A. Text Books

T1. Jain P.C. and Jain M., Engineering Chemistry, Dhanpat Rai and Sons, Delhi, Revised, 15th Edn. 2006

T2. Engineering chemistry, Wiley India Pvt. Ltd., 2018.

T3. Kuriacose J.C., Raja R. J., Chemistry in Engineering and Technology, Vol. I/II TMH 1988

A. Reference Books

R1. Fischer T., Materials Science for Engineering Students, Academic Press, London, 2009

R2. Fuel Science &Technology Hand Book, James G Speight; Marcel Dekker, New York.

Development of civilization

Stone age → Bronze age → Iron age → Polymer age

- The Stone Age, Bronze Age, and Iron Age mark key stages in human civilization, defined by the dominant materials used for tools and technologies.
- The transition from stone to metals like bronze and iron brought significant advancements in agriculture, warfare, and construction.
- Today, the Polymer Age symbolizes modern reliance on synthetic materials like plastics, revolutionizing industries, healthcare, and everyday life through lightweight, durable, and versatile materials that shape the world around us.

Syllabus

Module 1 (7 hrs): Advanced materials and polymers: Introduction, Definition, classification of polymers – based on origin, thermal behaviour, Polymerization reactions and applications, Tacticity. Functionality, Degree of polymerization, Co-polymerization – alternating, random, block and graft polymers. Mechanism of free radical polymerization and ionic polymerization. Mechanism of coordination polymerization, Condensation polymerization reactions, Glass transition temperature & factors affecting it. Molecular weight of polymers, Number average and weight average molecular weights, Numerical problems. Preparation, properties, and applications of Polythene (LDPE and HDPE), Nylon (6:6, 6, 6:10, 11), PF resins and Polyester. Natural rubber, Processing of Natural Rubber, Vulcanization, Compounding of rubber; Synthetic Rubber: Buna-N, Buna-S. Composites, biomaterials, their properties, and applications.

Module 1 – Advanced Materials and Polymers

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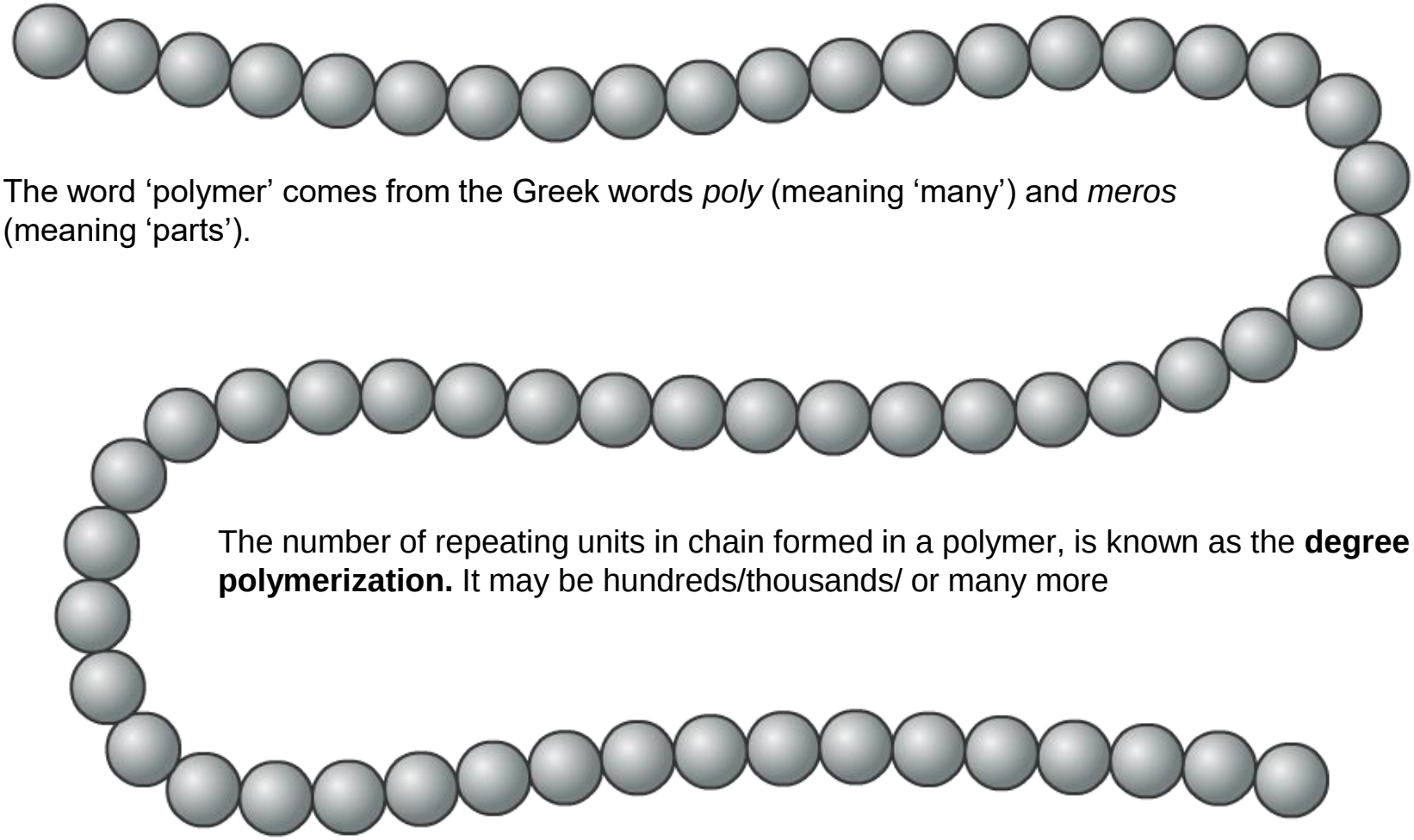
Composites and biomaterials: properties and applications

A world of polymer

What are polymers?

A ***polymer*** is a high molar mass molecular compound made up of many repeating chemical units (Monomers).



The word ‘polymer’ comes from the Greek words *poly* (meaning ‘many’) and *meros* (meaning ‘parts’).

The number of repeating units in chain formed in a polymer, is known as the **degree of polymerization.** It may be hundreds/thousands/ or many more

The process by which monomers are transformed into polymers is called *polymerization.*

Few Queries???

- What are some of the polymers that you encounter every day?
  Sandwich bags, carpets, nylon stockings, stackable chains, milk cartons, etc.
- Why do different polymers have different properties?
  They have different chemical compositions (different monomer units), different structures, different ways of being fabricated, etc.
- Imagine samples of LDPE (sandwich bag, squeeze bottle) and HDPE (milk jug, grocery bag). What are some of the differences in the physical properties of these substances?
  LDPE – more transparent, flexible, waxy
  HDPE – more opaque, rigid, non-waxy

POLYMERS

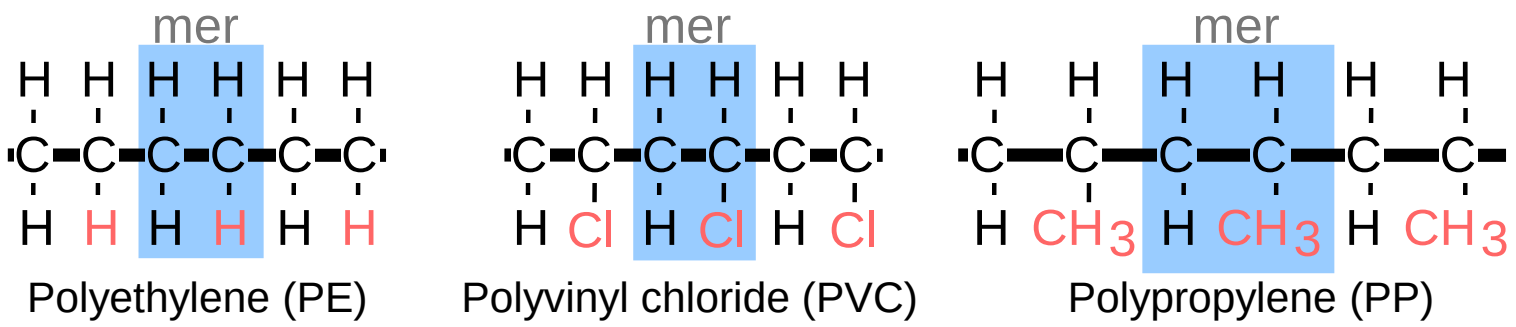
DEFINITION:

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

poly and *meors*

many *parts or units*

e.g.

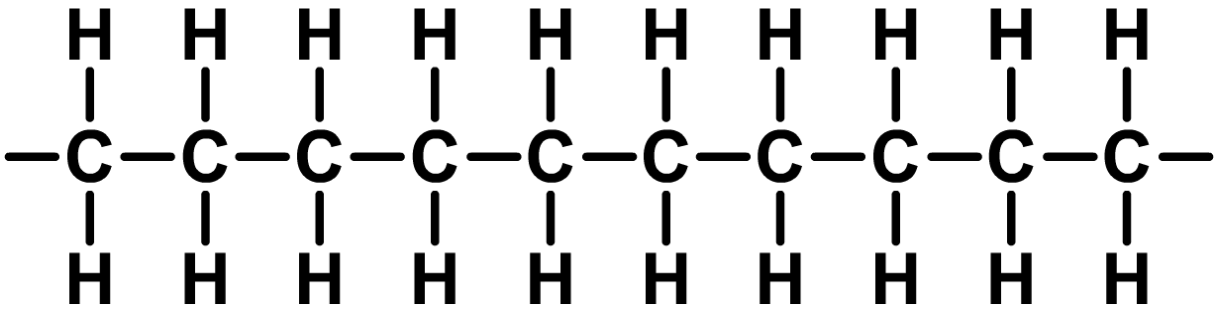


Polymers are macro molecules formed by linking smaller molecules repeatedly, called *monomers*.

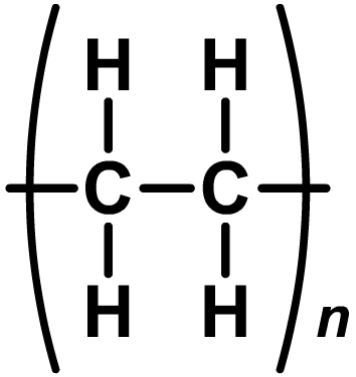
Drawing polymers – shorthand formulae

Polymers contain thousands of molecules, so how can their structures be easily drawn?

Part of the polymer molecule can be drawn:

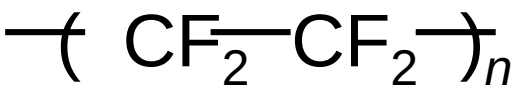


A better way is to show a **shorthand formula**:

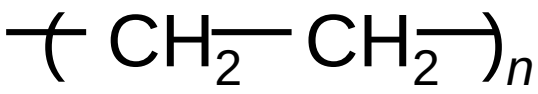


The '*n*' means that the polymer contains a very large number of the repeating unit shown in the brackets.

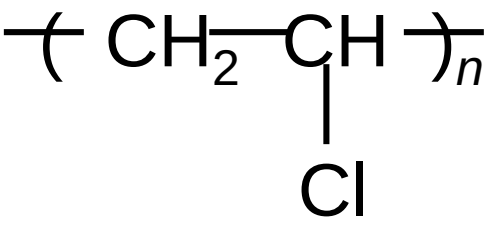
1) ***Homopolymer*** is a polymer made up of only one type of monomer



Teflon

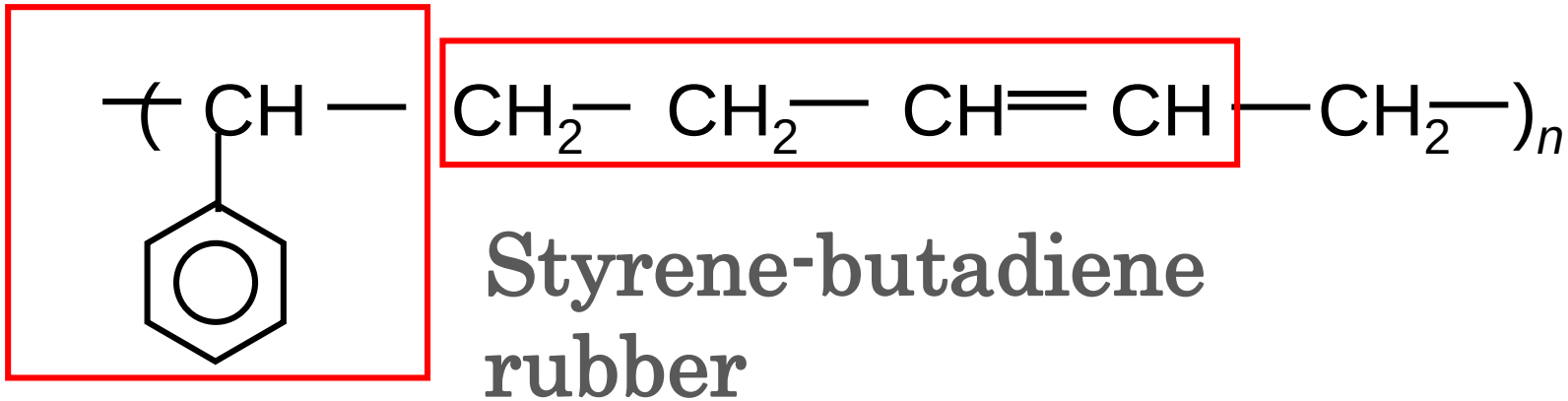


Polyethylene



PVC

2) ***Copolymer*** is a polymer made up of two or more monomers



Styrene-butadiene rubber

Copolymers

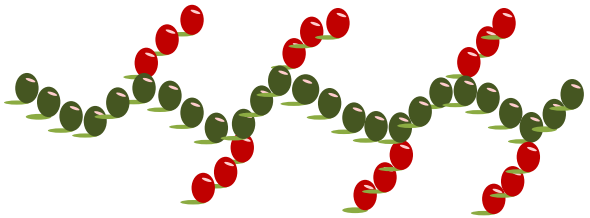
two or more monomers polymerized together

Alternating **A** and **B** alternate in polymer chain

Block large blocks of **A** units alternate with large blocks of **B** units

Random **A** and **B** randomly positioned along chain

Graft chains of **B** units grafted onto **A** backbone



Classification of Polymers:

1. Based on origin:

A. Natural Polymers

These occur in nature in plants and animals and are very essential for life. For e.g., proteins, nucleic acids, Starch, cellulose, protein, silk, wool and natural rubber are some natural polymers.

B. Synthetic Polymers

Synthetic polymers are man-made polymers which include fibers like teflon and dacron, synthetic rubbers, Polyethylene, Polystyrene, polyvinylchloride, nylone, polyester

2. based on polymerization reactions:

Based on the mode of polymerization, polymers are classified as:

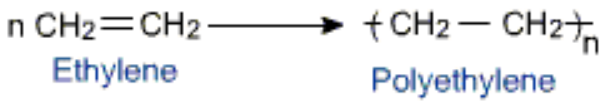
1. *Addition polymers*
2. *condensation polymers*

Addition polymers

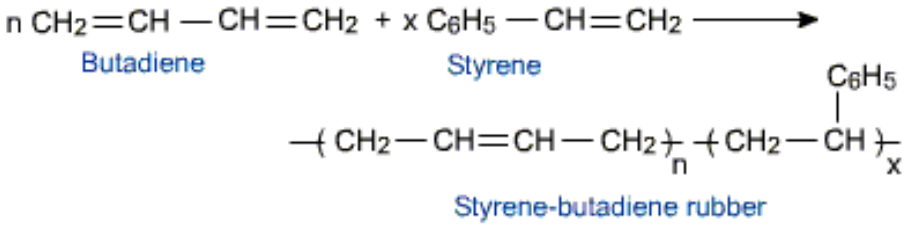
Addition polymers are formed when monomer units are separately added to form long chains without elimination of any by-product molecules. These polymers are formed by reactions between monomer molecules possessing multiple bonds.

