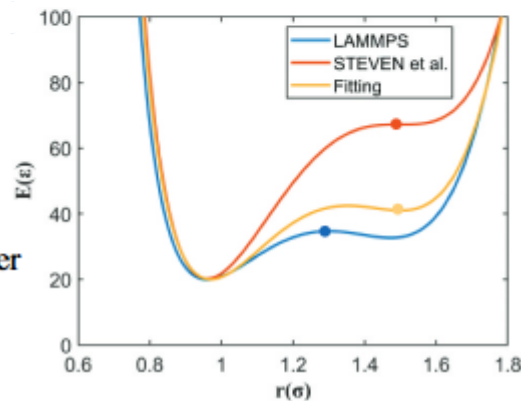
➤ Tensile strength increases with molecular weight until saturation. Low molecular weight polymers have weak van der Waals forces and low strength, while high molecular weight polymers gain strength from chain entanglement.

Properties Of Polymers

1. Mechanical Properties of Polymers



- inner chain bead
- unreacted terminal bead
- reacted terminal bead
- no fully reacted cross-linker
- fully reacted cross-linker



1.1.2 Cross-linking:

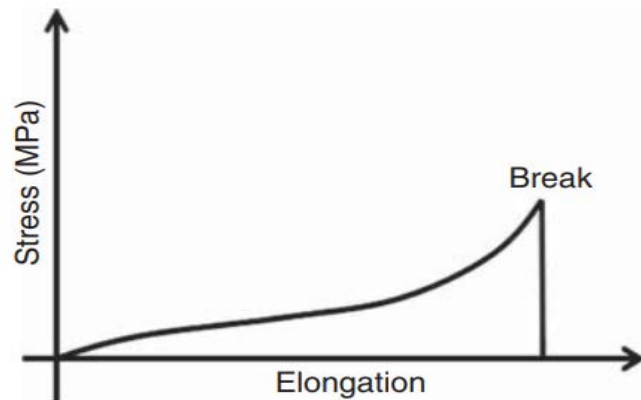
- The cross-linking restricts the motion of the chains and increases the strength of the polymer.

1.1.3 Crystallinity:

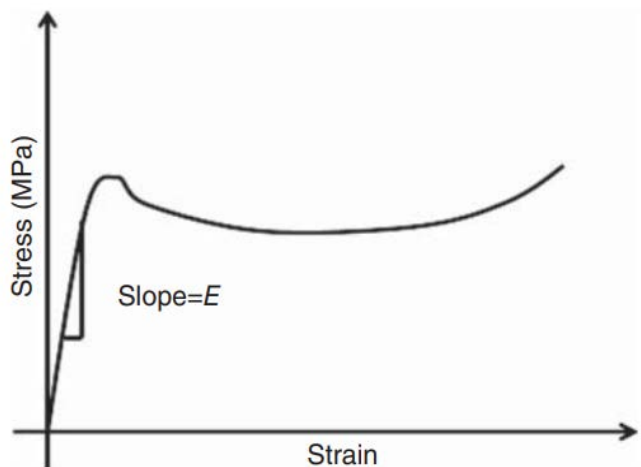
- The crystallinity of the polymer increases strength, because in the crystalline phase, the intermolecular bonding is more significant. Hence, the polymer deformation can result in the higher strength leading to oriented chains.

Properties Of Polymers

1. Mechanical Properties of Polymers



Elongation to break of the polymer.



Young's modulus of the polymer.

1.2 Percent Elongation to Break (Ultimate Elongation):

- It is the strain in the material on its breakage, as shown in Fig. It measures the percentage change in the length of the material before fracture. It is a measure of ductility. Ceramics have very low (<1%), metal have moderate (1-50%) and thermoplastic(>100%), thermosets (<5%) value of elongation to break.

