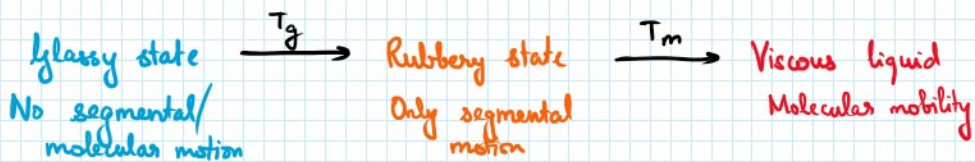


### 3. Glass Transition Temp, Structure-Property Relationship

30 November 2023 10:00

#### GLASS TRANSITION TEMPERATURE

- All amorphous polymers have a certain temperature  $\rightarrow$  glass transition temperature ( $T_g$ )
  - BELOW: stiff, hard, brittle, glossy
  - ABOVE: soft, flexible, rubbery
- The rubbery state on heating melts at a certain temperature  $\rightarrow$  melting point ( $T_m$ )

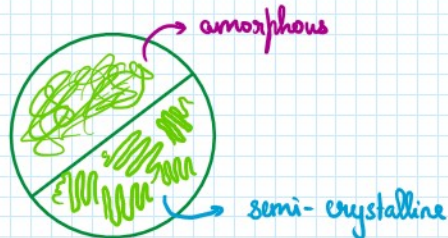


- Value of  $T_g$   $\rightarrow$  measure of flexibility, predicts response to mechanical stress
- Knowledge of  $T_g$  and  $T_m$   $\rightarrow$  useful in selecting right temperature range for fabrication
- $T_g$  also gives us an idea of thermal expansion, heat capacity, electrical & mechanical properties

#### STRUCTURE - PROPERTY RELATIONSHIP OF POLYMERS

##### CRYSTALLINITY

- Degree of crystallinity  $\rightarrow$  depends on structure, configuration
- Polymers have both amorphous and crystalline regions
- Crystalline regions  $\rightarrow$  polymer chains are arranged in an orderly fashion, parallel and close to each other.



**NOTE:**  
High crystallinity  
 $\downarrow$   
sharper melting point,  
greater rigidity, strength,  
density

##### Structure

- Polymer w/ linear chains with no bulky pendant groups  $\rightarrow$  more crystalline  
eg: Polyethylene is more crystalline than polyvinylacetate.



- Polymer w/ linear chains with no bulky pendant groups  $\rightarrow$  more crystalline

eg: Polyethylene is more crystalline than polyvinylacetate  $\rightarrow$  bulky group

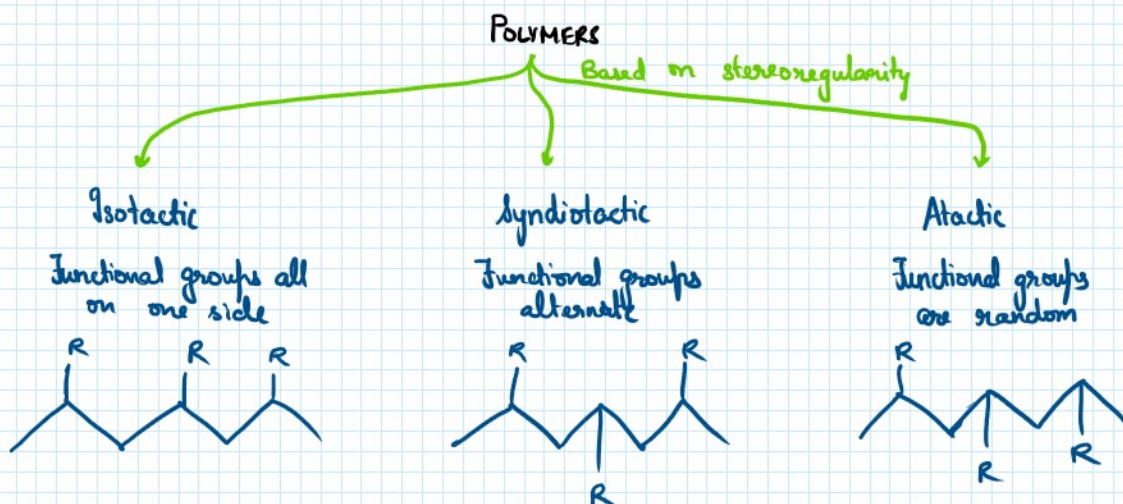
- Polymers containing polar groups are more crystalline.