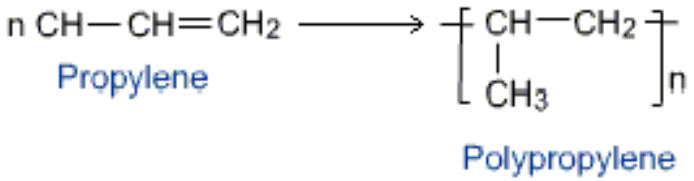
Example: Ethylene undergoes polymerization to form polythene.

The empirical formula of the monomer and polymer are the same. Other examples:
Polypropylene is an addition polymer of propylene.



Styrene-butadiene rubber is an addition polymer formed by addition reactions between butadiene and styrene.

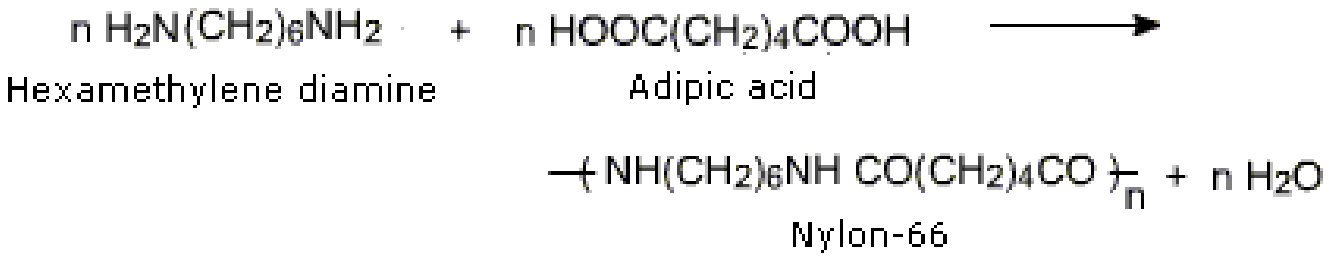




Condensation polymers

Condensation polymers are formed when the monomers containing active functional groups (generally two), which react together with the elimination of a small molecule like water, ammonia, alcohol etc.

Examples: Nylon-66, polyester, Bakelite etc.Nylon-66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:



3. Based on thermal behavior

The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecular structure.

Thermoplastics and Thermosets are the 2 categories.

1. A **thermoplastic** is a polymer that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently. Thus thermoplastics can be moulded on heating. Most thermoplastics are high-molecular-weight polymers whose chains associate through weak Van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon).

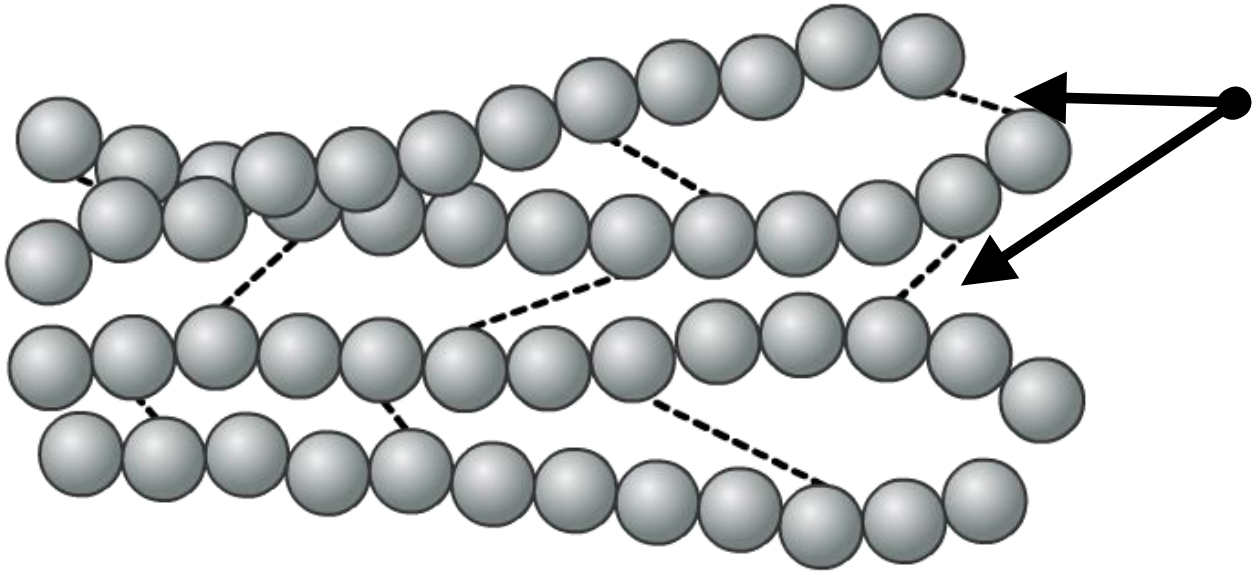
These polymers have no cross-linking between chains. Examples: Polyethylene, polystyrene etc.

2. **Thermosetting** polymers

Thermosetting polymers made from relatively low molecular mass semi-fluid polymers which when heated in a mould forms an insoluble hard mass which is infusible. This is due to extensive crosslinks between the different polymer chains forming three dimensional network of bonds.

Example: Bakelite and melamine

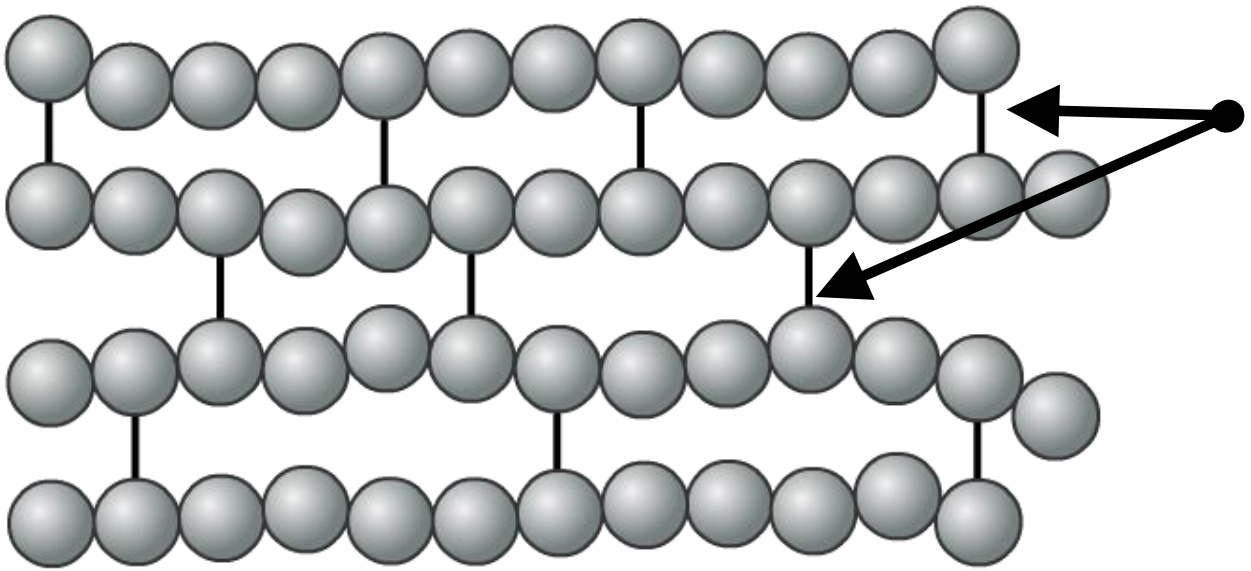
Thermoplastic polymer	Thermosetting polymer
1. They soften on heating readily.	1. They do not soften on heating. On prolong heating, however, they burn.
2. They consist of long chain linear macromolecules.	2. Their set molecules have three dimensional network structure, joined by strong covalent bonds.
3. They are formed mostly by addition polymerization reaction.	3. They are formed by condensation polymerization reaction.
4. They are usually soft, weak and less brittle.	4. They are usually hard, strong and more brittle.
5. They can be reclaim from wastes.	5. They cannot be reclaim from wastes.
6. They are usually soluble in some organic solvents.	6. Due to the strong bonds and cross-linking they are insoluble in almost all organic solvents



weak intermolecular forces –

these let the chains slide past each other

Plastics made of these polymers are stretchy and have a low melting point. They are called **thermoplastic polymer**.



strong intermolecular forces (cross-links) – these hold the chains firmly in place

Plastics made of these polymers cannot be stretched, are rigid and have a high melting point. They are called **thermosetting** plastics (or ‘thermosets’).

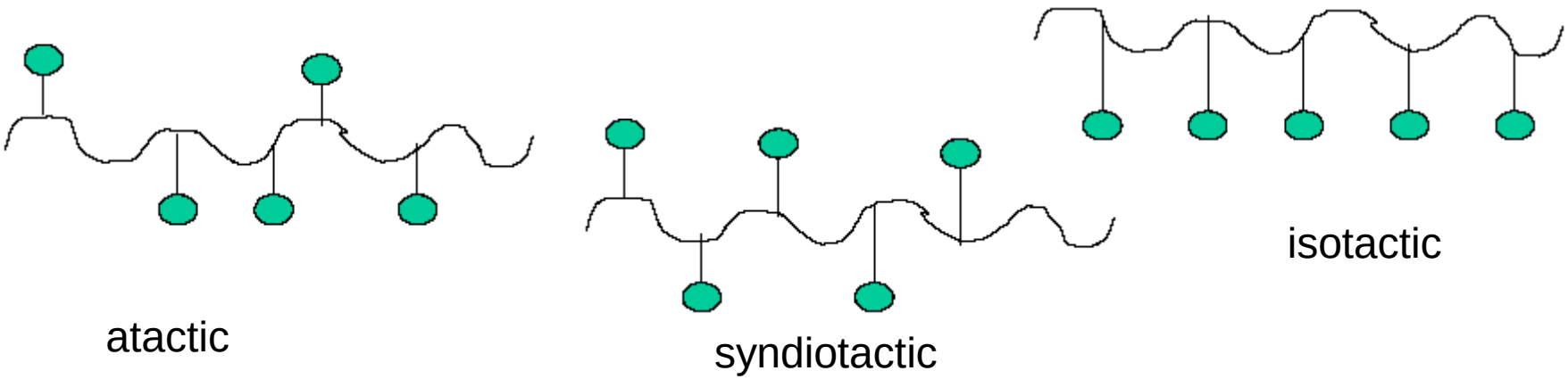
Classification by Chain Configuration

The orientation of monomeric units in a polymer can take place in orderly or disorderly fashion with respect to the main chain. The differences in configuration of polymer is known as tacticity.

Configuration : Is defined by polymerization method. A change in configuration require the rupture of covalent bonds .

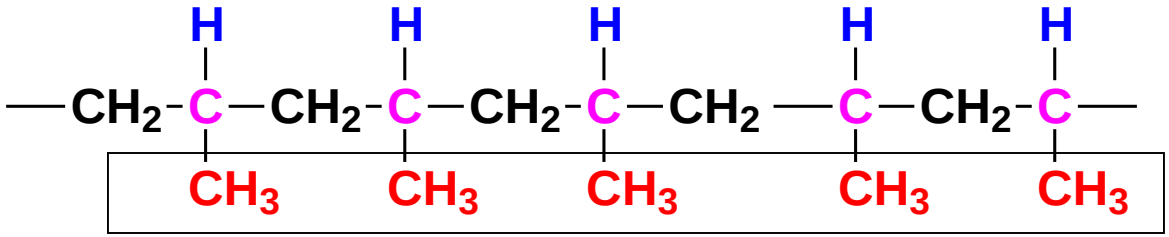
Stereoisomerism or tacticity

- Isotactic
- Syndiotactic
- Atactic



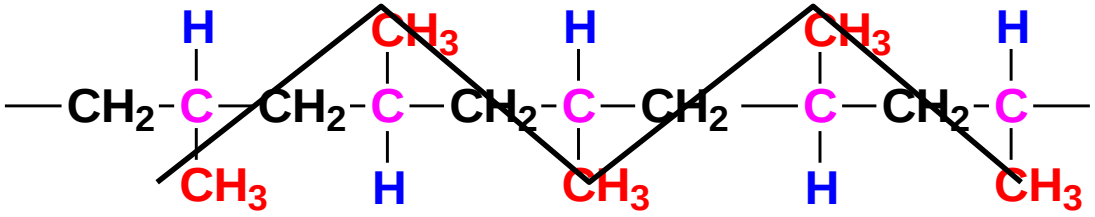
Tacticity- Plane representation of polypropylene polymer

1. Isotactic polymers



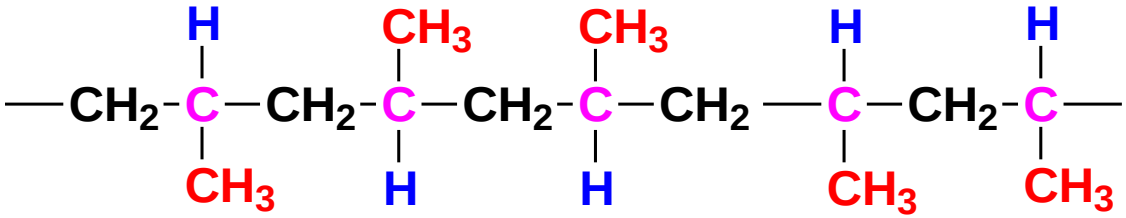
Functional groups on the same side of the main carbon skeleton

2. Syndiotactic polymers



Functional groups arranged in the alternate fashion of the main carbon skeleton

3.Atactic polymers



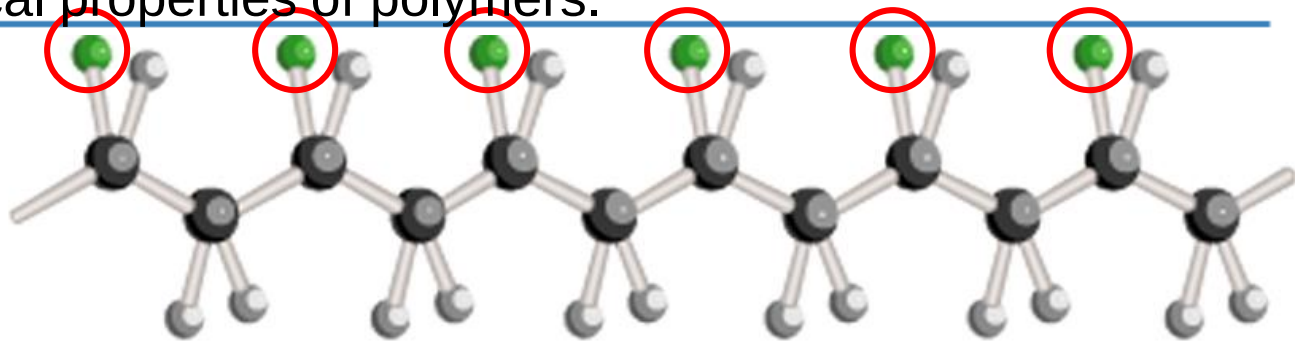
Functional groups arranged in a random manner around the main carbon skeleton

Tacticity : the orientation of monomeric units in a polymer molecule

It affects the physical properties of polymers.