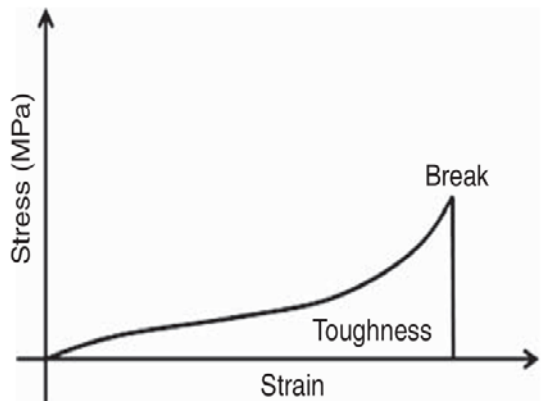
1.3 Young's Modulus (Modulus of Elasticity or Tensile Modulus):

- Young's Modulus is the ratio of stress to the strain in the linearly elastic region. Elastic modulus is a measure of the stiffness of the material.

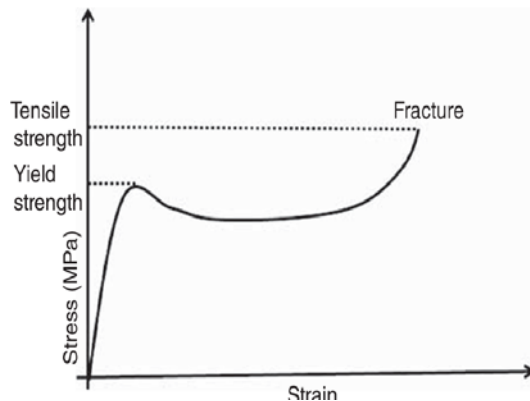
$$E = \frac{\text{Tensile Stress}(\sigma)}{\text{Tensile Strain}(\epsilon)}$$

Properties Of Polymers

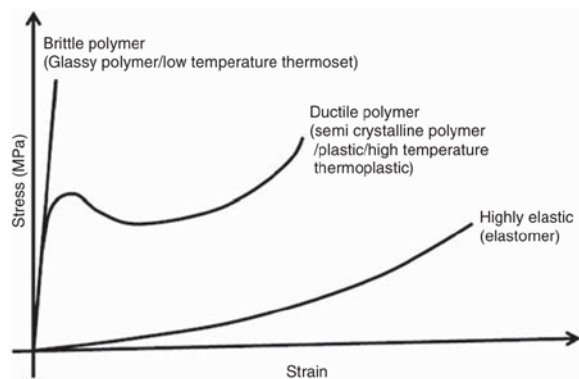
1. Mechanical Properties of Polymers



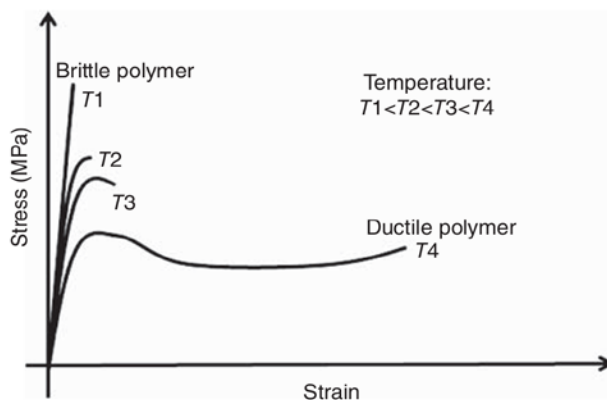
The toughness of polymer material.



Yield strength and tensile strength of polymer



Stress-strain behavior of different types of materials.



Effect of temperature on the mechanical properties of polymer.