WHY: strong secondary forces (dipole-dipole, hydrogen bonding)  $\rightarrow$  close packing between polymeric chains

eg: PVC is more crystalline than PE

## Configuration

- Crystallinity  $\rightarrow$  depends on stereoregularity of polymer



- Isotactic  $\rightarrow$  most crystalline
- Syndiotactic  $\rightarrow$  less crystalline
- Atactic  $\rightarrow$  least crystalline

## TENSILE STRENGTH

Amount of stress a polymer can take before permanent deformation

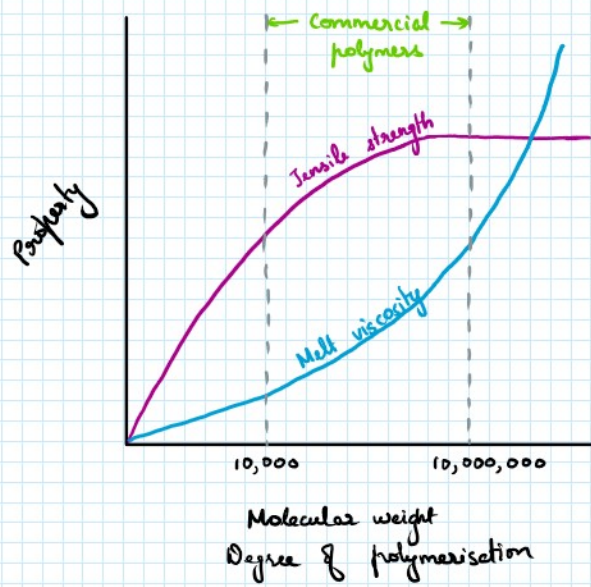
It depends mainly on the following:

### Molecular mass

- Low molecular mass  $\rightarrow$  soft and gummy
- High molecular mass  $\rightarrow$  tough and heat resistant
- On increase of molecular mass, tensile strength increases to a certain extent and then becomes constant
- Melt viscosity initially shows a gradual increase then increases steeply with higher molecular weight



maximum weight



### Structure

- Polymer has polar groups  $\rightarrow$  tensile strength increases  
WHY: Force of attraction between chains prevents them from slipping against each other  
Eg: PVC, Nylon
- Cross-linking  $\rightarrow$  increases tensile strength

### CHEMICAL RESISTANCE

Resistance to swelling, dissolving and/or degradation in the presence of a solvent/chemical

- Depends on chemical nature of monomeric units and their molecular arrangement

### Presence of polar and non-polar groups

Like dissolves like

- Polymers with polar groups  $\rightarrow$  dissolved by polar liquids (water, alcohols)
- Polymers with non-polar groups  $\rightarrow$  swell & dissolve in non-polar solvents (petrol, benzene, carbon tetrachloride)

### Residual unsaturation

Polymers with residual double bonds  $\rightarrow$  attacked & degraded in UV light  $\rightarrow$  oxidative degradation

### Packing

Dense packing  $\rightarrow$  solvent cannot penetrate the layers  $\rightarrow$  resistance increases



0  
Dense packing  $\rightarrow$  solvent cannot penetrate the layers  $\rightarrow$  resistance increases  
Eg: Teflon

### Molecular mass

Swelling character decreases as molecular mass increases

### Degree of cross-linking

Greater the degree of cross-linking, lesser the solubility

### ELASTICITY

Property of the polymer by which it deforms on applying force and regains its original shape on release of force

