High polymers

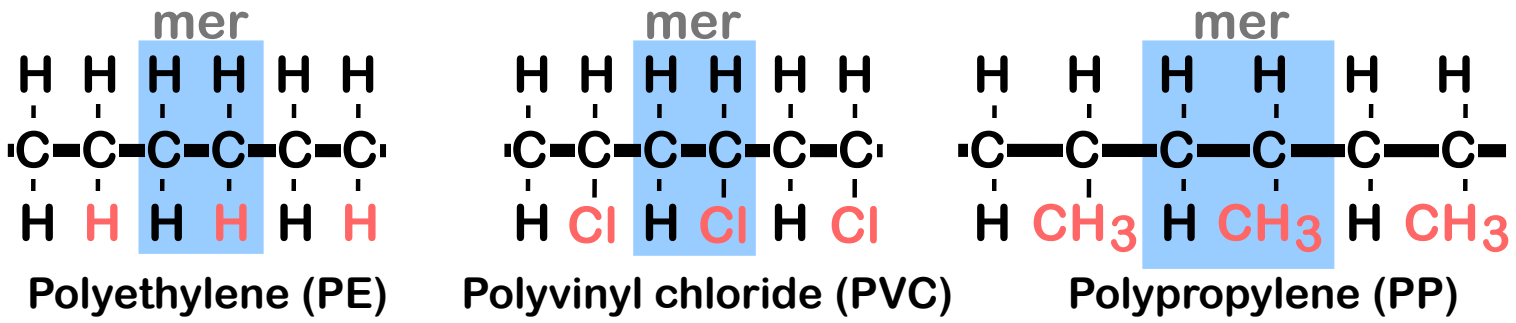
DEFINITION:

The word *polymer* is derived from the two greek words

poly **and** ***mers***

many ***parts or units***

e.g.

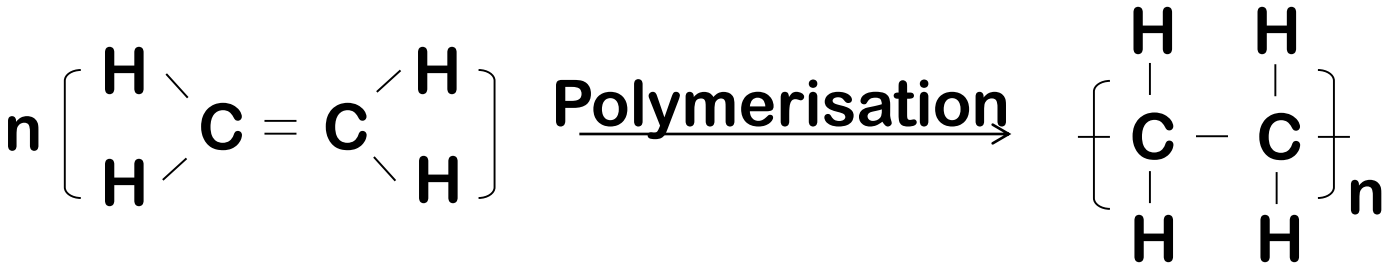


Polyethylene (PE) **Polyvinyl chloride (PVC)** **Polypropylene (PP)**

Polymers are macro molecules formed by linking smaller molecules repeatedly, called *monomers*.

Examples:

Polyethylene is formed by linking a large number of ethylene molecules



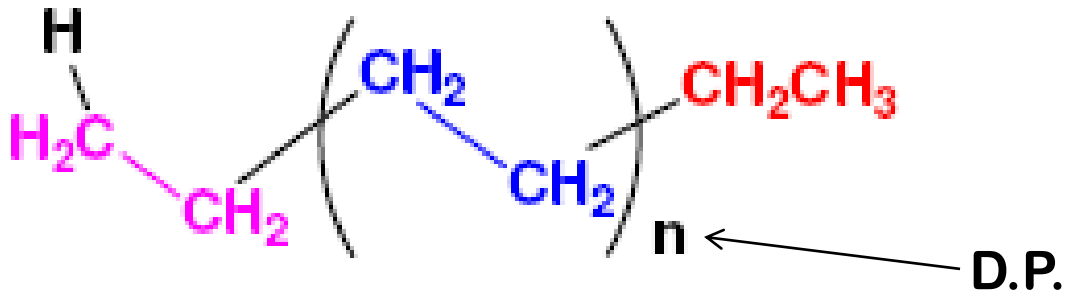
Ethylene polyethylene

polystyrene is formed by linking styrene molecules

styrene polystyrene

The number of repeating units (n) in the chain is known as the degree of polymerization.

e.g.,



Polymers with high degree of polymerization are called high polymers and these have very high molecular weights (10^4 to 10^6).

Polymers with low degree of polymerization are called oligomers.

Classification of Polymers

Polymers can be classified in several ways, based on

- origin
- structure
- methods of formation
- response to heat
- properties (or applications)

Based on the origin

polymers can be classified as

- Natural polymers
- synthetic polymers

Natural polymers are those which are obtained naturally

e.g., Cellulose, Silk, Starch, RNA, DNA, Proteins etc.,

Synthetic polymers are those which are made by man

e.g., polyethylene, polystyrene, PVC, polyester, etc.,

semi-synthetic polymers which are chemically modified natural polymers

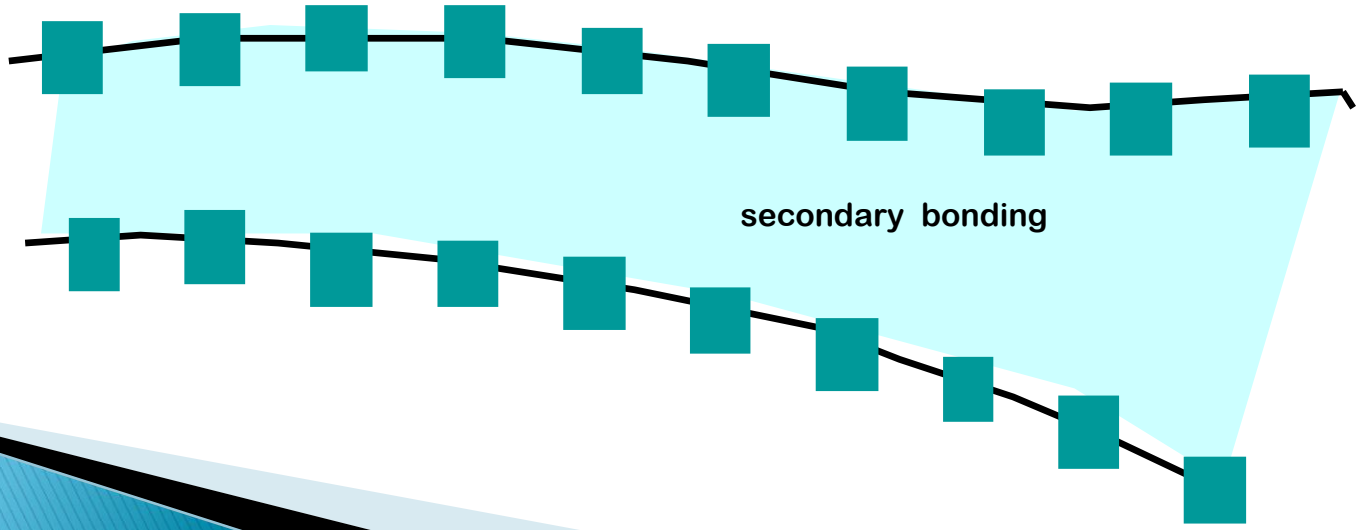
e.g., cellulose acetate, cellulose nitrate, halogenated rubbers etc.,