1.4 Toughness:

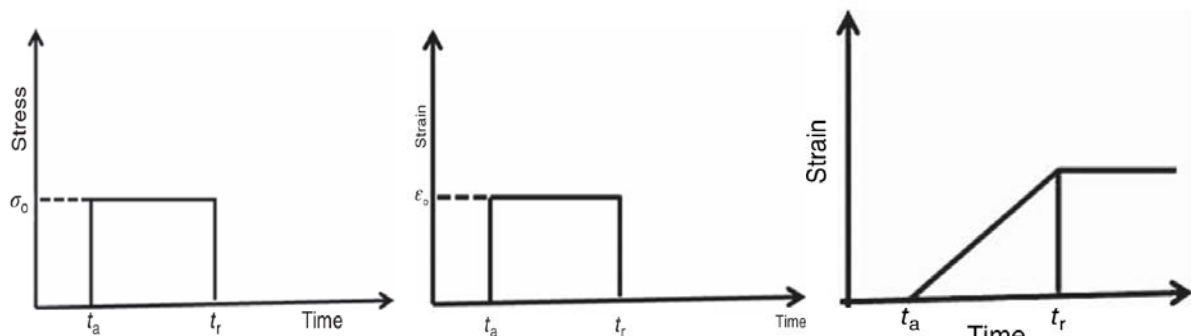
The toughness of a material is given by the area under a stress–strain curve

$$\text{Toughness} = \int \sigma \, d\epsilon$$

- Toughness represents the energy a material absorbs before breaking. Rigid polymers have high Young's modulus but low fracture toughness, while ductile polymers share similar modulus with greater toughness. Elastomers, being rubbery, exhibit low modulus. Yield strength marks the end of the elastic region, whereas tensile strength corresponds to fracture and can be higher or lower than yield strength. Mechanical properties vary with temperature: as temperature rises, elastic modulus and tensile strength decrease, while ductility increases.

Properties Of Polymers

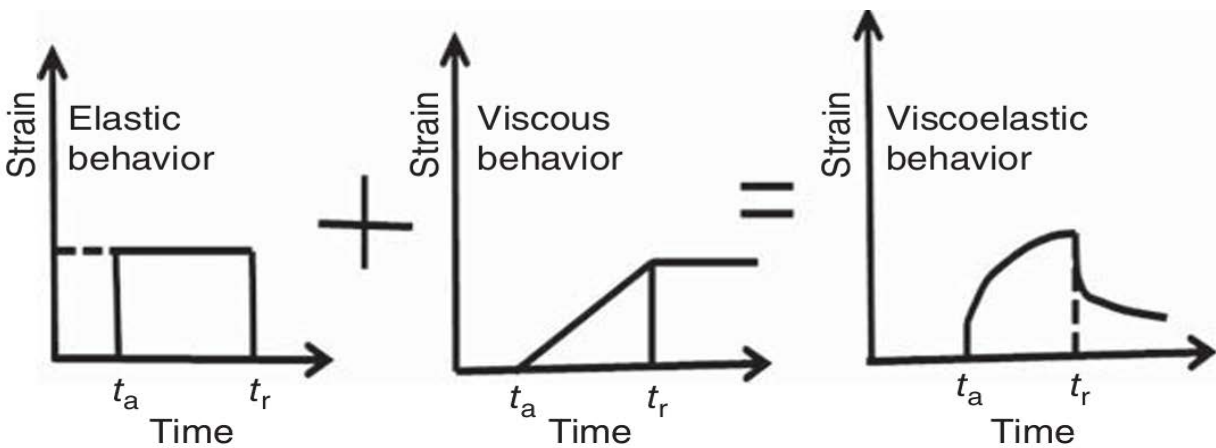
1. Mechanical Properties of Polymers



Constant stress applied to a polymer.

Elastic deformation.

Viscous deformation.



Viscoelastic deformation: the combined behavior of viscosity and elasticity.

Viscoelasticity: **Deformation is of two types: elastic and viscous.** Under constant stress, elastic deformation occurs instantly and remains until the stress is removed. On unloading, the material fully recovers its original dimensions, making the deformation reversible.

$$\sigma = E\epsilon$$

where E is the elastic modulus, σ is applied stress, and ϵ is the strain developed

Viscous deformation is time-dependent; strain increases gradually under constant load. After unloading, the material does not fully recover, making the deformation irreversible.