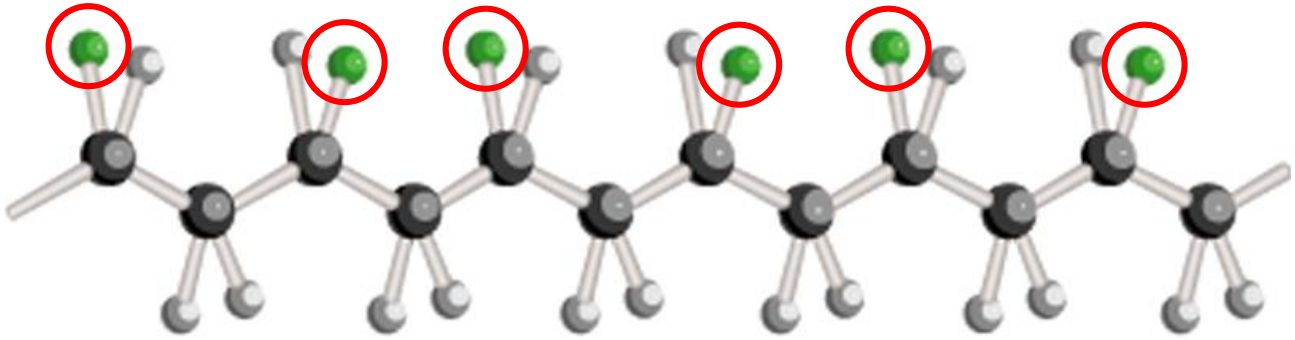
R groups on same side of chain

Isotactic



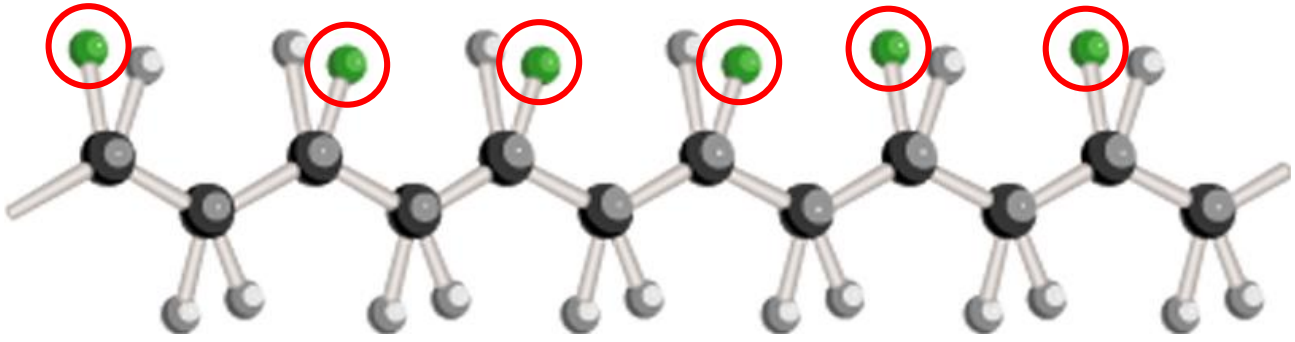
R groups alternate from side to side

Syndiotactic



R groups disposed at random

Atactic



Functionality

The number of bonding sites in a monomer is referred as its functionality

Bifunctional: eg. alkene

Trifunctional: eg. Monomethylsilicon trichloride ($MeSiCl_3$)

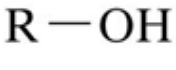
Polyfunctional: eg. Silicon tetrachloride ($SiCl_4$)

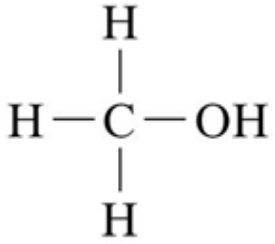
Functionality

the number of reactive sites or bonding sites

Some mono functional hydrocarbons

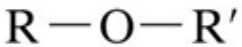
Alcohols

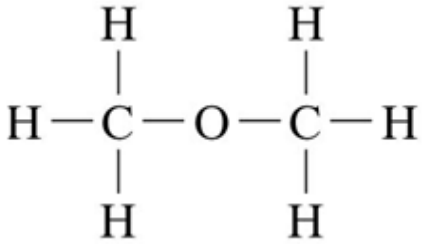




Methyl alcohol

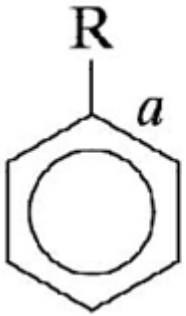
Ethers

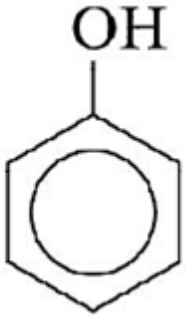




Dimethyl Ether

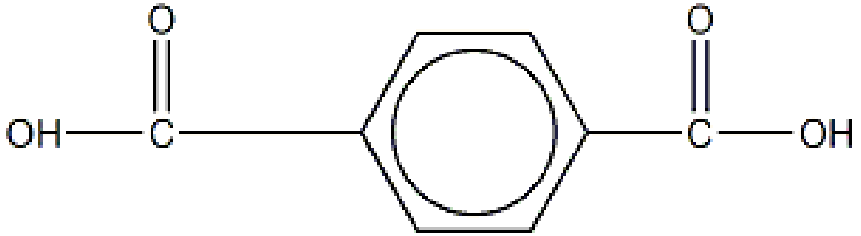
Aromatic hydrocarbons



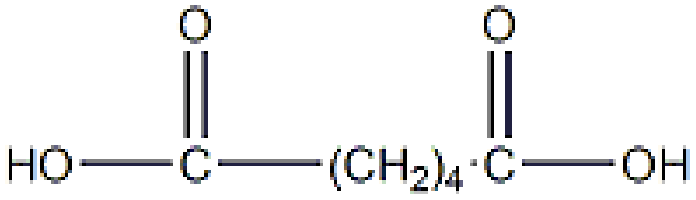


Phenol

Some bi functional hydrocarbons

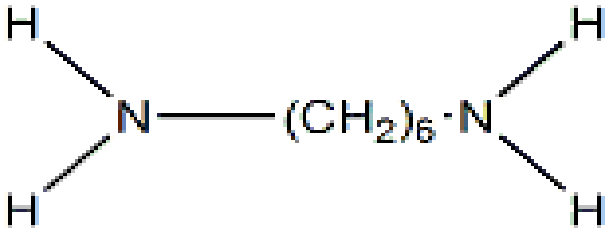


Terephthalic acid



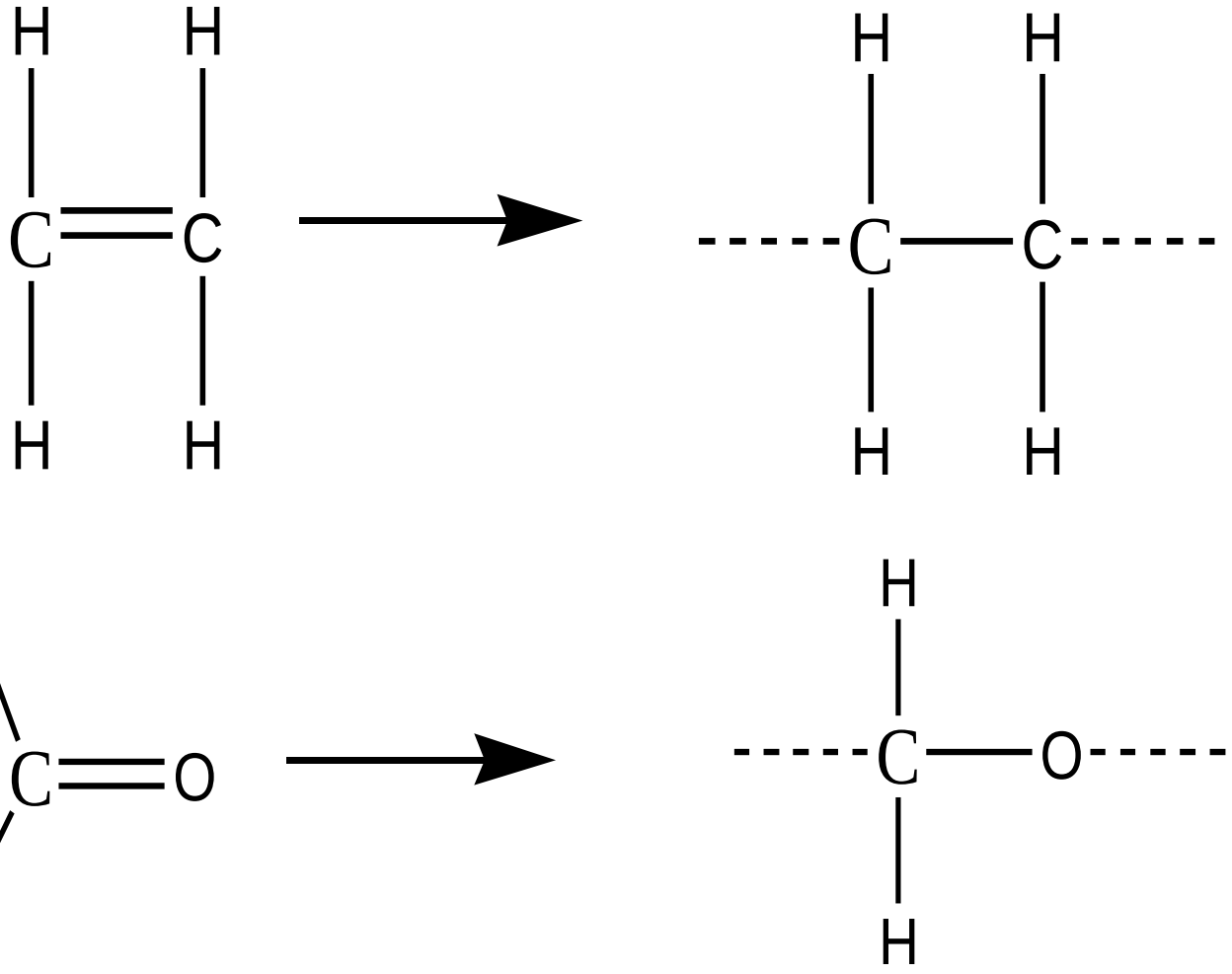
adipic acid (hexanedioic acid)

ethylene glycol



1,6-hexanediamine

Ethylene is considered to be bifunctional

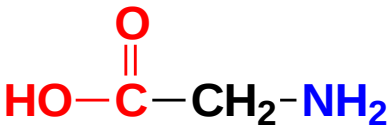


Functionality

The number of reactive sites present in a monomer is called functionality

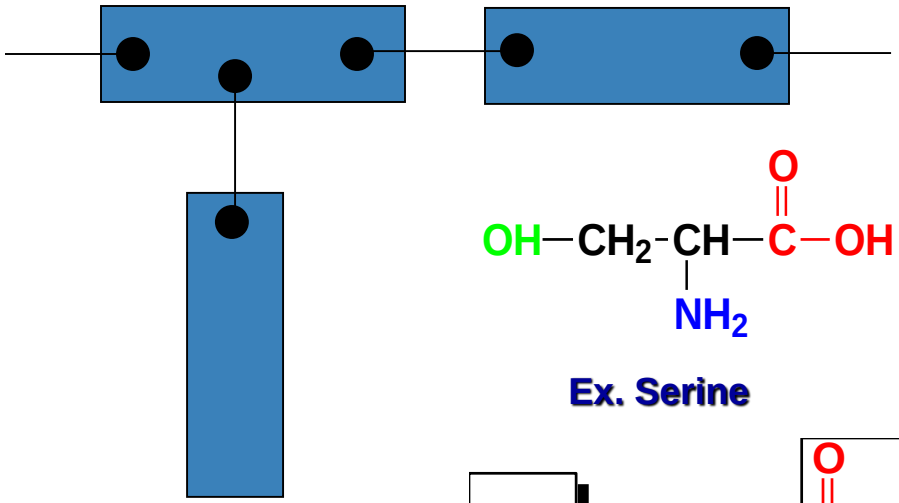
1.

Linear chain polymer is formed if the functionality of the monomer is only two (Bifunctional)

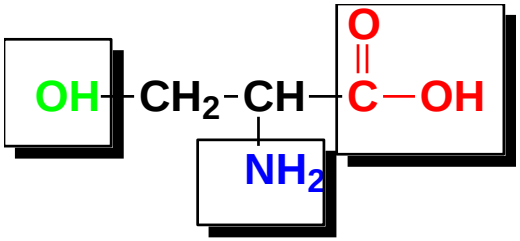


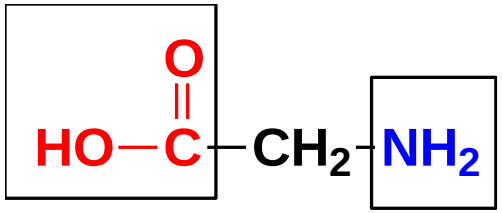
Ex. Glycine

2.



Ex. Serine



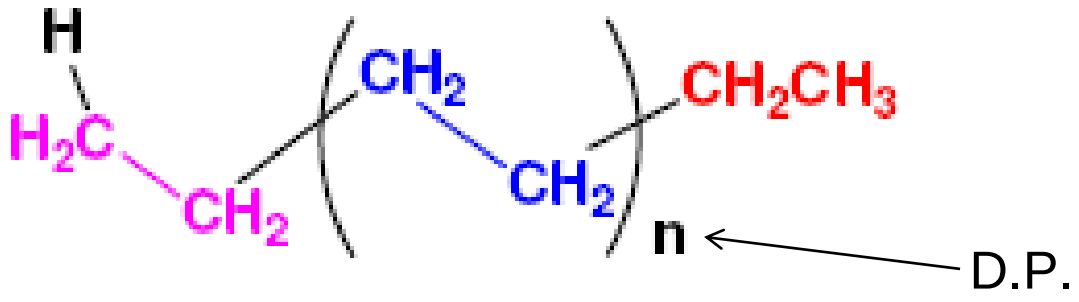


Glycine

Cross linked chain polymer is formed if the functionality of the monomer is more than two (multifunctional)

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

e.g.,

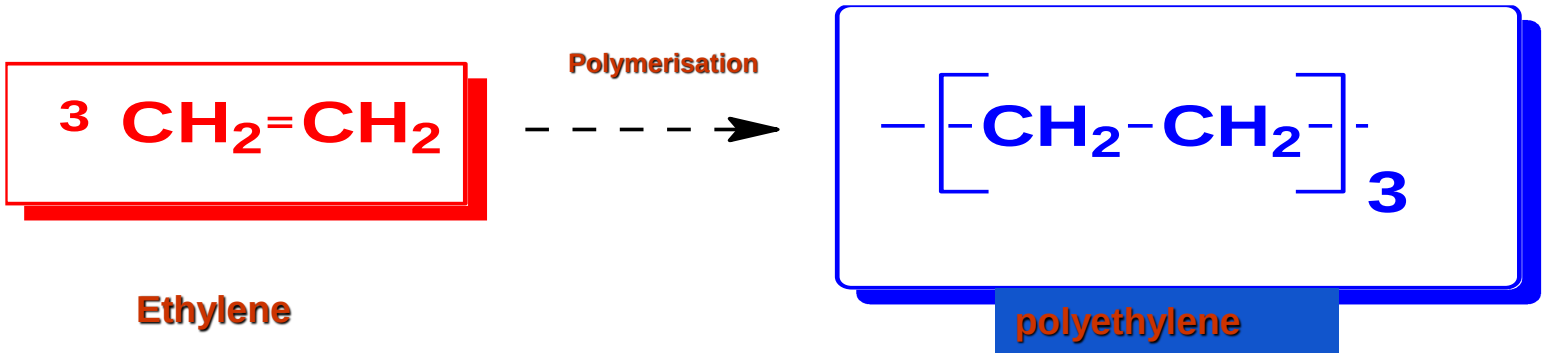


Polymers with high degree of polymerization are called high polymers and these have very high molecular weights (10^4 to 10^6).

Polymers with low degree of polymerization are called oligomers.

Degree of Polymerization (P) = M/m;

Where, M= Mass of Polymer; m = mass of monomeric unit



Degree of polymerisation (P) = 3

Mass of this polymer M = (28 x 3) = 84Da

General method of polymerization

Two major methods generally used for preparing polymers:

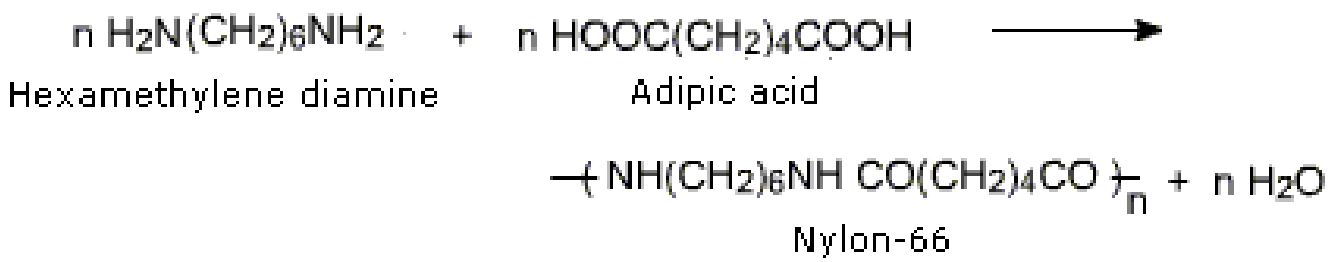
1. Addition polymerization

2. Condensation polymerization

Addition Polymerization
It is a reaction that yields a product, which is an exact multiple of the original monomeric molecule. Such a monomeric molecule usually contains one or more double bonds, which by intermolecular rearrangement may make the molecule bifunctional. The addition polymerization reaction must be instigated by the application of heat, light, pressure or a catalyst for breaking down the double covalent bonds of monomers.