Based on the molecular structure

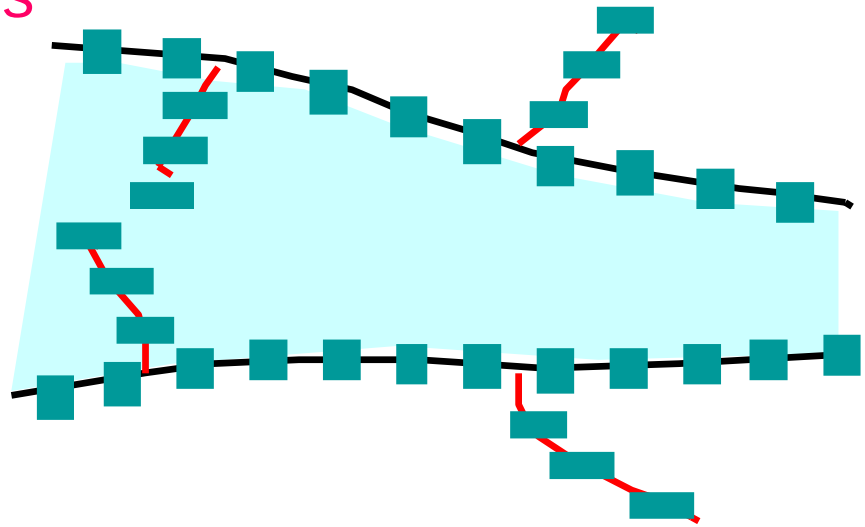
polymers can be classified as

- Linear
- Branched
- Cross-linked

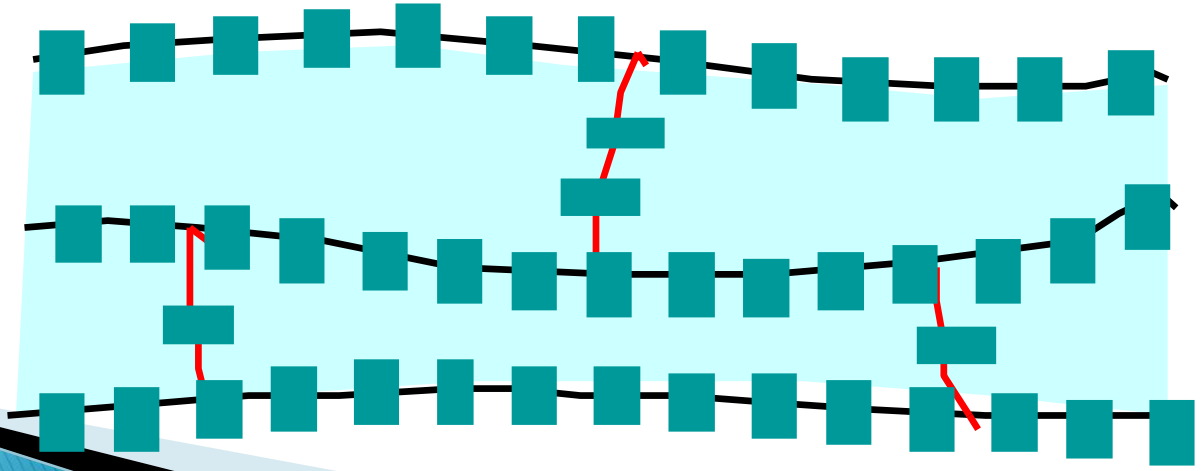
In linear polymers,
the monomeric units combine linearly with each other



Branch polymers



Cross linked polymers



Based on the method of formation

- Addition polymers
- Condensation polymers

Addition polymers are formed by self-addition of monomers
The molecular mass of a polymer is an integral multiple of the molecular mass of a monomer

Condensation polymers are formed by condensation reaction

i.e., reaction between two or more monomer molecules with the elimination of simple molecules like water, ammonia, HCl etc.,

Based on the response to heat

- **Thermo softening**
- **Thermosetting**

thermo softening or thermoplastics

soften on heating and can be converted into any shape and can retain its shape on cooling

thermosetting polymers

under go chemical change on heating and convert themselves into an infusible mass

Based on the properties or applications

- Plastics
- Elastomers
- Fibers
- Resins

Plastics

The polymers, which are soft enough at some temperature to be moulded into a desired shape and hardened on cooling so that they can retain that shape.

e.g., polystyrene, polyvinylchloride, polymethylmethacrylate etc.,

Elastomers

The polymers in which the structural units are either zig zag or in helical chains.

They undergo elastic changes when subjected to an external force but readily regain their original shape when the force is withdrawn

e.g., natural rubber, synthetic rubbers, silicone rubbers etc.,

Fibers

In these polymers, the molecular chains are arranged parallel to each other in a spiral or helical pattern and
the molecular length is at least 100 times its diameter

e.g., nylons, terylene, etc.,

Resins

These polymers have a glossy appearance

These constitutes the major essential part of the plastics

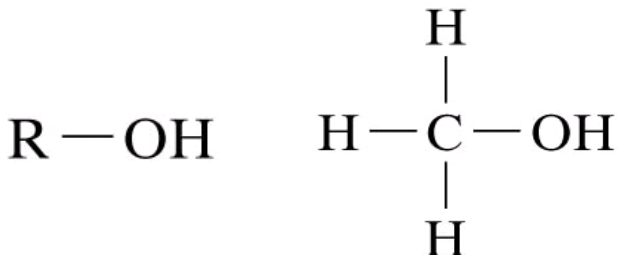
These undergo the polymerization reactions and impart different properties to plastics

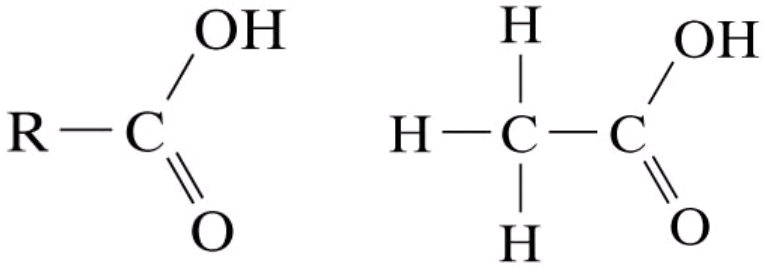
e.g., polysulphide sealants, epoxy adhesives, etc.,

Functionality

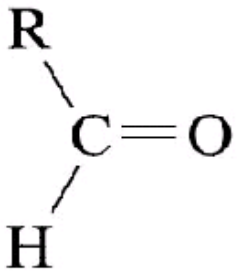
the number of reactive sites or bonding sites