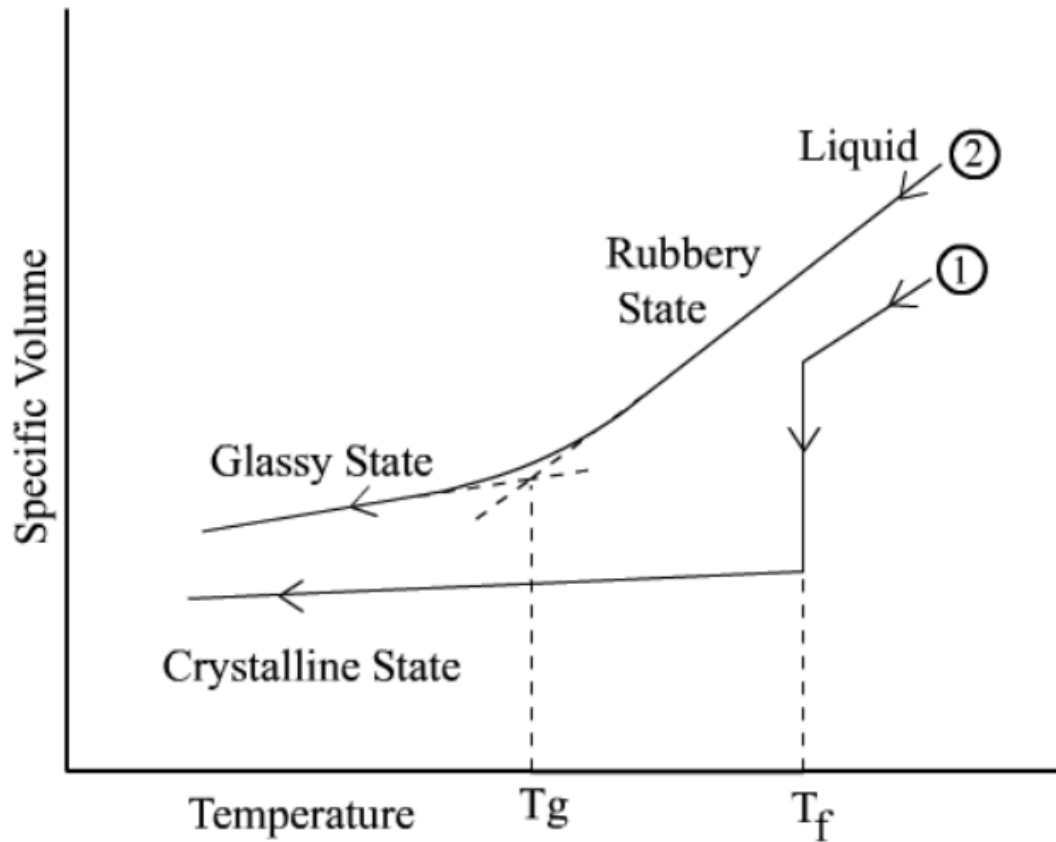
$$\sigma = \gamma \frac{d\epsilon}{dt}$$

where γ = viscosity, and $d\epsilon/dt$ = strain rate

Polymers exhibit viscoelastic behavior, combining elasticity and viscosity. At low temperature/high strain rate, they act elastically; at high temperature/low strain rate, they behave viscously; and at intermediate conditions, both effects appear.