Condensation polymerization
May be defined as a reaction occurring between simple polar-group-containing monomers with the formation of polymer and elimination of small molecules like water, HCl etc.

Examples: Nylon-66, polyester, Bakelite etc.Nylon-66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:

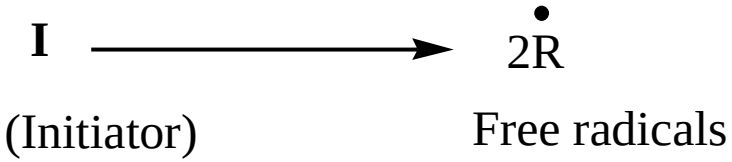


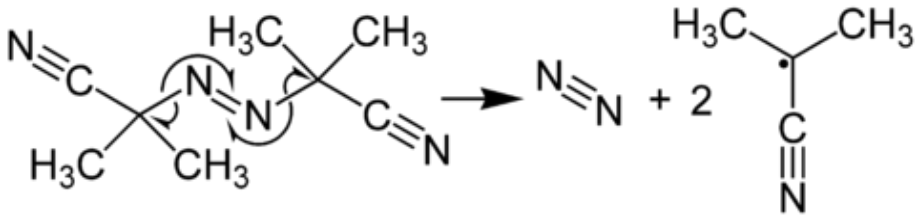
Mechanism of addition polymerization:

1. Free radical polymerization
2. Cationic polymerization
3. Anionic polymerization
4. Coordination polymerization or Ziegler-Natta polymerization

Free redical polymerization mechanism:

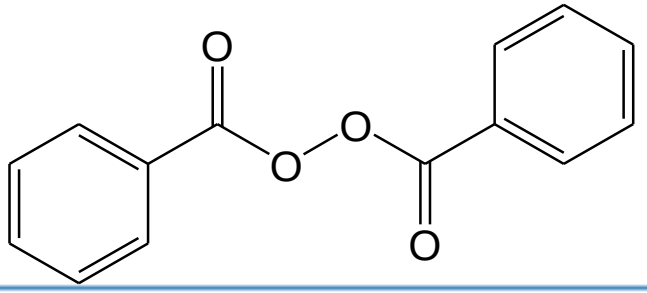
(i) ***Initiation step*** is considered to involve two reactions. The first step is the production of free radicals by **homolytic dissociation** of an initiator to yield pair of radicals.(**benzoylperoxide**, ***tert*-butylperoxide**, **AIBN**)



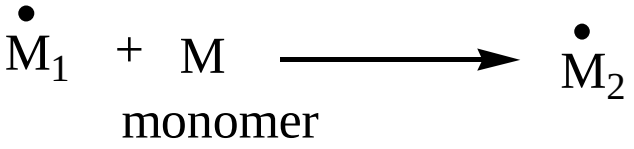


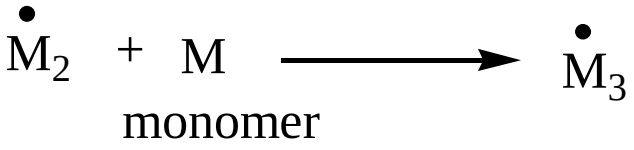
Azobisisobutyronitrile

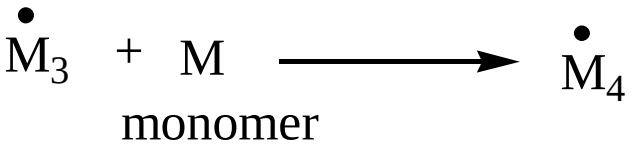
The second part of the initiation steps involves the reaction of this radical with first monomer unit (M) to produce chain initiating species



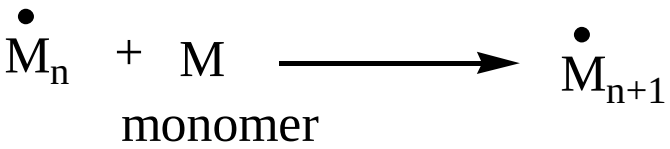
(ii) Propagation step consists of the growth of M_1 free radical by successive reaction of large numbers of monomers molecules







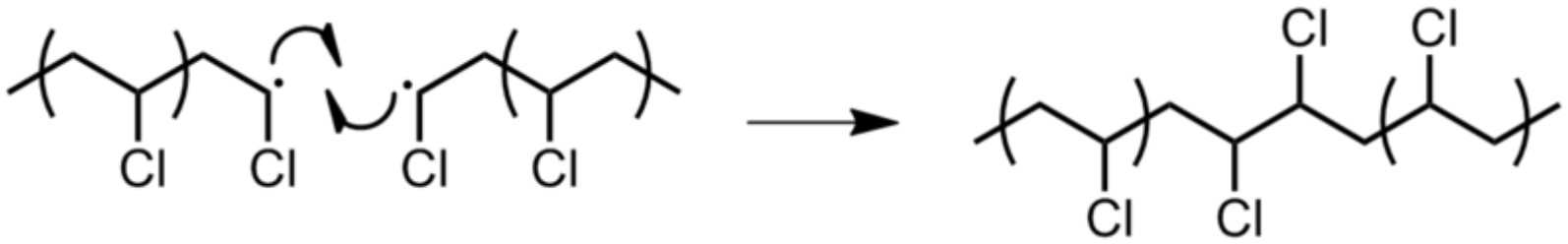
In general



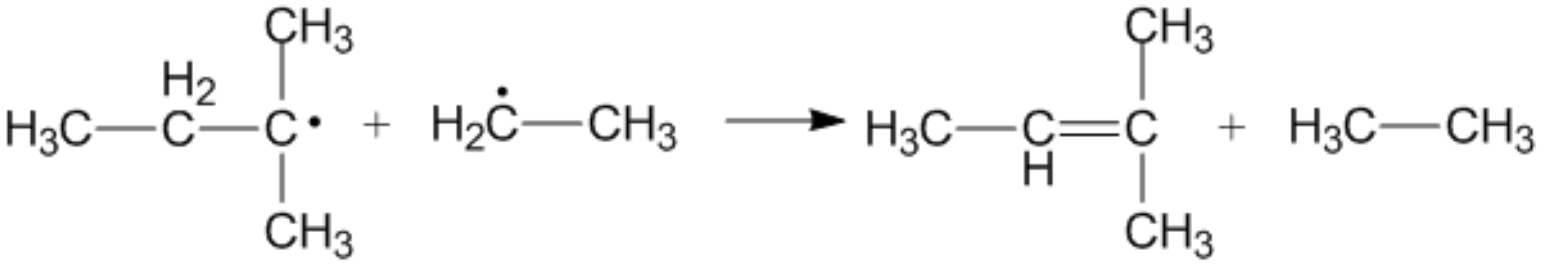
Termination steps

a)Termination by coupling

b) Termination by disproportionation



Termination by coupling



Termination by disproportionation

IONIC CHAIN POLYMERIZATION

Ionic polymerization is more complex than free-radical polymerization

Whereas free radical polymerization is non-specific, the type of ionic polymerization procedure and catalysts depend on the nature of the substituent (R) on the vinyl (ethenyl) monomer.

Cationic initiation is therefore usually limited to the polymerization of monomers where the R group is electron-donating This helps stabilize the delocalization of the positive charge through the p orbitals of the double bond

Anionic initiation, requires the R group to be electron withdrawing in order to promote the formation of a stable carbanion

Using catalyst, not initiator

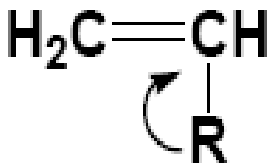
Highest reaction rate

Termination step is just disproportionation

Environment must be pure

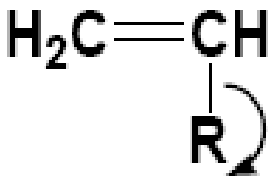
Ionic Polymerization

Cationic



R - Electron donating

Anionic



R - Electron withdrawing

A). Anionic Polymerization

Involves the polymerization of monomers that have strong electron-withdrawing groups, e.g., acrylonitrile, vinyl chloride, methyl methacrylate, etc.

typical catalyst include KNH_2, n-BuLi, and Grignard reagents such as alkyl magnesium bromides

If the monomer has only a weak electron-withdrawing group then a strong base initiator is required, eg, butyllithium; for strong electron-withdrawing groups only a weak base initiator is required, eg, a Grignard reagent.

Steps of polymerization

i) Initiation: KNH_2 initiates the reaction and carbanion is formed

ii) Propagation

iii) Termination

B) Cationic Polymerization

- Involves the polymerization of monomers that have strong electron-donating groups, eg, propylene etc.

- typical initiators (catalysts) are compounds with electron acceptor properties eg. $AlCl_3$, $SnCl_4$, $TiCl_4$, and BF_3

- Steps of polymerization

  i) Initiation : $AlCl_3$ initiates the reaction and carbocation is formed

  ii) Propagation

  iii) Termination

Coordination polymerization (Ziegler-Natta catalysts)

Coordination polymerization is a form of addition polymerization in which monomer adds to a growing macromolecule through an organometallic active center.

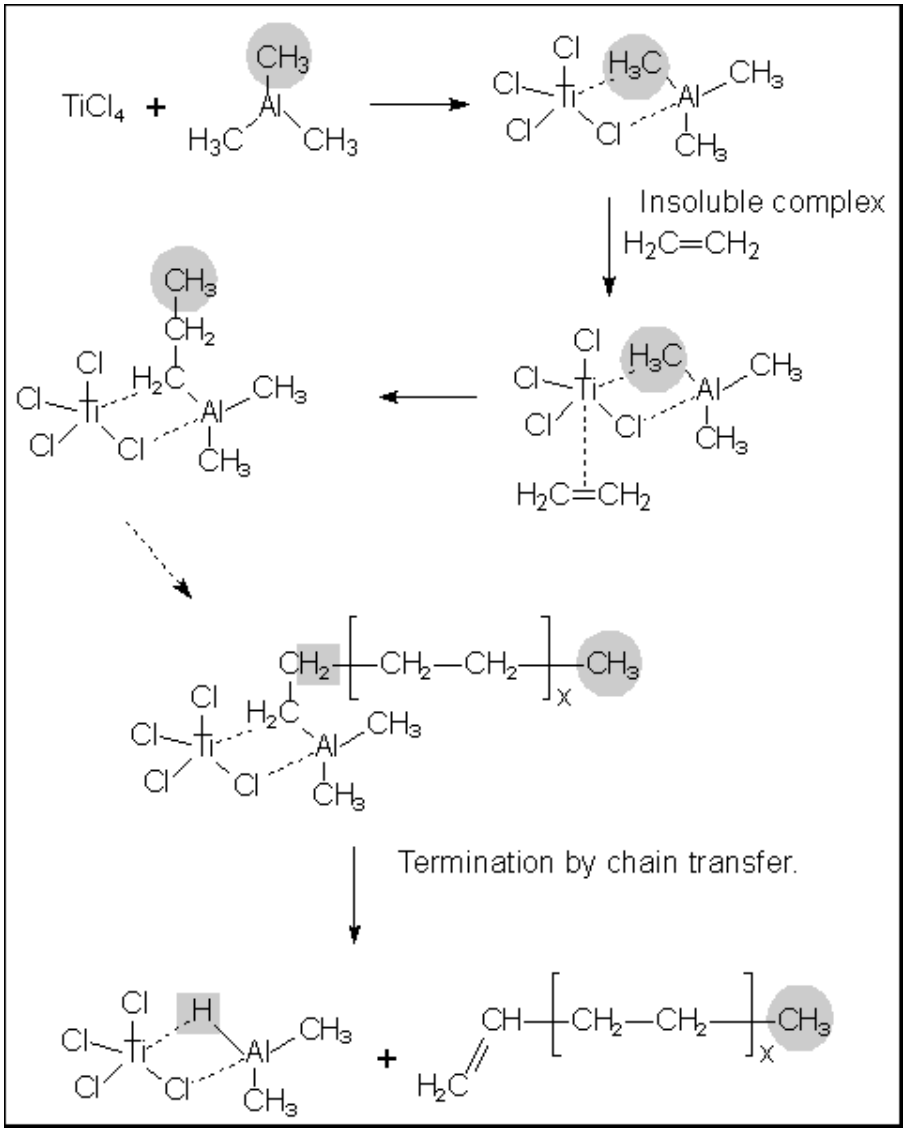
The development of this polymerization technique started in the 1950s with heterogeneous Ziegler-Natta catalysts based on **titanium tetrachloride** and an **aluminium co-catalyst ($TiCl_4$ + R_3Al)**

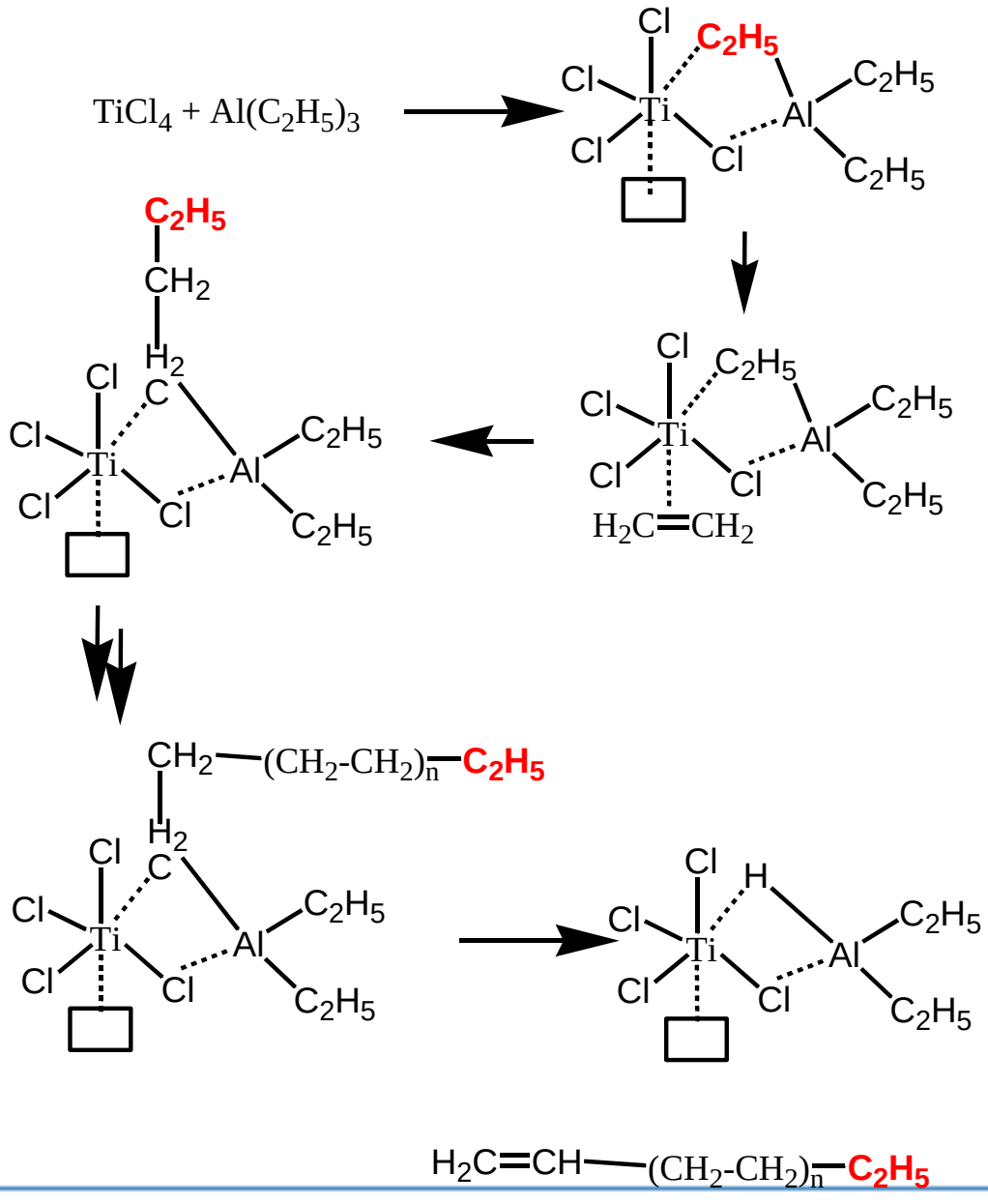
Coordination polymerization has a great impact on the physical properties of vinyl polymers such as polyethylene and polypropylene compared to the same polymers prepared by other techniques such as free radical polymerization.

