**Polymer:** A large molecule (macromolecule) built up by repetitive bonding (covalent) of smaller molecules (monomers)

- Generally not a well defined structure, or molecular weight.
- Need to use statistical properties to describe.

Polymers are formed by linking monomers through chemical reaction—called polymerization. You don’t end up with a unique molecule.

\[
i \text{ monomers} \quad \rightarrow \quad \text{chain of monomers}
\]

\[
i A \quad \rightarrow \quad (A-A-A)_{i/3}
\]

**Homopolymer:** all A identical

- The most produced/used polymers are homopolymers of terminal alkenes.
- Produced by radical polymerization.

\[
i \text{ CH}_2=\text{CH}_2 \quad \rightarrow \quad (\text{CH}_2-\text{CH}_2)_i
\]

ethylene polyethylene

\[
i \text{ H}_2\text{C}=C\backslash \text{CH}_3 \quad \rightarrow \quad \{\text{H}_2\text{C}-\text{C}\}_i\backslash \text{CH}_3
\]

methylmethacrylate PMMA
Copolymers:
made up of different monomers

\[ i \ A + i \ B \rightarrow -(A-B)_{i} - \]

\[ i \ \text{H}_{2}\text{C} = \text{CHCl} + i \ \text{H}_{2}\text{C} = \text{CCl}_{2} \rightarrow \left(\text{H}_{2}\text{C} - \text{CH} - \text{CH}_{2} - \text{C} - \right)_{i} \text{Cl} \text{Cl} \]

vinyl chloride  vinylidene chloride

poly(vinylchloride-co-vinylidene chloride)  \rightarrow  Saran

---

\[ -\text{A-B-A-B-A-B-} - \text{ alternating copolymer} \]


Both of these are rare. Most common is a statistical copolymer, which has a statistical distribution of repeat units.

Block copolymers—Two long sequences of repeat units


**Structural characteristics** – Closely related to material properties

- **linear** (uninterrupted straight chain)
- **branched** (occasional branches off longer chain)
- **networked** (many interconnected linear chains; one giant molecule)

**Stereochemistry of Linkages**

- **ISOTACTIC** – R groups on same side of backbone
- **SYNDIOTACTIC** – R groups on alternating sides of backbone
- **ATACTIC** — Random (most common)

Ziegler-Natta catalysts used for iso- and syndio-
**Classification of polymers:**

**Polymers** (synthetic)

1) *Thermoplastics* (plastics) — linear, some cross-linking can be melted and reformed on heating
   a) *Amorphous*—no ordered structure  
   b) *Semi-crystalline*—composed of microscopic crystallites—domains of crystalline structure. Can be ordered.
   
   **Fibers** (nylon, polyester)

2) *Elastomers* (rubbers) — moderately cross-linked can be stretched and rapidly recover their original dimension

3) *Thermostats*—(resins)—massively cross-linked very rigid; degrade on heating

4) *Dendrimers*—multiply branched—multiple consecutive (regular) branches

**Biopolymers**

polypeptides—proteins-amino acid heteropolymer
nucleic acids—RNA/DNA
polysaccharides—sugars
Characterization

1) How do polymers respond to an applied force?
(study of flow and deformation: rheology)

- An elastic medium is described by Newton’s Law:
  \[ F = -kx \]

- If you apply a force (a stress), the material displaces by an amount x:
  \[ x = -\frac{F}{k} \]

  - small k: weak spring \(\rightarrow\) easily displaced
  - big K: stiff spring \(\rightarrow\) difficult to displace

- Polymers are often non-Newtonian

For polymers, we apply a stress, and it leads to internal distortion \(\rightarrow\) strain.

\[ \sigma = mS \]

- small \(m\) \(\rightarrow\) stretches easily/compresses easily (rubber)
- large \(m\) \(\rightarrow\) small strain produced by stress \(\sigma\) (hard plastics—PMMA)
The elastic modulus $m$ is highly temperature dependent!

Rubber has small $m$ at room temperature $\rightarrow$ ball bounces

At low $T$, $m$ much larger $\rightarrow$ rubber ball in liquid N$_2$ shatters when bounced $\rightarrow$ hard plastic

Also, plastics heated above room temperature are less stiff.

Typical plot of $m(T)$

Where is room temperature on this plot? (depends on whether you have a rubber or plastic)

The various temperatures characterize polymers.
2) **Molecular Weight – Molar Mass (M)**

\[ M_i = i M_0 \]

- \( M_i \) : molar mass of polymer molecule \( i \)
- \( M_0 \) : molecular weight of monomer

Typically have distribution of masses (all chain lengths aren’t equally long)

- **monodisperse**—equal chain lengths → purified proteins, dendrimers
- **polydisperse**—unequal lengths

Characterize the polydispersity through \( F(M_i) \): distribution of molar masses.

\[
M_i = \int_0^\infty M F(M) dM
\]

*We can find several statistical ways of describing the molar mass. Comparison of these numbers helps describe \( F(M) \).*

A) Number-average molar mass, \( \bar{M}_n \)

\[
\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad \Rightarrow \quad \int_0^\infty M F(M) dM = \bar{M}_n
\]

\( N_i \): # of molecules with degree of polymerization \( i \)
\( M_i \): molar mass for degree of polymerization \( I \)
B) Mass- or Weight-average molar mass, $\bar{M}_w$

$$\bar{M}_w = \sum_i w_i M_i$$

$w_i$ is the weight fraction: the total mass of molecules with mass $M_i$ divided by the total mass of all molecules

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

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \Rightarrow \int_0^\infty F(M) M^2 dM \over \int_0^\infty F(M) M dM$$

(second moment of M.M.)

C) In experiment 4, we are studying viscosity-average molar mass, $\bar{M}_v$

$$(\bar{M}_v)^a = \frac{\int_0^\infty M^{1+a} F(M) dM}{\int_0^\infty F(M) dM}$$

**Polydispersity**—We can describe the polydispersity through the width of the distribution of molar masses.

$$\bar{M}_n < \bar{M}_v < \bar{M}_w$$

$$\frac{\bar{M}_w}{\bar{M}_n} \geq 1$$

perfectly monodisperse = 1
3) **Chain dimensions**

**Contour length:** length along backbone

\[ n \text{ bonds of length } | \rightarrow n \cdot | \]

**End-to-end distance:** More common - measure of the coiled system

The distribution of \( \vec{r} \) is characterized by the rms end-to-end distance \( \sqrt{\langle r^2 \rangle} \)

For a freely jointed chain with \( n \) links and no restrictions on bond angle:

\[ \sqrt{\langle r^2 \rangle} = \sqrt{n} \ell \]

**Radius of gyration, \( R_g \)**

\( R_g \) is the rms distance of a chain segment from the center of mass of the polymer.

\[ R_g = \sqrt{\frac{\langle r^2 \rangle}{6}} \]

Define a center of mass; then each chain segment has a certain distance from the center of mass

\[ [\eta] \propto \frac{R_g^3}{M} \]

average \( x^2 \) to get \( R_g \)

\[ \langle x^2 \rangle^{1/2} = R_g \]

intrinsic viscosity

\( \)