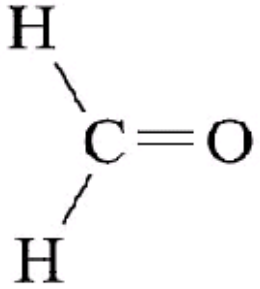
Some mono functional hydrocarbons

Alcohols  **Methyl alcohol**

Acids  **Acetic acid**

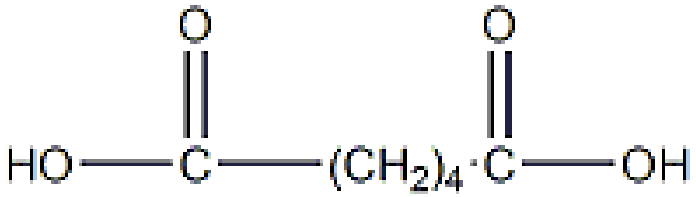
Aldehydes



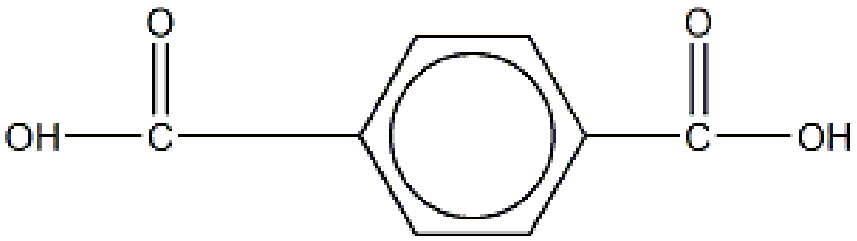


Formaldehyde

Some bi functional hydrocarbons

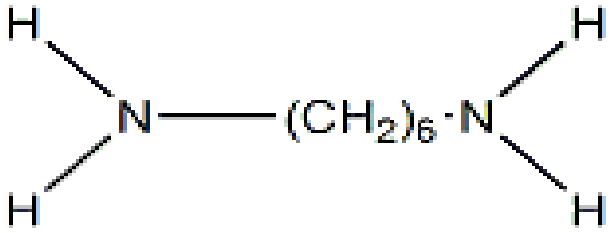


adipic acid (hexanedioic acid)



Terephthalic acid

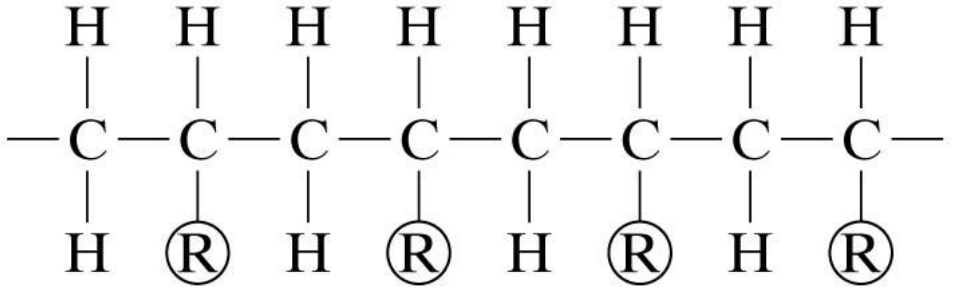
ethylene glycol



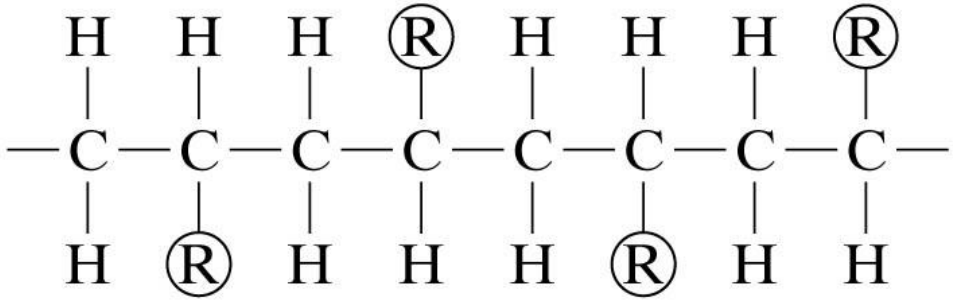
1,6-hexanediamine

Stereo regular polymers (or) Tacticity of Polymers

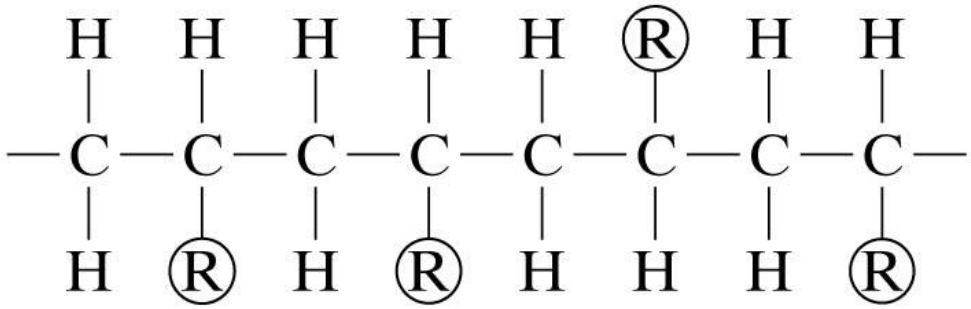
Isotactic
On one side



Syndiotactic
Alternating sides



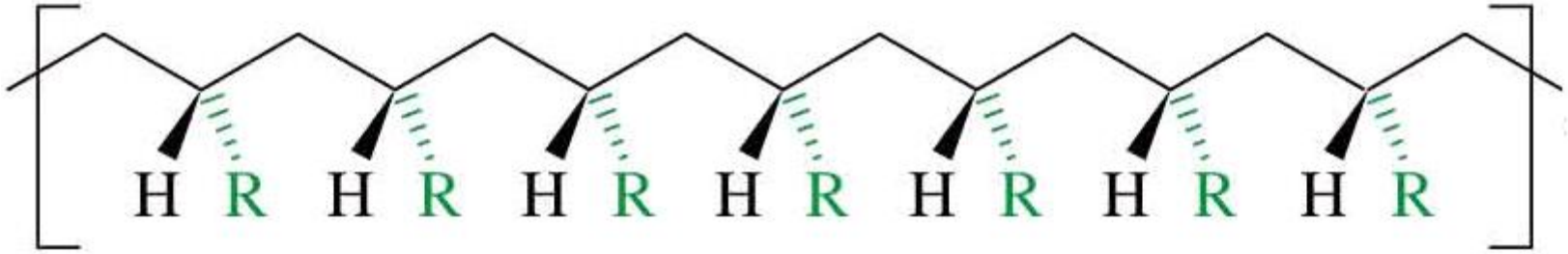
Atactic
Randomly placed

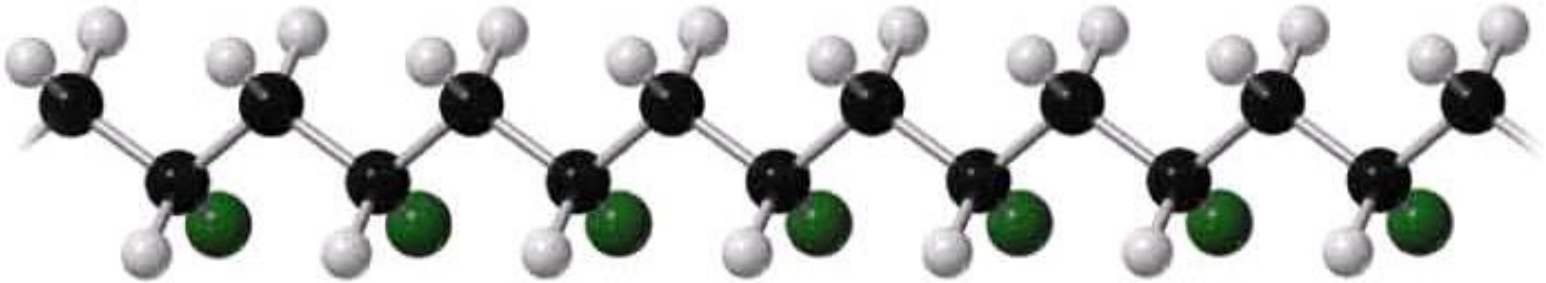


- Conversion from one stereoisomerism to another is **not** possible by simple rotation about single chain bond; bonds must be severed first, then reformed!