The polymers tend to be linear and not branched and have much **higher molar mass**. Coordination type polymers are also stereoregular and can **be isotactic or syndiotactic** instead of just **atactic**. This tacticity introduces crystallinity in otherwise amorphous polymers.

From these differences in polymerization type the distinction originates between low-density polyethylene (LDPE), high-density polyethylene (HDPE) .

Mechanism: **Coordination polymerization**




TiCl4 + Al(C2H5)3
Cl
C2H5
Ti
Al
C2H5
CH2
H2
C
H2C=CH2
CH2-(CH2-CH2)n-C2H5
H
H2C=CH-(CH2-CH2)n-C2H5

CONDENSATION POLYMERIZATION

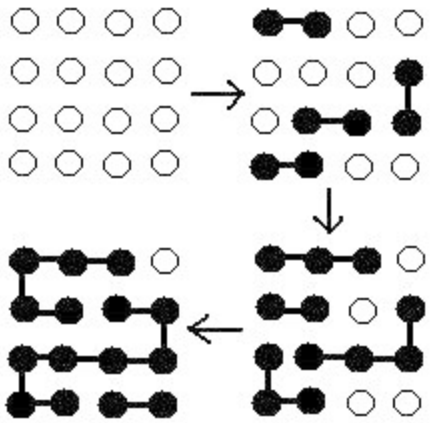
Minumum two functional groups required

Usually linear

Molecular weight increases slowly at low conversion

High extents of reaction are required to obtain high chain length

Step-growth polymerization refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers. Many naturally occurring and some synthetic polymers are produced by step-growth polymerization, e.g. polyesters polyamides, polyurethanes, etc. Due to the nature of the polymerization mechanism, a high extent of reaction is required to achieve high molecular weight. The easiest way to visualize the mechanism of a step-growth polymerization is a group of people reaching out to hold their hands to form a human chain — each person has two hands (= reactive sites). There also is the possibility to have more than two reactive sites on a monomer: In this case branched polymers are produced.



A generic representation of a step-growth polymerization. (Single white dots represent monomers and black chains represent oligomers and polymers)

Differences between step-growth polymerization and chain-growth polymerization

Step-growth polymerization	Chain-growth polymerization
Growth throughout matrix	Growth by addition of monomer only at one end of chain
Rapid loss of monomer early in the reaction	Some monomer remains even at long reaction times
Same mechanism throughout	Different mechanisms operate at different stages of reaction (i.e. Initiation, propagation and termination)
Average molecular weight increases slowly at low conversion and high extents of reaction are required to obtain high chain length	Molar mass of backbone chain increases rapidly at early stage and remains approximately the same throughout the polymerization
Ends remain active (no termination)	Chains not active after termination
No initiator necessary	Initiator required

Glass transition temperature: (Tg)

• At low temperatures, all amorphous polymers are stiff and glassy

• On Warming, polymers soften in a characteristic temperature range known as the glass-rubber transition region.

• The glass transition temperature (Tg), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states.

• Tg constitutes the most important mechanical property for all polymers. In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured.

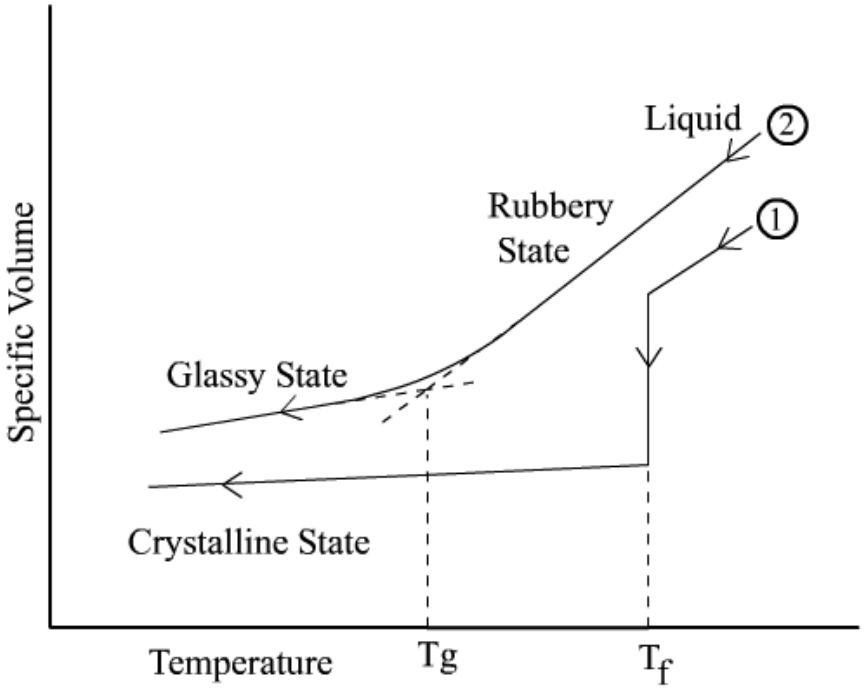
So, the *glass transition temperature* can be defined as the temperature below which an amorphous polymer is brittle, hard and glassy and above the temperature it becomes flexible, soft and rubbery.

Glassy state ⟶ rubber state

(Hard brittle plastic) (soft flexible)

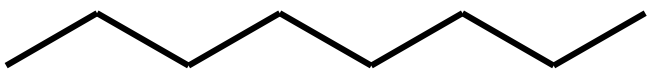
In the glassy state of the polymer, there is neither molecular motion nor segmental motion.

To become more quantitative about the characterization of the liquid-glass transition phenomenon and T_g, we note that on cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point, T_f. Instead, at the glass transition temperature, T_g, there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the figure below. Note that the intersections of the two straight line segments of curve (2) defines the quantity T_g.

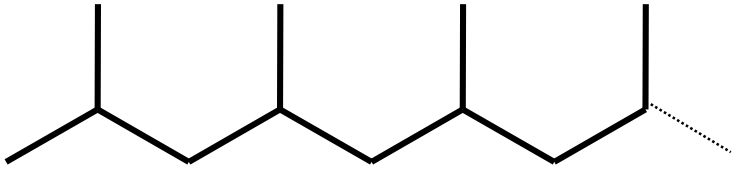


Factors affecting Tg

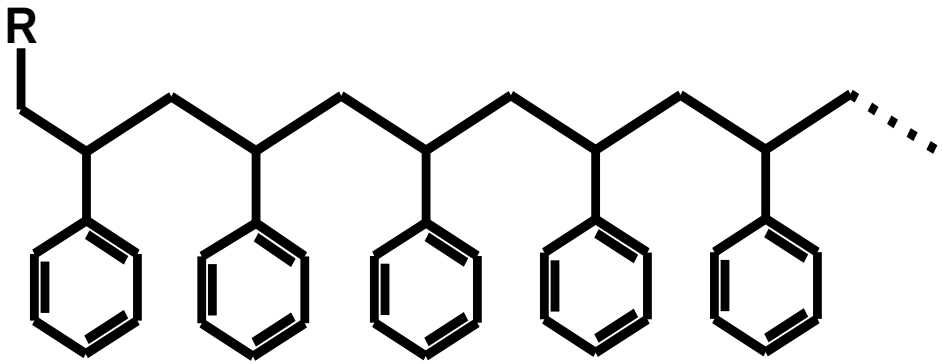
the bulky groups on chain, increases the Tg of the polymer



Polyethylene
Tg = -110 ^{0}C



Polypropylene
Tg = -25 ^{0}C

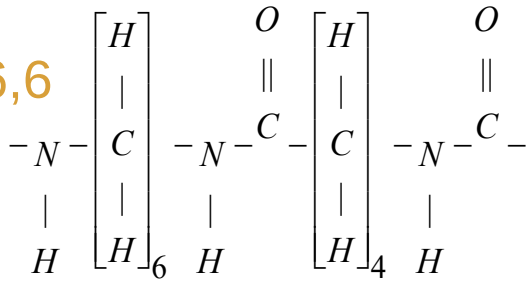


Polystyrene
Tg = 100 ^{0}C

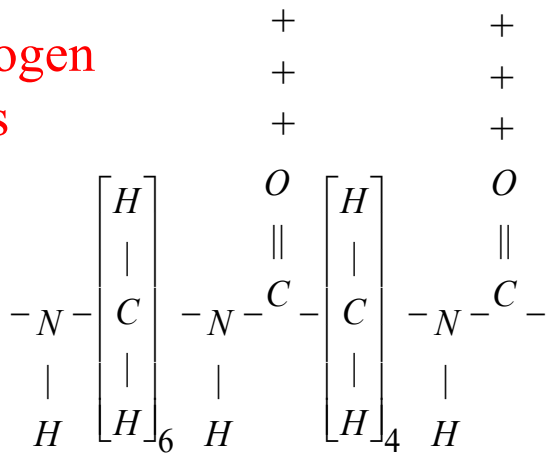
The presence of H-bonds between the polymer molecules increases the Tg

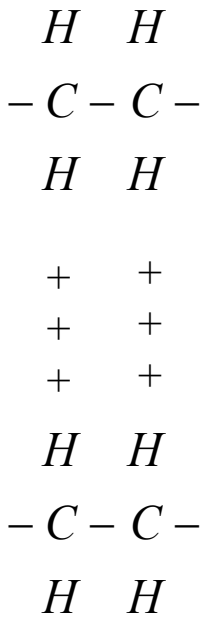
- e.g., the Tg of *nylon 6,6* (Tg = 50 ^{0}C) is higher than *PE* (Tg = -110 ^{0}C)

nylon 6,6



Hydrogen bonds





polyethylene

Van der Waals bonds

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

The Tg of a polymer is influenced by its molecular weight

With increase in molecular mass, the Tg increases

e.g.,

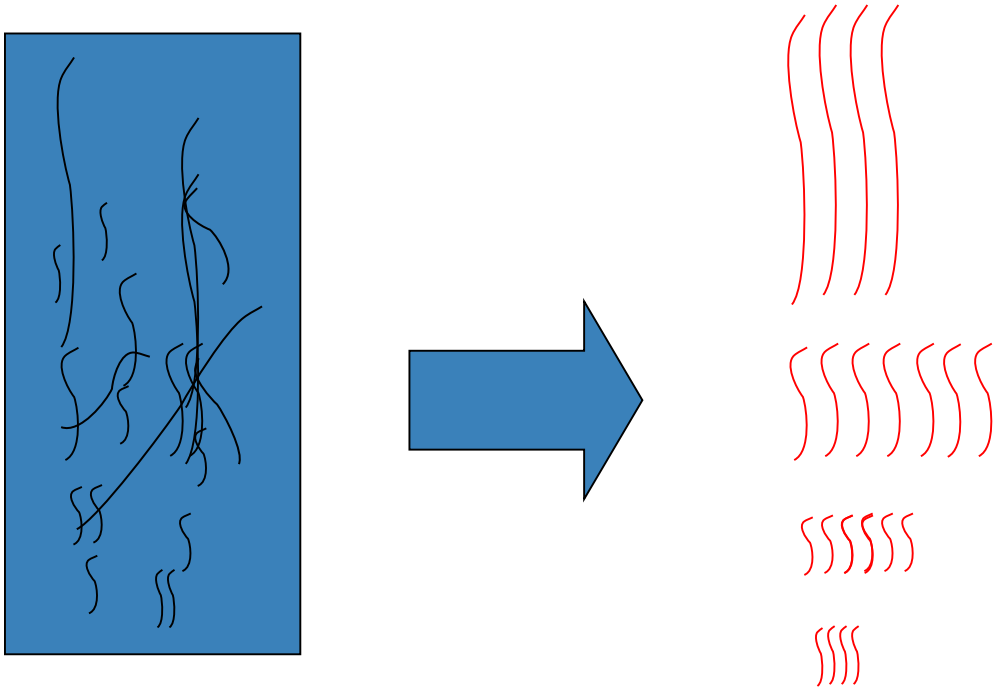
PE (low M_w)	-110 ^{0}C
PE (high M_w)	- 90 ^{0}C

Thus,

1) The presence of bulky side groups increase T_g.
2) Polar side atoms or groups of atoms increase T_g.
3) Double chain bonds and aromatic chain groups which tend to stiffen the molecular backbone increases T_g.
4) Increase in the molecular weight also tends to raise the glass transition temperature.
5) A small amount of branching will tend to lower Tg; on the other hand , a high density of branches reduces chain mobility, and elevates glass transition temperature.

Some Numericals

Molecular Weight of Polymers



The molecular weight of a polymer can only be viewed statistically and expressed as some average of the Mol. Wt.s contributed by the individual molecules that make the sample

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

(i) Number – average

(ii) weight – average

Number average molecular mass of a polymer can be defined as the total mass of all the molecules in a polymer sample divided by the total number of molecules present

The molecular mass of a polymer can use either *number fractions* or the *weight fractions* of the molecules present in the polymer

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

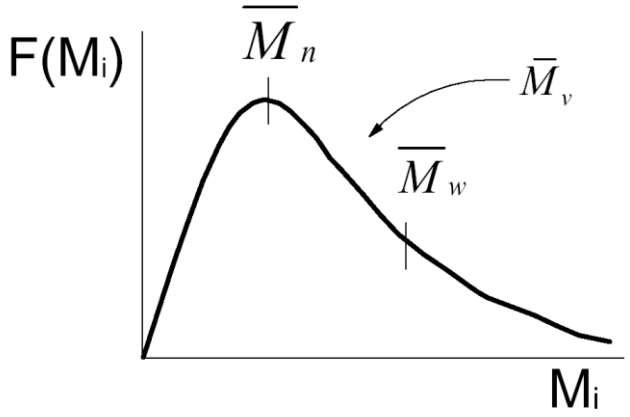
Polymers: Molecular Weight

N_i: no. of molecules with degree of polymerization of i

M_i: molecular weight of i

number average, M_n

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$



- weight average, M_w

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

The dispersity index, or formerly polydispersity index (PDI)= $\mathbf{M_w / M_n}$

Polymers: Molecular Weight

N_i: no. of molecules with degree of polymerization of i

M_i: molecular weight of i

number average, M_n

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\mathbf{N1M1 + N2M2 + N3M3 \ldots}}{\mathbf{N1 + N2 + N3 \ldots}}$$

- weight average, M_w

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\mathbf{N1M1^2 + N2M2^2 + N3M3^2 \ldots}}{\mathbf{N1M1 + N2M2 + N3M3 \ldots}}$$

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

ultra-centrifugal techniques

Numerical

Consider a polymer sample containing 50 molecules of molecular weight 10000, 35 molecules of molecular weight 12000 and 15 molecules of molecular weight 14000. Determine **Number Average Molecular Weight** and **Weight Average Molecular Weight.** If the polymer is **polypropylene,** what will be the **degree of polymerization?**

$$\overline{M_n} = \frac{(50x10000) + (35x\ 12000) + (15x14000)}{(50+35+15)}$$

Ans. =11,300 (Number Average Molecular Weight)

$$\overline{M_w} = \frac{50(10000)^2 + 35(12000)^2 + 15(14000)^2}{(50x10000)+(35x12000)+(15x14000)}$$

Ans. =11,486.7 (Weight Average Molecular Weight)

$$DP = \frac{\overline{M_n}}{\text{Molecular weight of monomer}}$$

Ans. = 269 (DP)

Q 1. A polymer sample consists of 10% by weight of macromolecules of molecular weight 10,000 and 90% by weight of macromolecules with molecular weight 100,000. Calculate $\bar{M}_n$ and $\bar{M}_w$

Solution:

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{N1M1 + N2M2}{N1 + N2} = \frac{W1 + W2}{N1 + N2}$$

If total weight of polymer = 100 gm
Macromolecule (1) = 10 gm = W1
Macromolecule (2) = 90 gm = W2

N1M1 = W1; Thus N1 = W1/M1 = 10/10000
N2M2 = W2; Thus N2 = W2/M2 = 90/100000

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{W1 + W2}{N1 + N2} = \frac{10 + 90}{(10/10^4) + (90/10^5)} = 5.26 \times 10^4$$

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{N1M1^2 + N2M2^2}{N1M1 + N2M2} = \frac{W1M1 + W2M2}{W1 + W2} = \frac{(10 \times 10^4) + (90 \times 10^5)}{(10+90)} = 9.1 \times 10^4$$

Q 2. A polymer mixture is prepared by mixing three polymers: A, B and C having $\bar{M}_n$, $\bar{M}_w$ and weights in mixture as given below:

Polymer	$\bar{M}_n$	$\bar{M}_w$	Wt. in mixture (gm)
A	1.2×10^5	4.5×10^5	200
B	5.6×10^5	8.9×10^5	200
C	10×10^5	10×10^5	100

Find $\bar{M}_n$ and $\bar{M}_w$ of mixture.