Properties Of Polymers

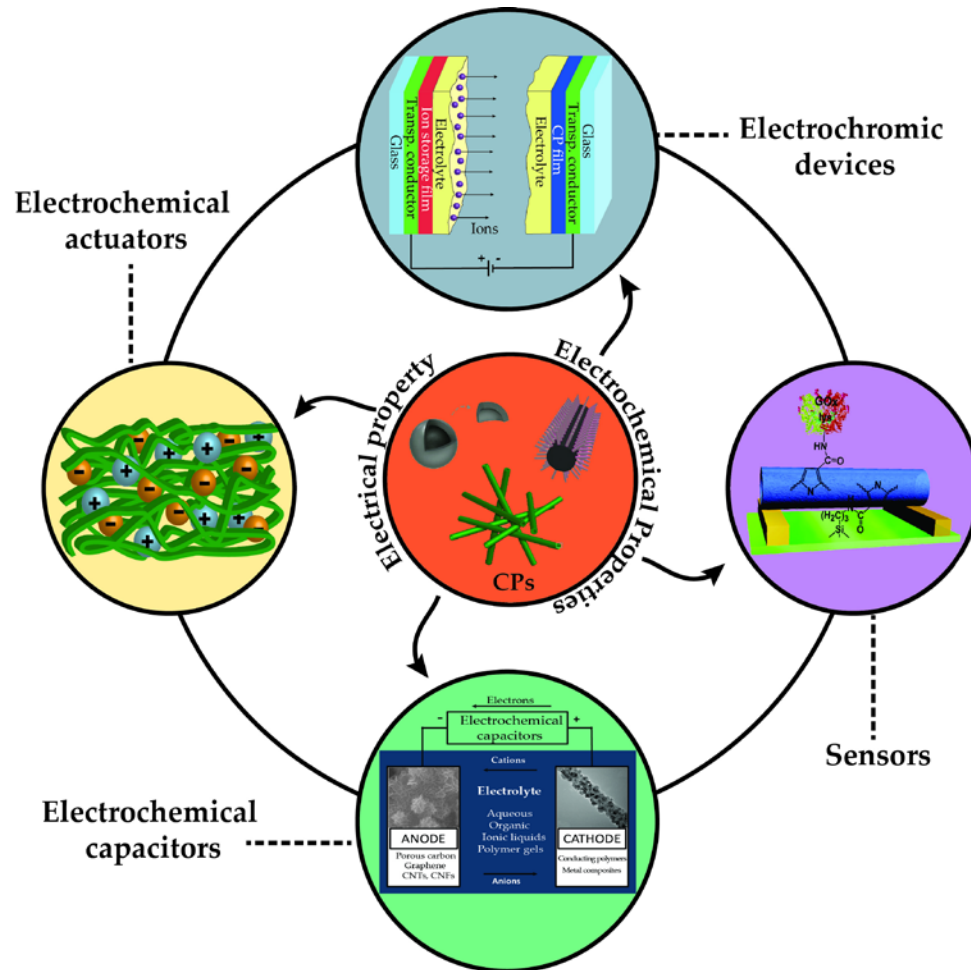
2. Thermal Properties



- ❑ **Glass Transition Temperature (T_g):** The temperature at which an amorphous polymer changes from a brittle glassy state to a rubbery state.
- ❑ **Melting Temperature (T_m):** For crystalline or semicrystalline polymers, the temperature where crystalline regions melt.
- ❑ **Thermal Stability:** Influenced by backbone rigidity, crosslinking, and presence of aromatic groups.
- ❑ **Coefficient of Thermal Expansion:** Polymers generally have higher expansion than metals or ceramics.

Properties Of Polymers

3. Electrical Properties



- ❑ Electrical properties of polymers are primarily related to dielectric behavior and electrical conductivity.
- ❑ A conductor allows current flow, while an insulator resists it.
- ❑ Most pristine polymers are insulators due to their covalent nature and lack of ionic/electronic pathways.
- ❑ Conducting nanomaterials (e.g., graphene, CNTs, carbon nanofibers) can be added to polymers to impart conductivity.
- ❑ Graphene sheets create percolated pathways for electron transfer, making the polymer nanocomposite conductive.
- ❑ Graphene is more efficient than CNTs, enabling the insulator-to-conductor transition at lower loading.
- ❑ **Example:** Adding 5 wt.% graphene to polyester increases conductivity from 3.32×10^{-9} to 2.05×10^{-3} S/cm, a 10^6 -fold enhancement.
- ❑ The improvement is due to interconnected graphene networks within the polymer matrix.