An isotactic polymer

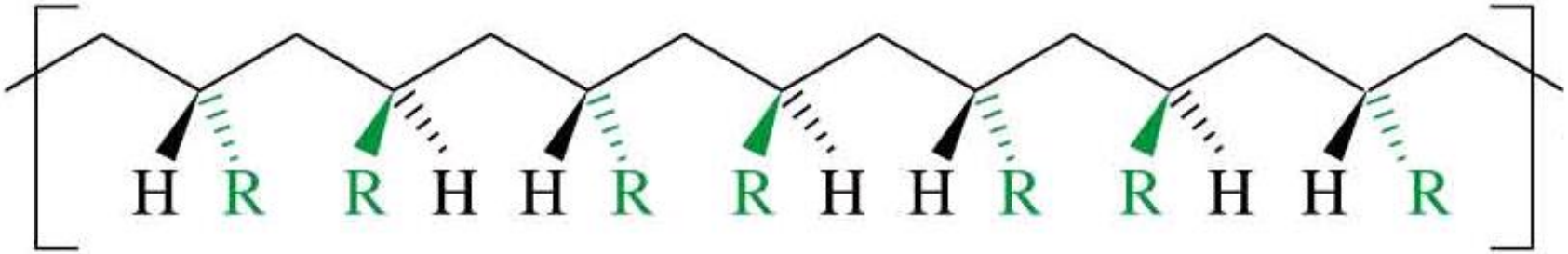
side groups on the same side of the backbone

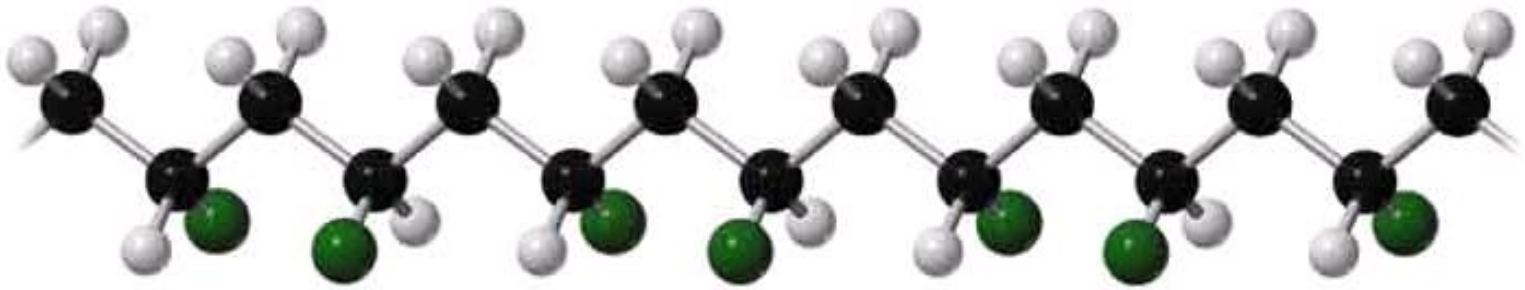




A syndiotactic polymer

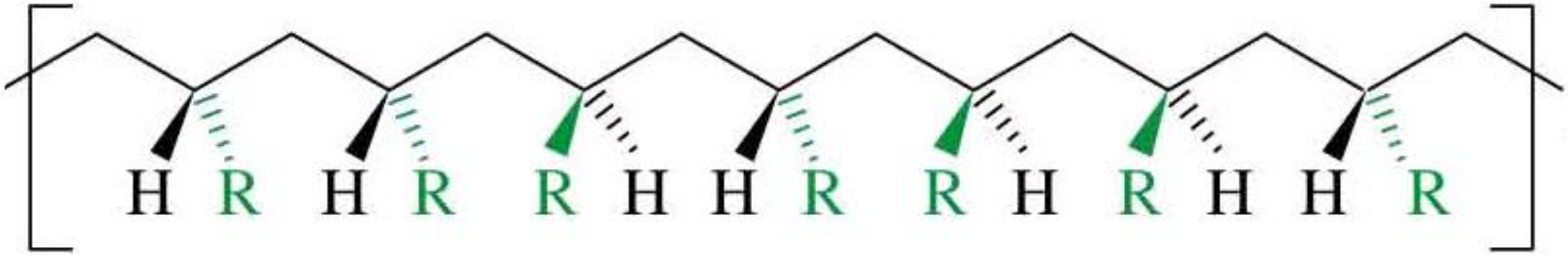
side groups on alternating sides of the backbone

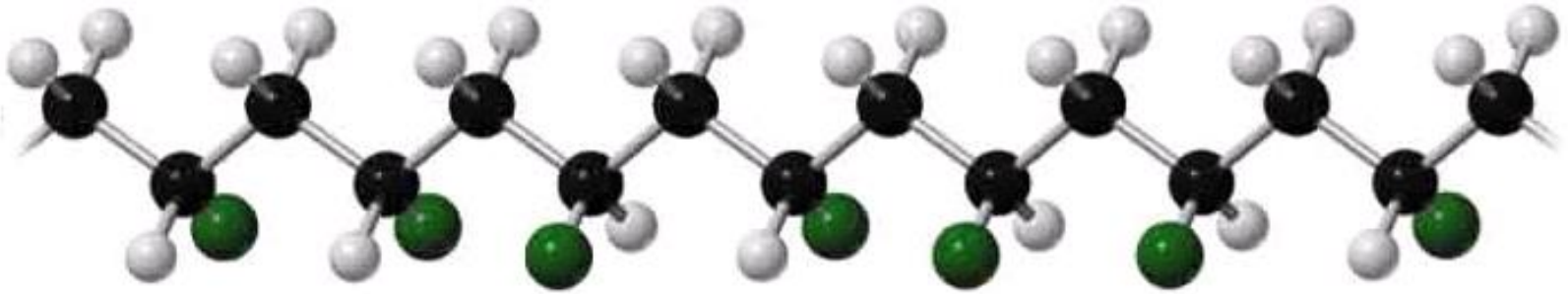




An atactic polymer

side groups on random sides of the backbone





Polymerization Reactions

- Polymerization = Reaction to convert monomers to a polymer.

- Two types of polymerization reaction:
  - Step-Growth Polymerization (Old = Condensation Polym.) applies to monomers with functional groups such as: -COOH, -COOR, -COOOC-, -COCl, -OH, -NH_2, -CHO, -NCO, epoxy.
  - Chain Polymerization (Old = Addition Polym.) applies to monomers having double bonds or ring structure.

- Both classes of reaction can lead to the formation of either linear polymers or polymer networks. Whether the linear chains or polymer networks are obtained only depends on the number of reactive entities per monomer.

Types of Polymerization

Polymerization occurs basically in two different modes.