Solution:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{N1M1+N2M2+N3M3}{N1+N2+N3} = \frac{W1+W2+W3}{N1+N2+N3} = \frac{200 + 200 + 100}{\frac{200}{1.2\times10^5} + \frac{200}{5.6\times10^5} + \frac{100}{10\times10^5}} = 2.35\times10^5$$

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{W1M1+W2M2+W3M3}{W1+W2+W3} = \frac{(200\times4.5\times10^5) + (200\times8.9\times10^5) + (100\times10\times10^5)}{200 + 200 + 100}$$

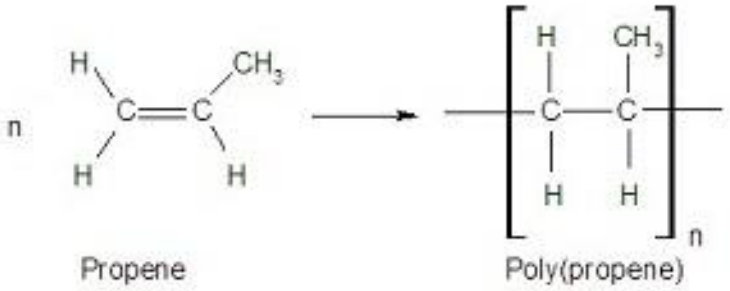
$$= 7.36 \times 10^5$$

Q 3. In a polymer, there are 100 molecules of molecular weight 100, 200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000. Find $\bar{M}_n$, $\bar{M}_w$ and PDI

PDI = Polydispersity index

Q 4. 42 gm of propene was polymerized by radical polymerization process and $\overline{DP}$ was found to be 1000. Calculate the number of molecules of PP produced.

Solution:



MW = 42

No of moles of Propene = Wt of Propene/MW of Propene

No of moles of Propene = 42 / 42 = 1

No of molecules in 1 mole of Propene = 1 x Avogadro Number

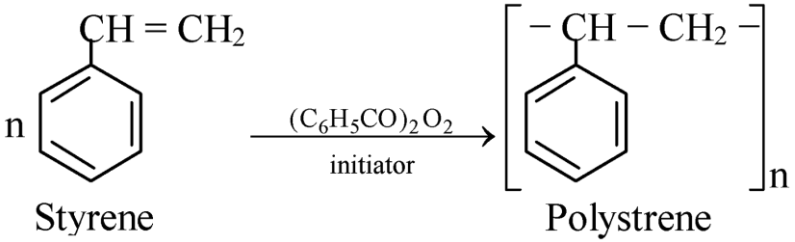
No of molecules in 1 mole of Propene = 1 x 6.023 x 10^{23} = 6.023 x 10^{23}

No of PP molecules (Polymer) = No of Propene molecules (Monomer) / DP

No of PP molecules (Polymer) = 6.023 x 10^{23} / 1000 = 6.023 x 10^{20} molecules

Q 5. The $\bar{M}_n$ of a polystyrene is 10^5 gm/mol. Find its $\overline{DP_n}$

Solution:



MW = 104 **MW = 10^5**

DP_n = MW of Polymer / MW of Monomer

DP_n = 10^5 / 104 = 961.54

Q 6. Find $\bar{M}_w$ for PP given its degree of polymerization as 10,000.

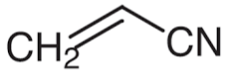
Q7. Which process is performed to improve the properties of the natural rubber? What are the structural changes happened in the process? Explain with diagram/structure.

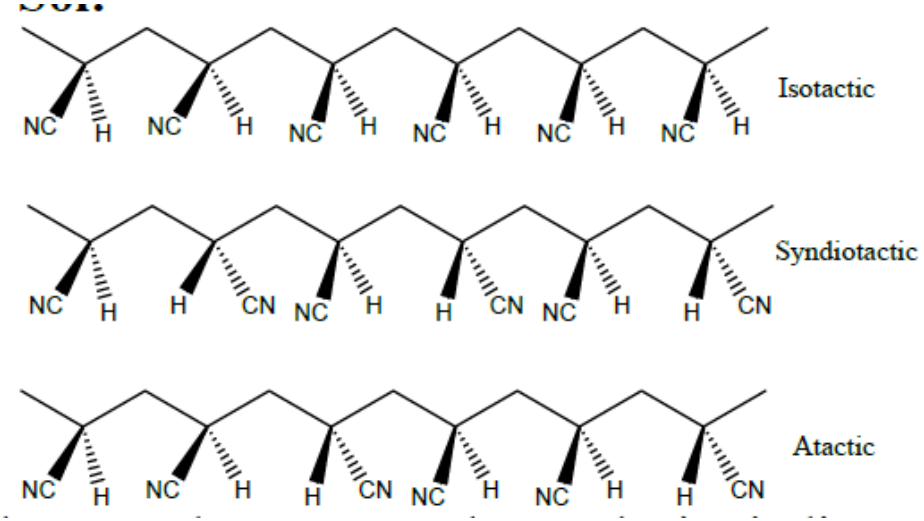
Solution

Vulcanization process.

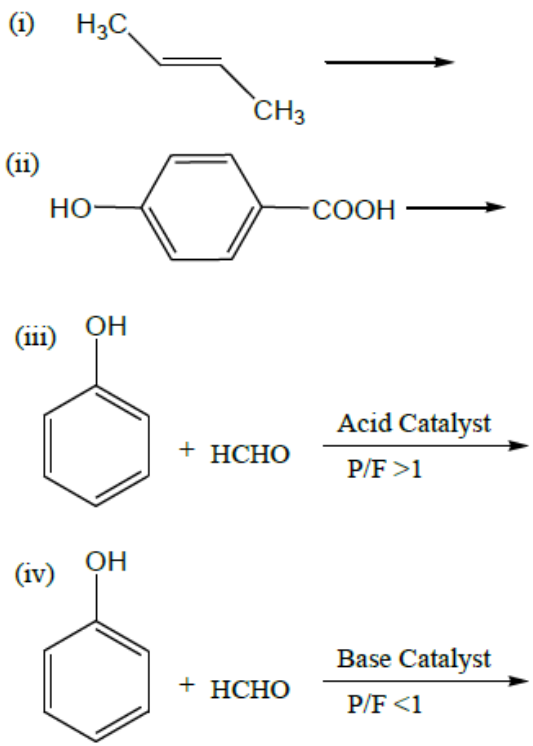
Q8. Draw the different structures of the polyacrylonitrile based on tacticity of the polymer.

Solution

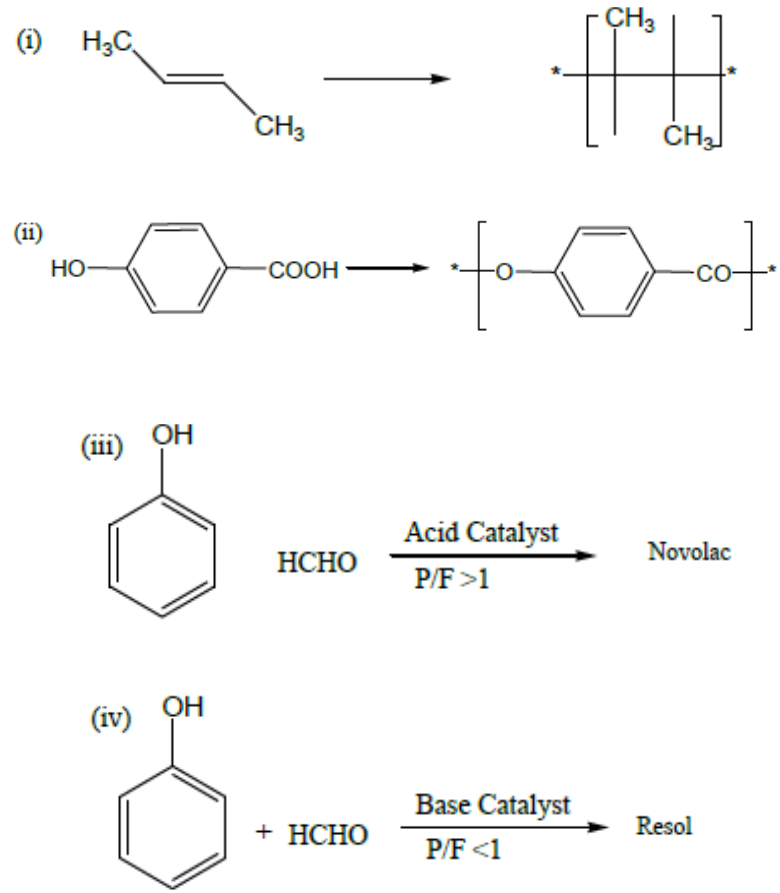




Q9. Predict the polymer product from the following:



Solution



Q10. In 10 g of a PVC sample (M_w= 100,000; Mn= 70,000), you add 20 g of another PVC sample with M_w 60,000, PDI=3. What will be the Mn of the new polymer mixture?

Solution

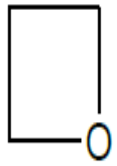
M_n = 26,250

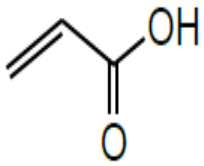
Q11. Justify /criticize the statement with reason:
(i) Methane can be polymerized
(ii) Methanol cannot be polymerized

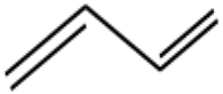
Solution

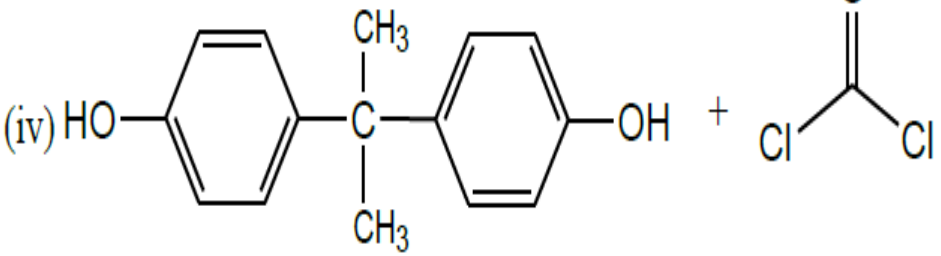
(i) Methane (CH_4) is without any functionality, so it cant **polymerize**.
(ii) Methanol cannot be polymerized, True, Reason, monofunctional.

Q12. Draw the repeat unit of the polymer that would be obtained in the polymerization of the following monomers.

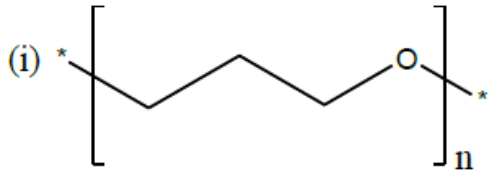
(i) 

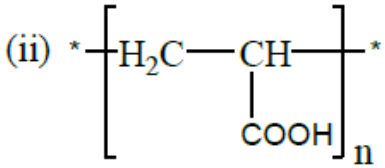
(ii) 

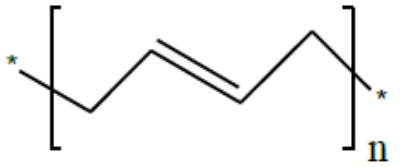
(iii) 

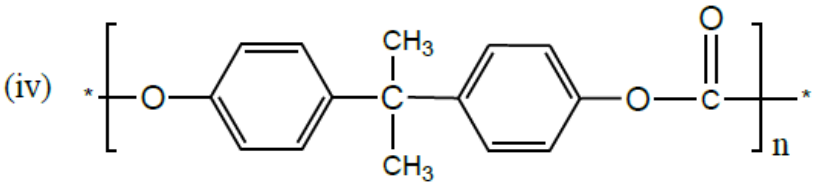
(iv) 

Solution

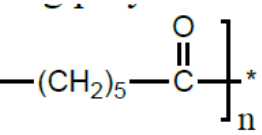
(i) 

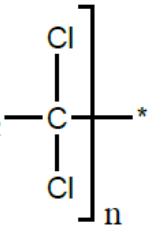
(ii) 

(iii) 

(iv) 

Q13. What is the no. average degree of polymerization (DP) of each of the following polymers with Mn 254,000?.

(i) 

(ii) 

Solution

(i) Mol. Wt. of repeating unit= 113.16; DP= 2244.6 (= ~2245)

(ii) Mol. Wt. of repeating unit= 96.93; DP: 2620.44 (= ~2620)

Q14. Write the name and draw the structure of polymer used for:
(a) Making the most chemical resistant reaction vessel;
(b) Making fiber.?

Solution

(a) Teflon, structure required to be mentioned
(b) Nylon , structure required to be mentioned

Q15. (i) Arrange the following polymers according to their T_g (from the lowest T_g to the highest T_g).

(a) Polystyrene (b) polypropylene and (c) polyvinyl chloride

Also justify your answer

Solution

Sol: Polypropylene(lowest) < polyvinyl chloride < polystyrene

Justification: increased intermolecular forces

Q16. Polyvinylchloride was prepared in presence of (i) peroxide initiator and (ii) $TiCl_4$-$Al(C_2H_5)_3$ catalyst. Describe the mechanism for each polymerization reaction and explain the tacticity of polymers formed in both the cases.

Solution

(i) Free radical mechanism (ii) Mechanism using Ziegler-Natta catalyst Tacticity (i) atactic (ii) syndiotactic and isotactic

Q17. How are polymers classified on the basis of mechanism of polymerization? Name and give structures of polymers formed by the following:
(i) Butadiene + acrylonitrile
(ii) Hexamethylene diamine + adipic acid
(iii) Caprolactam

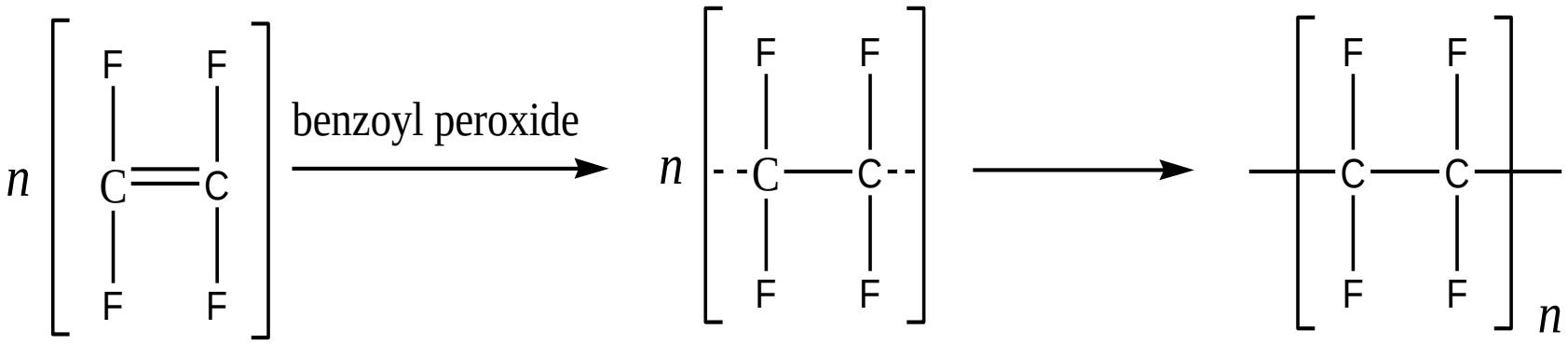
Solution

Polymer classified : (I) Addition and (II) condensation.
(i) Nitrile rubber or Buna-N rubber with structure
(ii) Nylon 6:6 with structure
(iii) Nylon 6 with structure

A polymer sample analysis indicated presence of **20% (by weight)** of macromolecules of **molecular weight 2000**, **30% (by weight)** of macromolecules of **molecular weight 3000** and **50% (by weight)** of macromolecules of **molecular weight 5000**. Calculate the number average and weight average molecular weight of the sample.