High elasticity  $\rightarrow$  elastomers

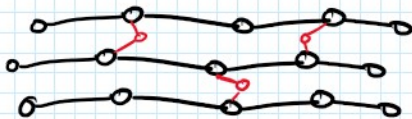
- Elastomers  $\rightarrow$  long coiled chains  $\xrightarrow[\text{stretch}]{\text{stress}}$  straighten and orient  $\xrightarrow{\text{release}}$  coil again
- Individual chains should not break on prolonged stretching for a polymer to show elasticity

### Structure

- Presence of polar groups  $\rightarrow$  strong force of attraction  $\rightarrow$  stiff and inflexible
- Non polar groups  $\rightarrow$  weak van der Waals forces  $\rightarrow$  more elastic
- Presence of bulky, aromatic & cyclic groups  $\rightarrow$  elasticity decreases

### NOTE: Improving elasticity

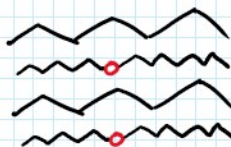
- Elastic materials: Introduce cross linking using vulcanisation



- Non-elastic materials: Use plasticisers (eg: triphenyl phosphate  $\text{Ph}_3\text{PO}_4$ )  $\rightarrow$  enter polymer chains and make it more flexible



PVC

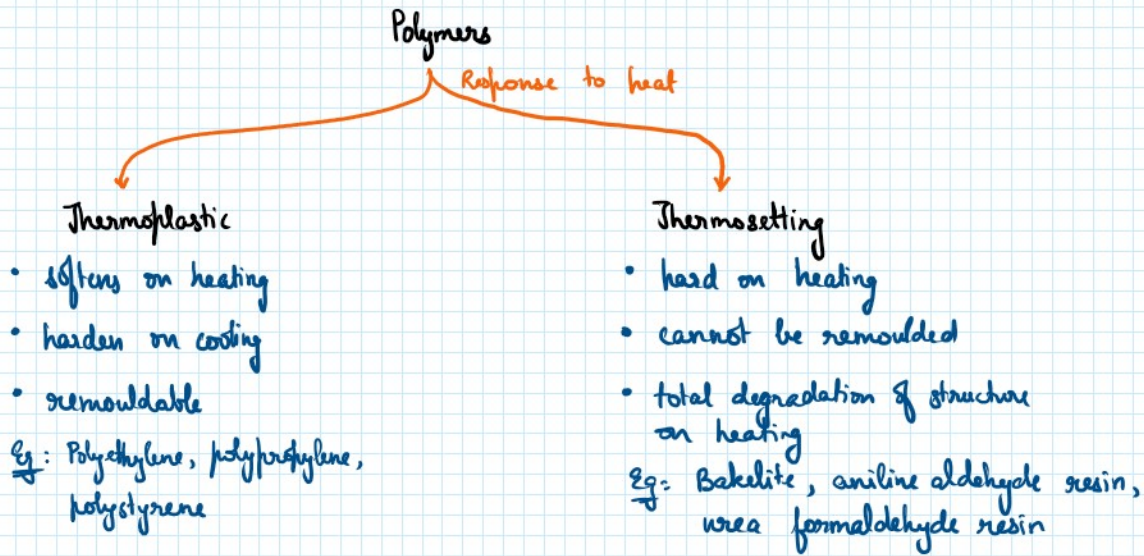


PVC with plasticiser

### PLASTIC DEFORMATION



Application of heat  $\rightarrow$  becomes soft and flexible } Plasticity / Plastic deformation  
Cooling  $\rightarrow$  returns to original shape



Why is there a difference in thermal behaviour?

- Thermoplastics  $\rightarrow$  relatively weak forces of attraction  $\rightarrow$  overcome when heated
- Thermosetting plastics  $\rightarrow$  cross linked with strong covalent bonds  $\rightarrow$  on heating results in charring & degradation