- addition (chain growth) polymerization
- condensation (step growth) polymerization

- Addition
  - monomers react through stages of initiation, propagation, and termination
  - initiators such as free radicals, cations, anions opens the double bond of the monomer
  - monomer becomes active and bonds with other such monomers
  - rapid chain reaction propagates
  - reaction is terminated by another free radical or another polymer

Condensation polymerization

- two monomers react to establish a covalent bond

- a small molecule, such as water, HCl, methanol or CO_2 is released.

- the reaction continues until one type of reactant is used up

DISTINGUISHING FEATURES OF ADDITION AND CONDENSATION POLYMERISATION

ADDITION	CONDENSATION
Monomers undergo self addition to each other without loss of by products	Monomers undergo intermolecular condensation with continuous elimination of by products such as H_2O, NH_3, HCl, etc.,
It follows chain mechanism	It follows step mechanism
Unsaturated vinyl compounds undergo addition polymerization	Monomers containing the functional groups (-OH, -COOH, $-NH_2$, ….) undergo this polymerization
Monomers are linked together through C – C covalent linkages	Covalent linkages are through their functional groups
High polymers are formed fast	The reaction is slow and the polymer molecular weight increases steadily throughout the reaction
Linear polymers are produced with or without branching	Linear or cross linked polymers are produced
e.g., polystyrene, plexiglass, PVC, etc.,	e.g., nylons, terylene, PF resins, etc.,

STRUCTURE – PROPERTY RELATIONSHIP OF POLYMERS

1. Tensile Strength

the forces of attraction and slipping power

Based on forces of attraction:

Strength of the polymer is mainly determined by

the magnitude and distribution of attraction forces

between the polymer chains

These attractive forces are of two different types

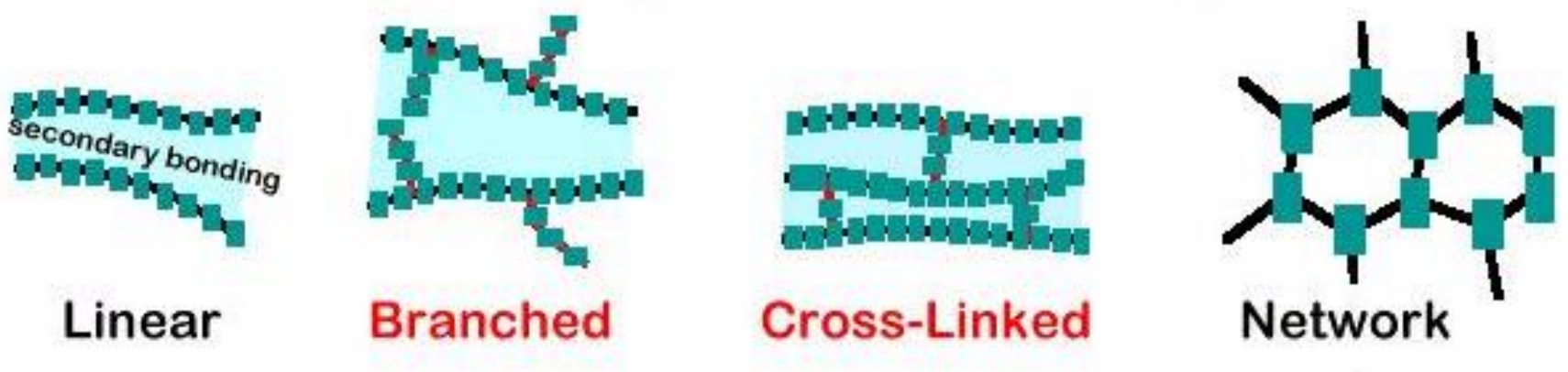
primary or covalent bond

secondary or intermolecular forces

In straight chain and branched chain polymers - weak intermolecular force of attraction

strength increases with increase in chain length -
as the longer chains are entangled (anchored) better

In cross-linked polymers, - covalent forces



Increase in Strength

Examples:

Linear Polymers: Polyethylene, polyvinyl chloride (PVC), polystyrene, polymethyl methacrylate (plexiglass), nylon, fluorocarbons (Teflon)

Branched Polymers: Many elastomers or polymeric rubbers

Cross-linked Polymers: Many elastomers or polymeric rubbers are cross-linked (vulcanization process); most thermosetting polymers

Network Polymers: Epoxies, phenol-formaldehydes.

Based on slipping power:

It is defined as the movement of molecules one over the other

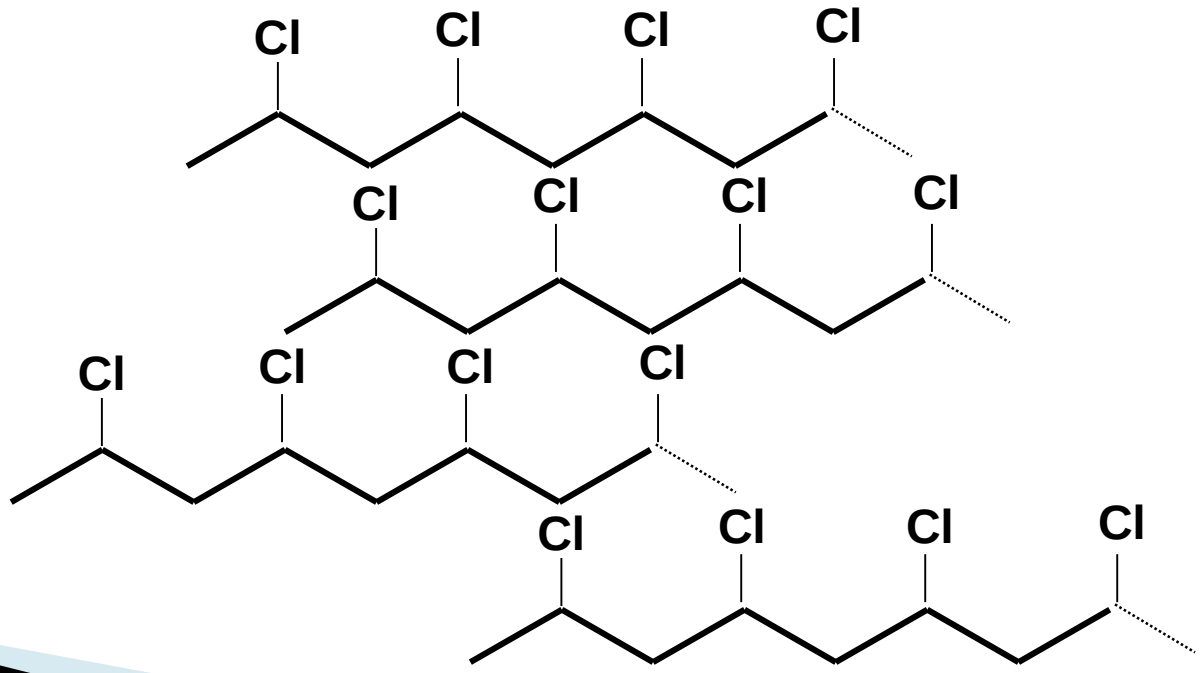
It depends on the shape of the molecule

the movement of molecules one over other is easy
i.e., slipping power is high

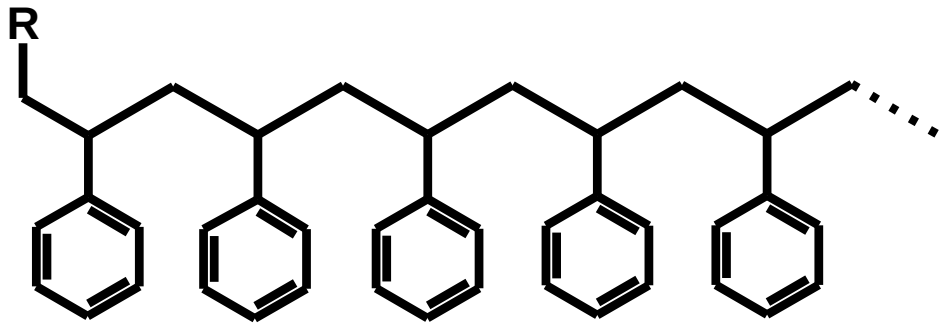
in case of poly vinyl chloride (PVC), the bulky chlorine atoms are present along the chain length hence movement is restricted

i.e., slipping power is less

Hence PVC has higher strength than PE



Polystyrene (PS) possess greater strength when compared to PE and PVC because of the presence of bulky phenyl group.