162 gram of poly 1,3-butadiene was treated with sulphur (S) to get a modified polymer. Calculate the amount of sulphur required to get the modified polymer. **(Atomic weight of S is 32)**

Polytetrafluoroethylene (TEFLON) or FLUON (PTFE)



Tetrafluoro ethene

Polytetrafluoroethene (PTFE)

Properties of TEFLON:

- They are extreme tough, high softening point, exceptionally high chemical-resistances towards all chemicals, high density, waxy touch.
- It can be punched, machined and drilled

Uses

- As an insulating materials (for motors, transformers, cables, wires, fitting)
- For making gaskets, packing, pump parts, tank, chemical-carrying pipe lines, tubing
- For coating
- In non-lubricating bearing and non-sticking stop-cocks.

Nylon: A man-made polymer

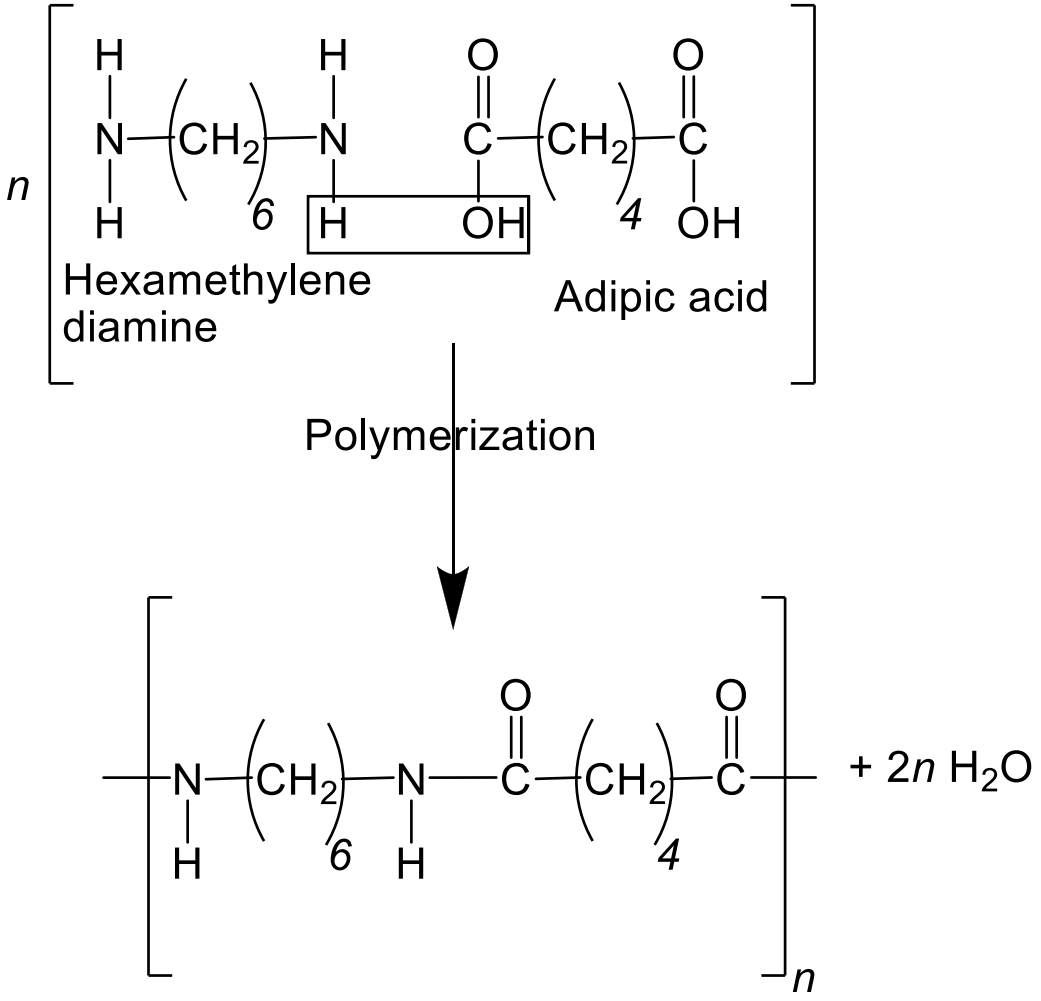
Nylon is used in clothes, shoes, jackets, belts, Tires, ropes and various accessories.

Polyamides are synthetic polymers, which have recurring amide groups. ***Nylons***, used mostly for making fibers, belong to ***polyamides***.

Nylon 6:6
Nylon 6
Nylon 11
Nylon 6:10

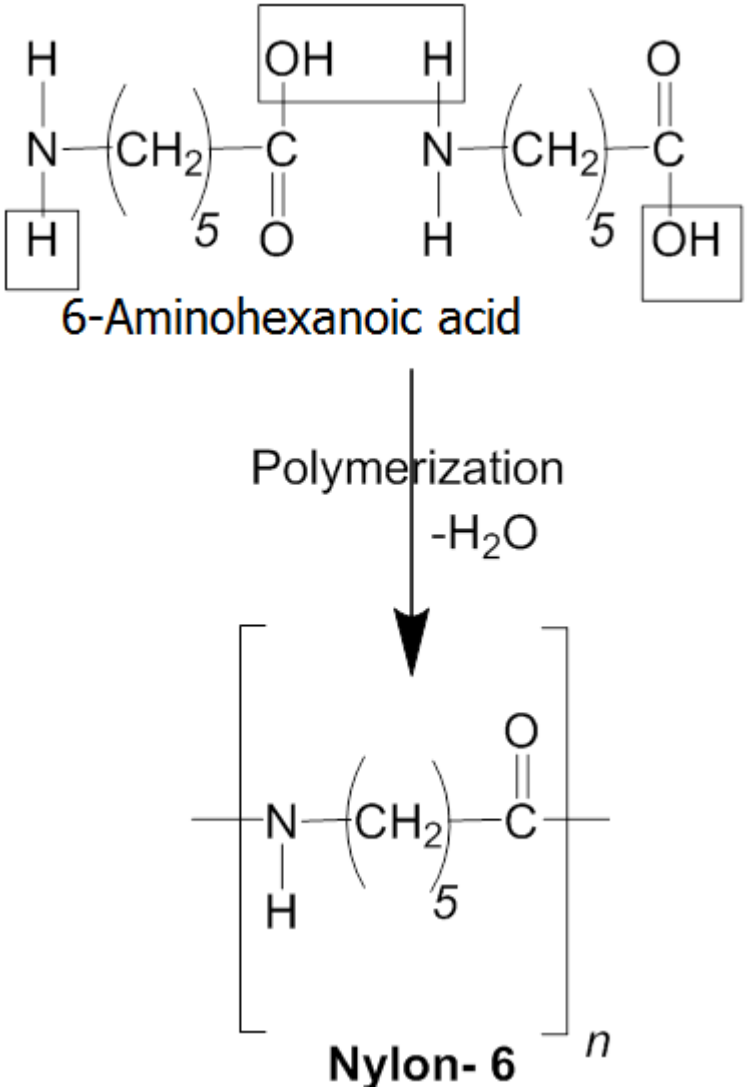
Nylon 6:6

Nylon 6:6 is obtained by the polymerization of adipic acid with hexamethylene diamine.

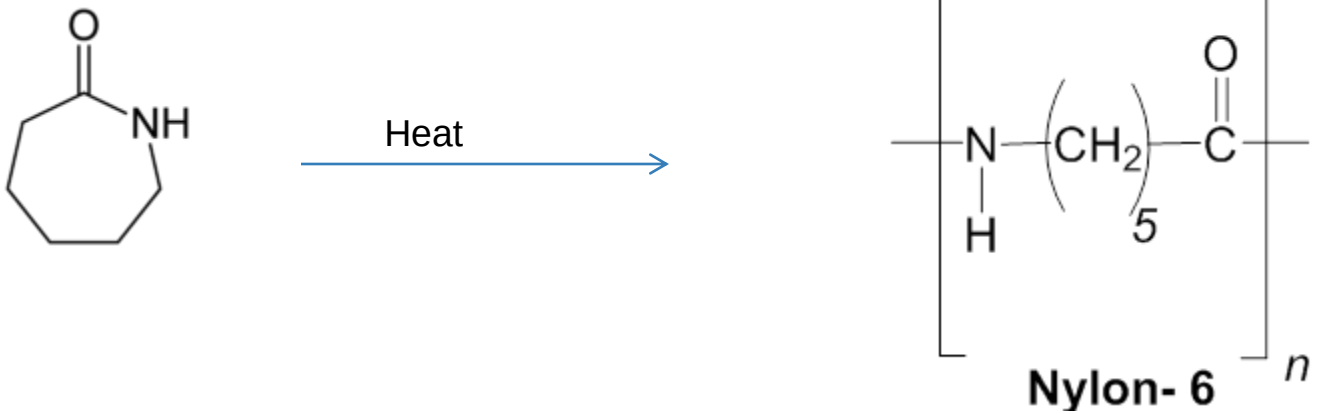


Nylon 6: Nylon-6 is produced by the following two methods:

1. Self-condensation of 6-aminohexanoic acid (ε-aminocaproic acid)

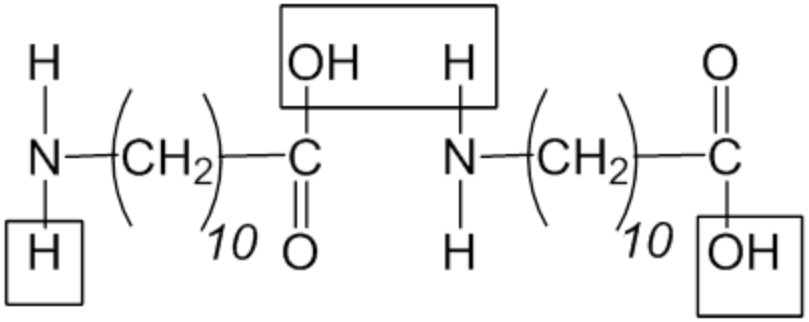


2. Ring opening polymerization of a caprolactum:



Nylon-11

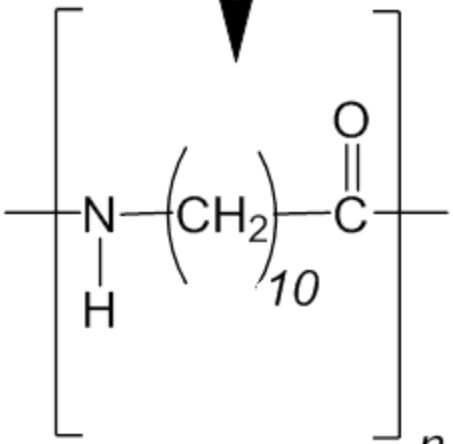
Nylon-11 is made by self condensation of 11-aminoundecanoic acid.



11-Amino undecanoic acid

Polymerization

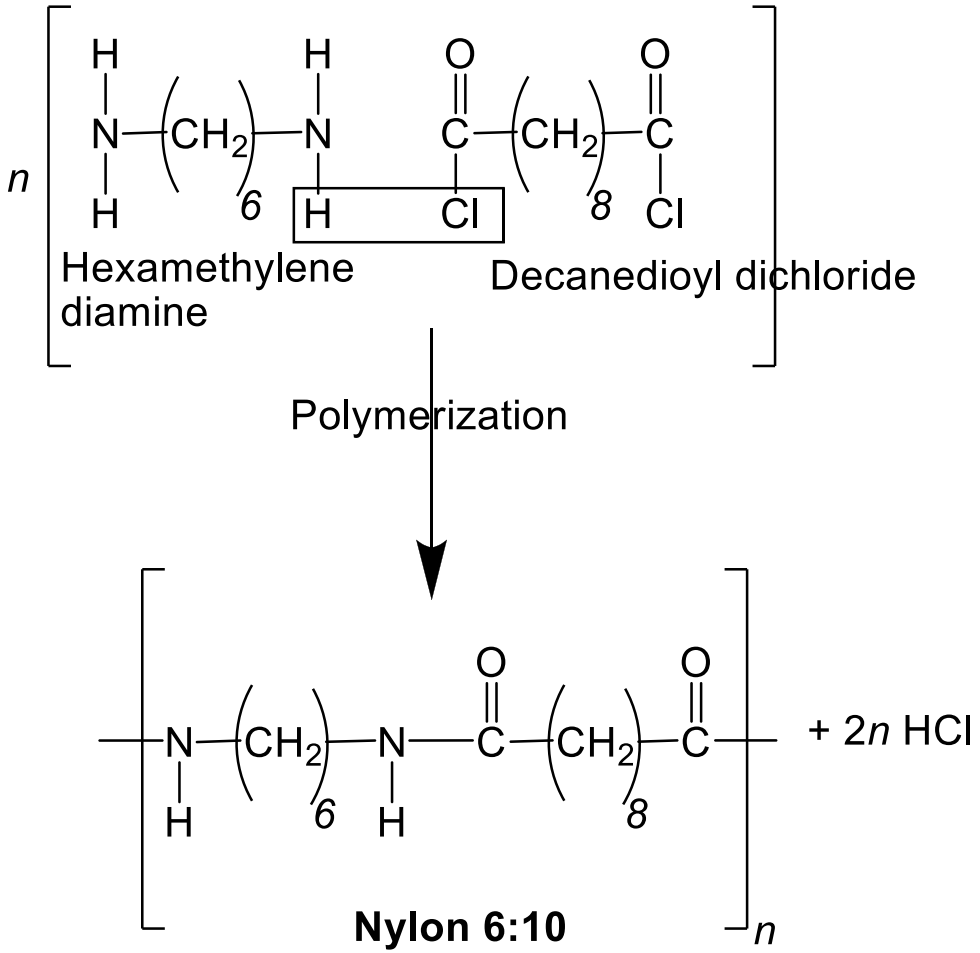
$-H_2O$



Nylon- 11

Nylon 6:10

Nylon 6:10 is obtained by the polymerization of Decanedioyl dichloride with hexamethylene diamine.



Properties of Nylon:

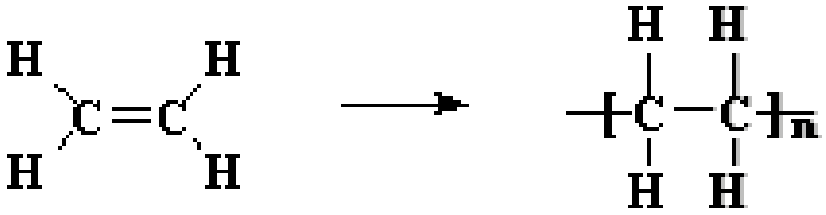
1. One of the very strong fibers. Extremely resistant to abrasion and flexing.
2. The specific gravity is 1.14 Very light, i.e., 80% of that of silk fibers, and 70% of that of cotton fibers.
3. Since nylon fibers absorb little water even though they are wetted., they dry fast and simple in laundering.
4. Excellent in elasticity and resistant to wrinkle.
5. Resistant to chemicals and oil. Non-attackable by sea water.
7. Non-attackable by molds and insects.

Uses:

1. Nylon-6:6 is primarily used for fibers, which find use in making socks, under-garments, dresses, carpets etc.
2. Nylon -6 and nylon-11 are mainly used for moulding purposes for gears, bearings etc. Nylon bearing and gears work quietly without any lubrication.
3. They are also used for making filaments for ropes, bristles for tooth brushes and films, tyre-cords etc.