In cross linked polymers, connected by strong covalent forces and so the movement of the intermolecular chains is totally restricted.

2. Plastic deformation

When a polymer is subjected to some stress in the form of heat or pressure or both, permanent deformation in shape takes place, which is known as plastic deformation

linear molecules - because of the presence of only the weak intermolecular forces show greatest degree of plastic deformation, under pressure .

Such type of materials are called thermoplastic materials

cross-linked molecules - covalent bonds - plasticity does not increase with rise in temperature or pressure or both in cross-linked molecules.

Such type of polymers are known as thermosetting polymers.

3. Chemical Resistance

Chemical resistance of the polymer depends upon the

- chemical nature of monomers and
- their molecular arrangement

Thus a polymer is more soluble in structurally similar solvent

polymers containing polar groups like – OH, - COOH etc., usually dissolve in polar solvents like water, ketone, alcohol etc., but these are chemically resistant to non-polar solvents

Similarly non-polar groups such as methyl, phenyl dissolve only in non-polar solvents like benzene, toluene, etc.,

polymers of more aliphatic character - soluble in aliphatic solvents, chemical resistance more in aromatic solvents

polymers with more aromatic groups dissolve more in aromatic solvents, chemical resistance more in aliphatic solvents

Polymers containing ester groups - Hydrolysis with strong alkalis at high temperature.

Polyamides like nylon containing –NHCO– group can undergo easily the hydrolysis by strong acid or alkali.

- Polymers containing residual unsaturation - degradative oxidation in air in presence of light or ozone.

- Because of the dissolution of polymers in suitable solvents, there occurs softening, swelling and loss of strength of polymer material

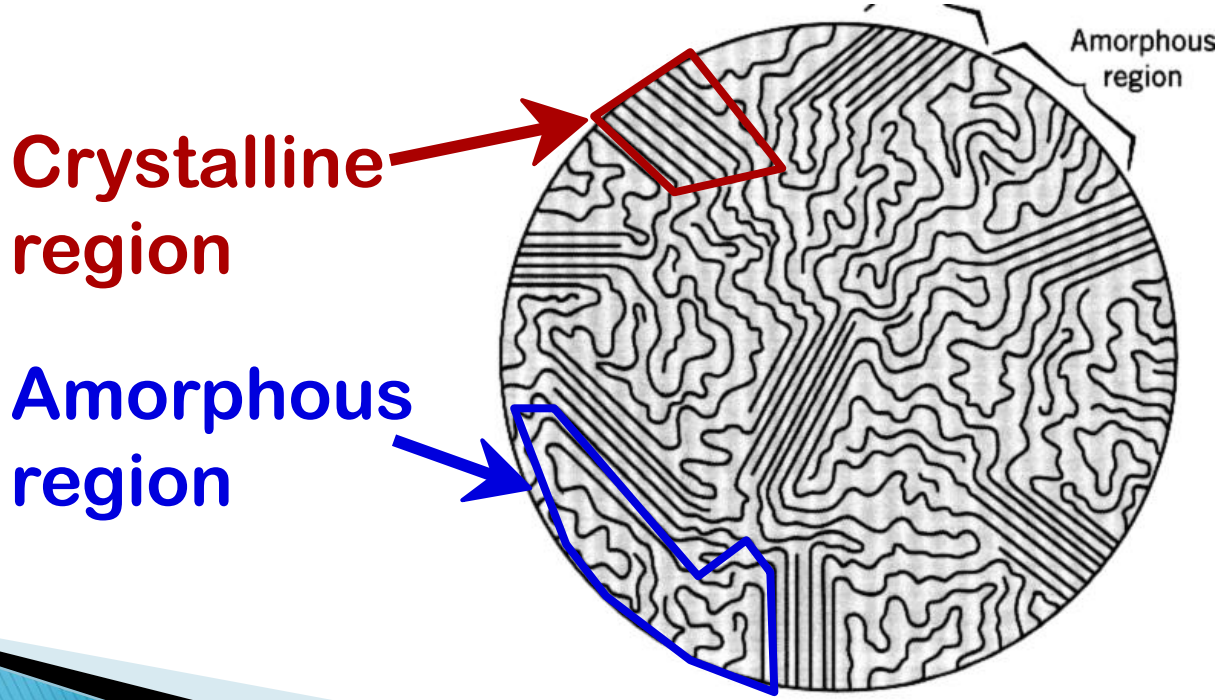
- Permeability of the solvents in the polymers also depends on crystallinity. Hence crystalline polymers exhibits higher chemical resistance than less crystalline polymers because of denser packing.

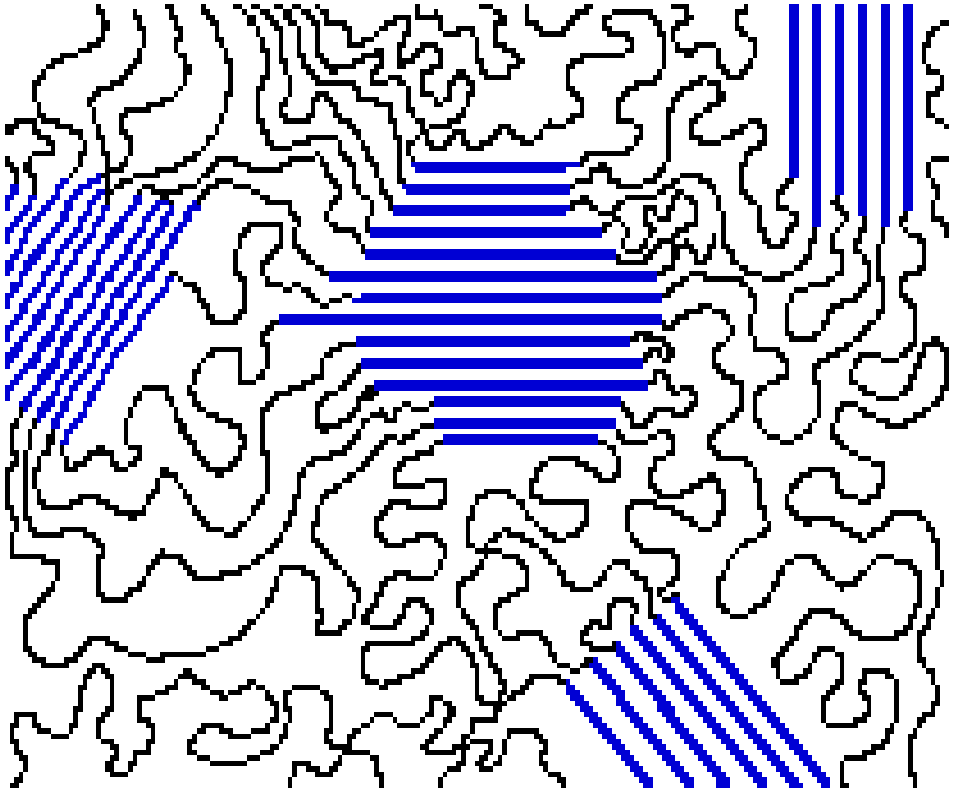
4. Crystallinity

Polymers are part crystalline and part amorphous

An amorphous state is characterized by complete random arrangement of molecules

crystalline form by regular arrangement of molecules





Some Highly Crystalline Polymers:

Polypropylene

Syndiotactic polystyrene

Nylon

Kevlar and Nomex

Polyketones

Some Highly Amorphous Polymers:

Poly(methyl methacrylate)

Atactic polystyrene

Polycarbonate

Polyisoprene

Polybutadiene

A linear polymer will have a high degree of crystallinity, and be stronger, denser and more rigid.

- The more branched the polymer, the less dense and less crystalline.

- Polymers with a long repeating unit or with low degree of symmetry do not crystallize easily .

- Isotactic and syndiotactic polymers are stronger and stiffer due to their regular packing arrangement.

- Optical properties: crystalline -> scatter light (Bragg)
  amorphous -> transparent.

5. Elasticity

Elasticity of the polymer is mainly because of the uncoiling and recoiling of the molecular chains on the application of force

When a polymer is stretched the snarls begin to disentangle and straighten out

i.e., the orientation of the chains occurs which in turn enhances the forces of attraction between the chains and thereby causing the stiffness of the materials

However when the strain is released snarls return to their original arrangement.

- introducing cross-linking at suitable molecular positions
- introducing bulky side groups such as aromatic and cyclic groups on repeating units
- introducing non-polar groups on the chains

By introducing a plasticizer the elasticity of polymer can be enhanced.

The glassy state and the glass transition

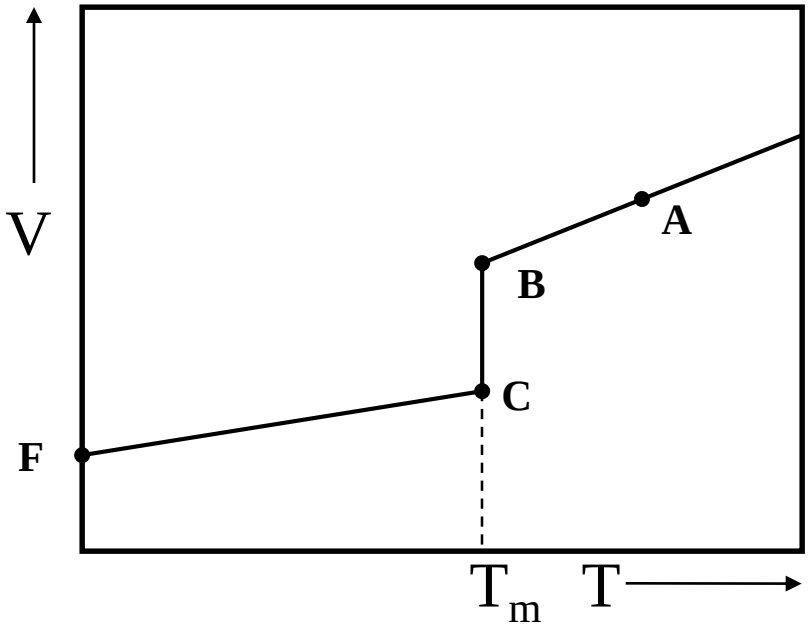
- ***In general for ordinary compounds of low molar mass:***

crystalline solid

melting

liquid

increase in volume at T_m



GLASS TRANSITION TEMPERATURE (T_g)

Amorphous polymers do not have sharp melting points They possess softening point .

At low temperature, polymers exist as glassy substances. Since the molecular chains can not move at all easily in this state, the solid tends to shatter, if it is hit .

If the solid polymer is heated, eventually it softens and becomes flexible . This softness and flexibility is obtained at the glass transition temperature.

The ***glass transition temperature*** can be defined as the temperature below which an amorphous polymer is brittle, hard and glassy and above the temperature it becomes flexible, soft and rubbery

Glassy state ⟶ rubber state

(Hard and brittle plastic) (soft and flexible)

In the glassy state of the polymer, there is neither molecular motion nor segmental motion

When all chain motions are not possible, the rigid solid results

On heating beyond T_g segmental motion becomes possible but molecular mobility is disallowed. Hence flexible.

Factors influencing the glass transition temperature

Glass transition temperature of a polymer depends on parameters such as

- chain geometry
- chain flexibility
- molecular aggregates
- hydrogen bond between polymer chains
- presence of plasticizers and
- presence of substrates in the polymer chains

A polymer having regular chain geometry show high glass transition temperature

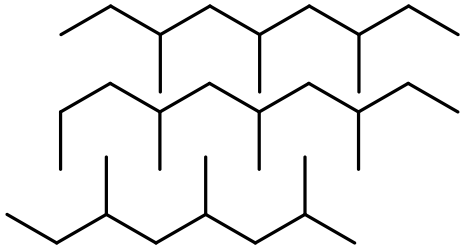
crystalline polymers have higher T_g's than amorphous polymers

HIGH-DENSITY POLYMERS

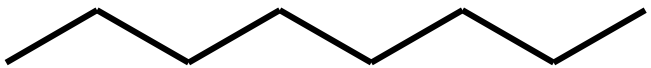
Linear polymers with chains that can pack closely together. These polymers are often quite rigid.

LOW-DENSITY POLYMERS

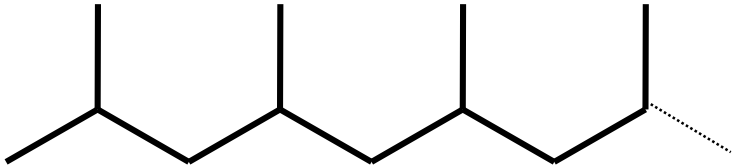
Branched-chain polymers that cannot pack together as closely. There is often a degree of cross-linking. These polymers are often more flexible than high-density polymers.



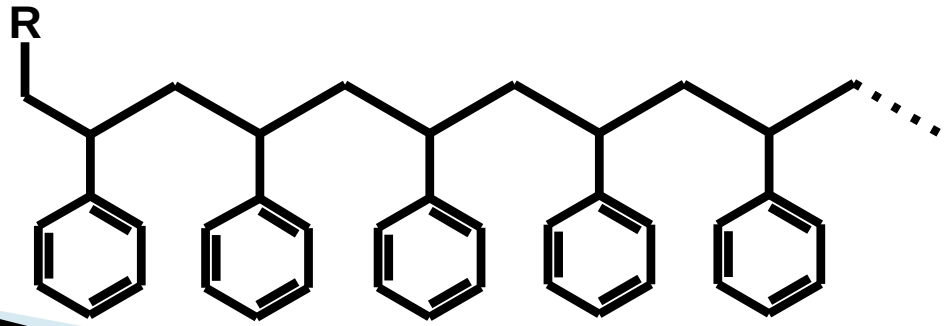
the bulky groups on chain, increases the Tg of the polymer



Polyethylene
Tg = - 110 ^{0}C



Polypropylene
Tg = - 18 ^{0}C

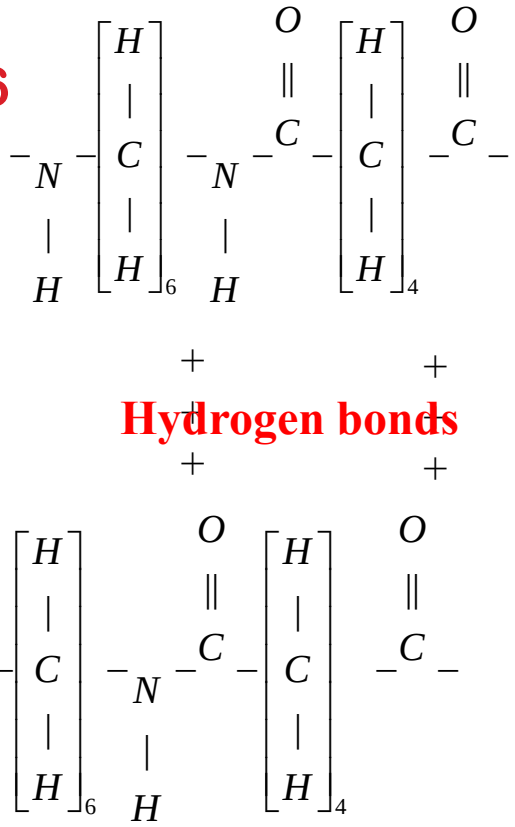


Polystyrene
Tg = 100 ^{0}C

The presence of H-bonds between the polymer molecules increases the Tg

- e.g., the Tg of *nylon 6,6* (Tg = 50 ^{0}C) is higher than *PE* (Tg = -110 ^{0}C)

nylon 6,6



Hydrogen bonds

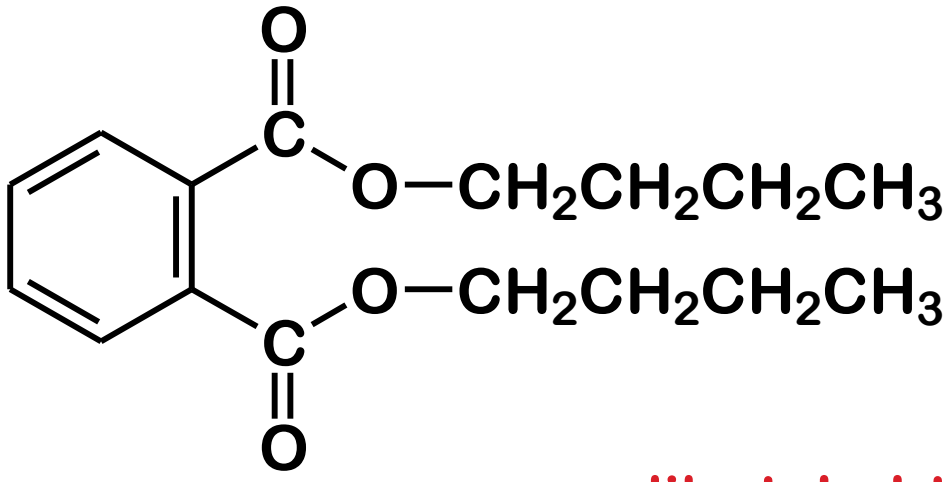
polyethylene

Van der Waals bonds

With H-bonds Vs vanderWaals bonds, nylon is expected to have (and does) higher Tg.

The presence of a plasticizer reduces the Tg of a polymer

The plasticizers are usually dialkyl phthalate esters, such as dibutyl phthalate, a high boiling liquid.



dibutyl phthalate

The plasticizer separates the individual polymer chains from one another. It acts as a lubricant which reduces the attractions between the polymer chains.

The Tg of a polymer is influenced by its molecular weight

With increase in molecular mass, the Tg increases

However, it is not significantly affected if molecular weight is around 20000

e.g., PE (low Mw) - 110 ^{0}C

PE (high Mw) - 90 ^{0}C

The glass transition temperature helps in choosing the right processing temperature

It also gives the idea of

thermal expansion

heat capacity

electrical and mechanical properties

Molecular Weight of Polymers

When a monomer is polymerized to form a polymer, a number of polymer chains start growing at any instant, but all of them do not get terminated after growing to the same size. The chain termination is a random process.

Hence, each polymer molecule formed can have a different number of monomer units and thus different molecular weights

So, a polymer sample can be thought of a mixture of molecules of the same chemical type, but of different molecular weights.

the molecular weight of a polymer can be expressed by two most and experimentally verifiable methods.

(i) Number – average molecular weight

(ii) Weight – average molecular weight

In computing the number average molecular mass of a polymer, we consider the number fractions.

In computing the weight average molecular mass of a polymer, we consider the weight fractions.

Number average molecular mass of the whole polymer is given by

$$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i}$$

Total mass (w) of all the molecules in polymer divided by total number of molecules present.

In computing the weight average molecular mass of a polymer, we consider the weight fractions

Total weight of the polymer (W) is given by

$$W_i = \Sigma n_i M_i$$

Weight of fraction 'one' = $W_1 = n_1 M_1$

Molecular weight contribution by fraction 'one'

$$M_w = w_1 M_1 / w_i$$

$$= \frac{n_1 M_1^2}{\sum n_i M_i}$$

Weight average molecular mass of the whole polymer is given by

$$\overline{M_w} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

- Ratio of M_w to M_n is known as the polydispersity index (PDI)
  - a measure of the breadth of the molecular weight
  - PDI = 1 indicates $M_w = M_n$, i.e. all molecules have equal length (monodisperse)
  - PDI = 1 is possible for natural proteins whereas synthetic polymers have $1.5 < PDI < 5$.

The number-average molecular mass (M_n) is determined by the measurement of colligative properties such as

lowering of vapour pressure

osmotic pressure

depression in freezing point

elevation in boiling point

The weight-average molecular mass (M_w) is determined by

light scattering and ultra-centrifugal techniques.

Polymer molecules with different degree of polymerization such as 500, 750, 850 and 1100 are mixed in molecular ratio 1: 2: 3: 4 in a sample of high polymer of styrene. Calculate the number average and weight average molecular weights. ($C_6H_5 — CH = CH_2$)

$$M_n = \frac{1 \times (500 \times 104) + 2 \times (750 \times 104) + 3 \times (850 \times 104) + 4 \times (1100 \times 104)}{10}$$

$$= 93080$$

$$M_w = \frac{1 \times (500 \times 104)^2 + 2 \times (750 \times 104)^2 + 3 \times (850 \times 104)^2 + 4 \times (1100 \times 104)^2}{1 \times (500 \times 104) + 2 \times (750 \times 104) + 3 \times (850 \times 104) + 4 \times (1100 \times 104)}$$

$$= 97{,}405.33$$

(1)A polypropylene [-CH_2–$CH(CH_3)$-] sample contains the following composition.

Degree of polymerization	**400**	**800**	**600**
% of composition	**25**	**35**	**40**

Calculate Mn & Mw of polypropylene sample by neglecting the end groups. Given that atomic masses of C = 12 and H = 1 amu.

2)Polymer molecules with different degree of polymerization 500,750,950 and 1500 are mixed in molecular ratio 1:2:3:4 in a sample of high polymer of ethylene. Calculate the no. average and Wt average molecular mass.