Polyethylene (PE)

Polyethylene (PE)is obtained by polymerization of ethylene.



Properties:

1) Polyethylene is a rigid , waxy, white translucent, non polar material.
2) Polyethylene exhibits considerable chemical resistance to strong acids, alkalis and salt solutions at room temperature.
3) It is good insulator of electricity.
4) It is swollen and permeable to most oils and solvents.

Low-density polyethylene (LDPE)

Low-density polyethylene (LDPE) is a linear polymer with branching. It is manufactured under high pressure (1000-3000 atm) and in the temperature range of 80-350°C using initiators such as benzoyl peroxide or oxygen.
Method: free radical polymerization.

Properties of LDPE

1)LDPE is defined by a density range of 0.910–0.925 g/cm^3.
2) It is not reactive at room temperatures, except by strong oxidizing agents, and some solvents cause swelling.
3)It can withstand temperatures of 80 °C continuously and 95 °C for a short time.
4)Made in translucent or opaque variations, it is quite flexible, and tough but breakable.
5) LDPE has more branching than HDPE.
6)Since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower. LDPE contains the chemical elements carbon and hydrogen.

Uses of LDPE

LDPE is widely used for manufacturing various containers, dispensing bottles, wash bottles, tubing, plastic bags for computer components, and various molded laboratory equipment. Its most common use is in plastic bags. Other products made from it include:

1)Trays and general purpose containers.
2)Corrosion-resistant work surfaces.
3)Parts that require flexibility, for which it serves very well
4)Juice and milk cartons are made of liquid packaging board, a laminate of paperboard and LDPE (as the water-proof inner and outer layer), and often with of a layer of aluminum foil (thus becoming aseptic packaging)
5) Parts of computer hardware, such as hard disk drives, screen cards, and optical disc drives

High-density polyethylene (HDPE)

High-density polyethylene (HDPE) is a linear polymer with little or no branching. It is manufactured under low pressure (1000-3000 atm) and below 100°C using Ziegler Natta catalyst (Et_3Al and $TiCl_4$) by coordination polymerization or using metal oxide catalyst by Phillips process.

Properties of HDPE

1)HDPE is known for its large strength to density ratio.
2)The mass density of high-density polyethylene can range from 0.941 to 0.97 g/cm^3.
3) Although the density of HDPE is only marginally higher than that of low-density polyethylene, HDPE has little branching, giving it stronger intermolecular forces and tensile strength than LDPE.The difference in strength exceeds the difference in density, giving HDPE a higher specific strength.
4) It is also harder and more opaque and can withstand somewhat higher temperatures (120 °C/ 248 °F for short periods, 110 °C /230 °F continuously). High-density polyethylene, unlike polypropylene, cannot withstand normally required autoclaving conditions. The lack of branching is ensured by an appropriate choice of catalyst (e.g., Ziegler-Natta catalysts) and reaction conditions.

HDPE is resistant to many different solvents and has a wide variety of applications, including:

3-D printer filament
Banners
Bottle caps
Chemical resistant piping systems
Food storage containers
Fuel tanks for vehicles
Electrical and plumbing boxes
Folding chairs and tables

P – F Resins

These are formed by condensation polymerization and are thermosetting polymers

There are two important commercial PF resins: Novolacs and Resoles

Both novolacs and resoles are linear, low molecular weight, soluble and fusible prepolymers

The nature of the product formed depends largely on the molar ratio of phenol to formaldehyde and also on the nature of the catalyst

During moulding operations, these two undergo extensive branching leading to the formation of highly cross linked, insoluble, hard, rigid and infusible products

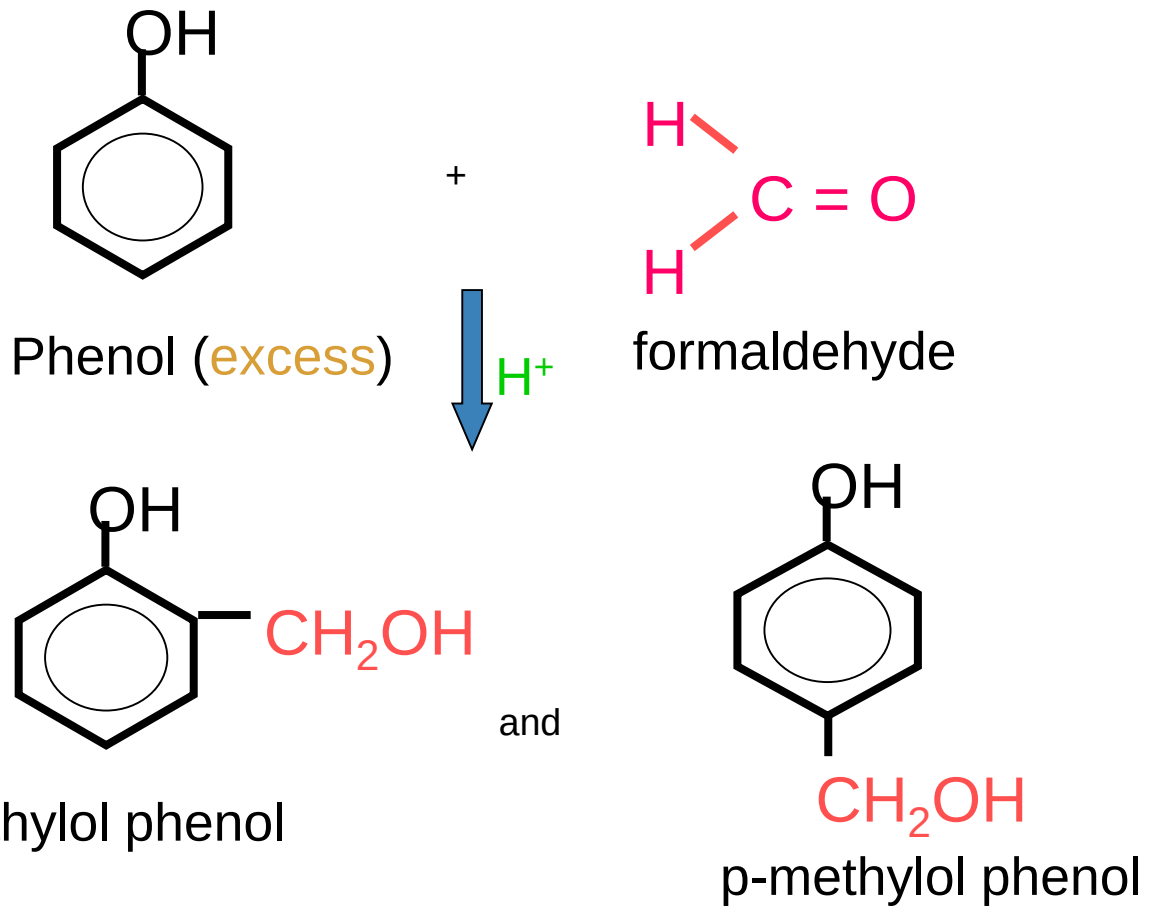
The phenol ring has three potential reactive sites while the formaldehyde has two reactive sites

The polycondensation reaction between these two are catalyzed by either acids or alkalies

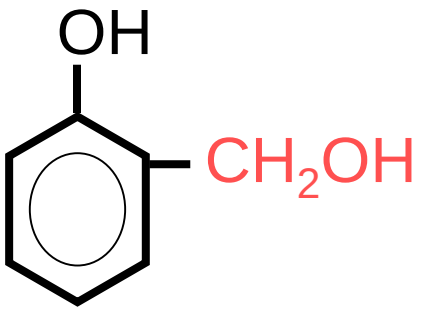
Novolacs

When P/F molar ratio is > 1 and the catalyst used is an acid, low mol. wt. polymers formed are called Novolacs

The first step in the reaction is the addition of formaldehyde to phenol to form *ortho* or *para* methylol phenols

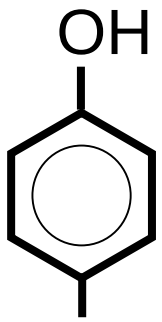


These methylol phenols condense rapidly to form Novolacs

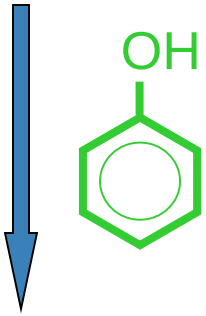


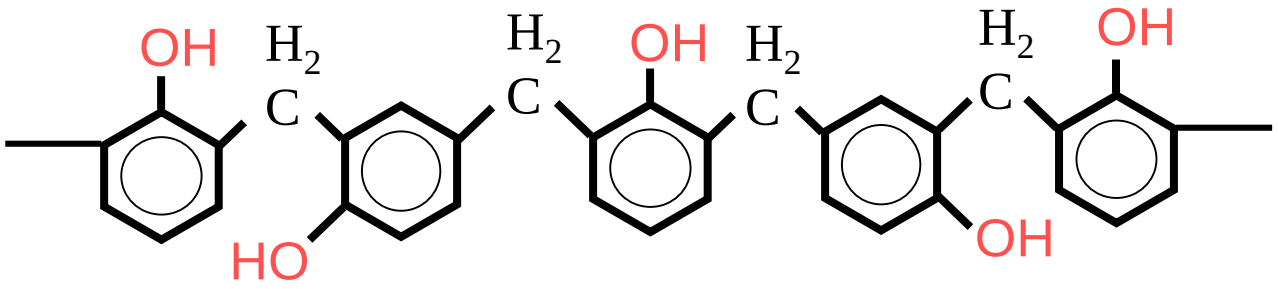
o-methylol phenol

or



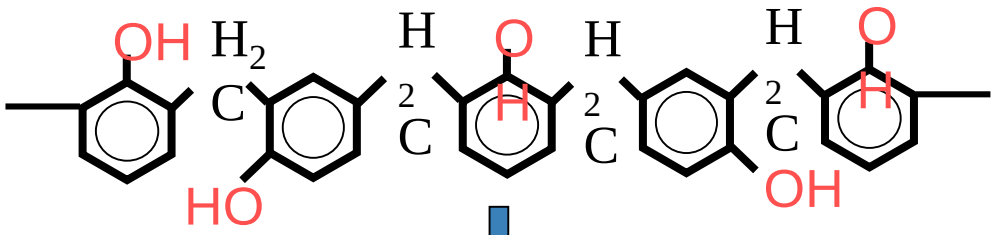
p-methylol phenol





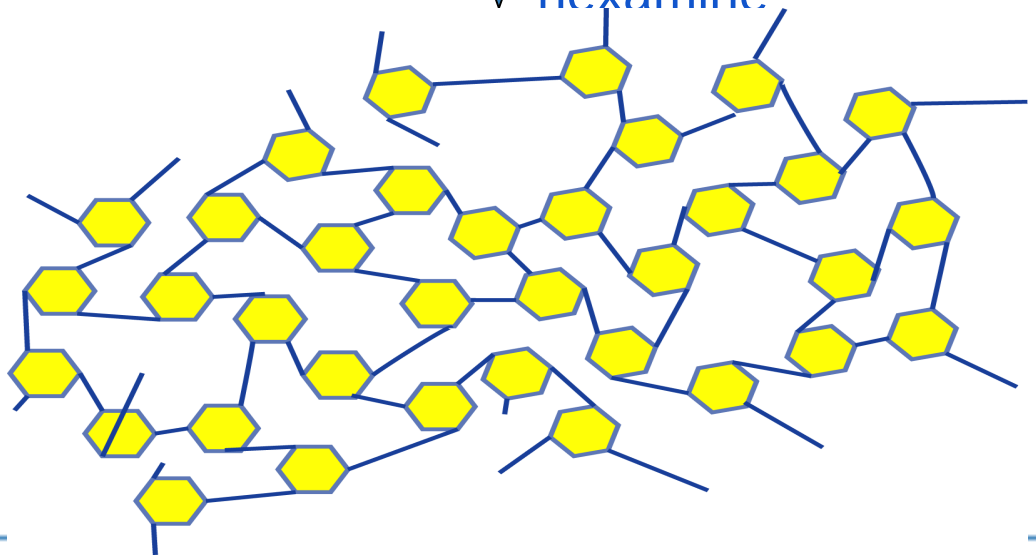
Novolacs

These novolacs are linear and low mol. wt. polymers. They are soluble and fusible. About 5 – 6 phenol rings per molecule are linked through methylene bridges
Since they contain no active methylol groups, they themselves do not undergo cross linking. However, when heated with formaldehyde or hexamine, they undergo extensive cross linking, resulting in the formation of infusible, insoluble, hard and rigid thermosetting product



Novolacs (prepolymer)

Curing with Formaldehyde or hexamine



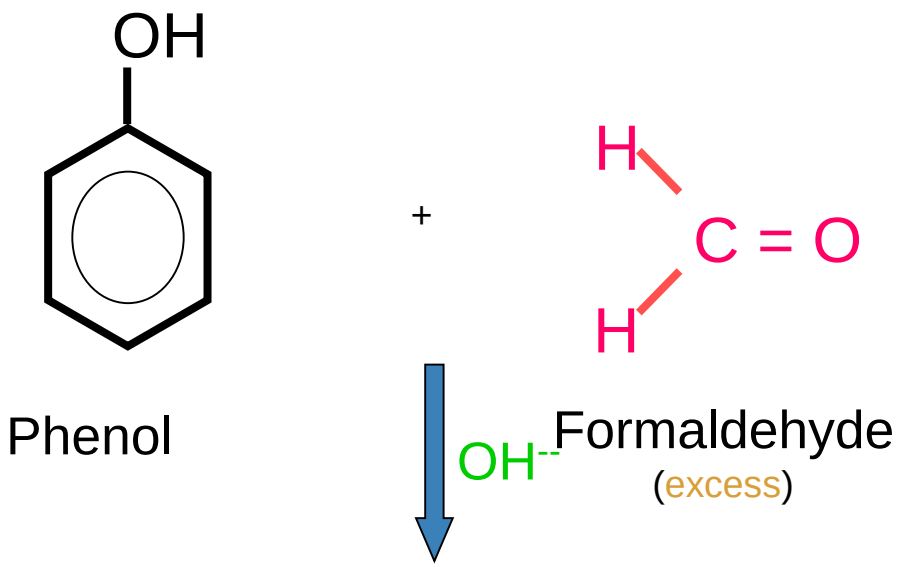
Resoles

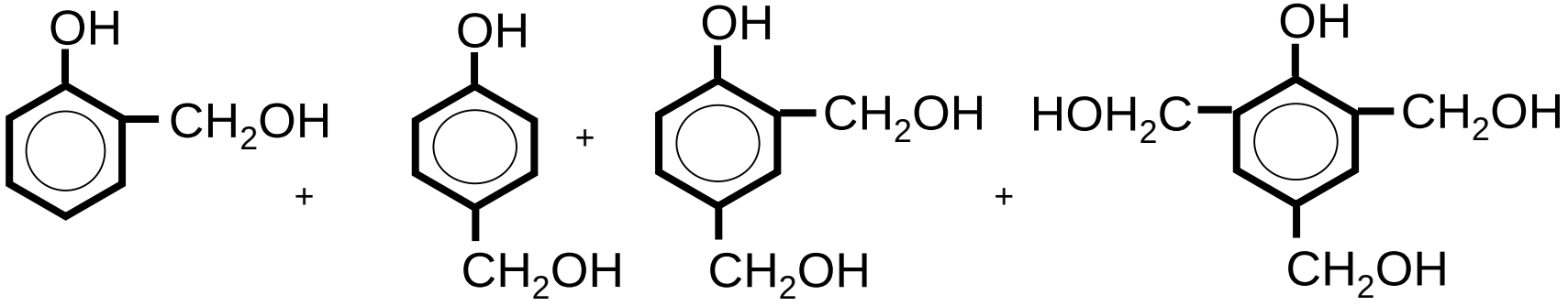
When the molar ratio of P/F is < 1 and the catalyst used is a base, the polymer formed are called Resoles

The first step in the reaction is the formation of mono, di and trimethylol phenols. They undergo condensation to form resoles

The resoles in which phenols are linked through methylene bridges are soluble and fusible

Since they contain alcoholic groups, further reaction during curing leads to cross linking, resulting in a network, infusible and insoluble product





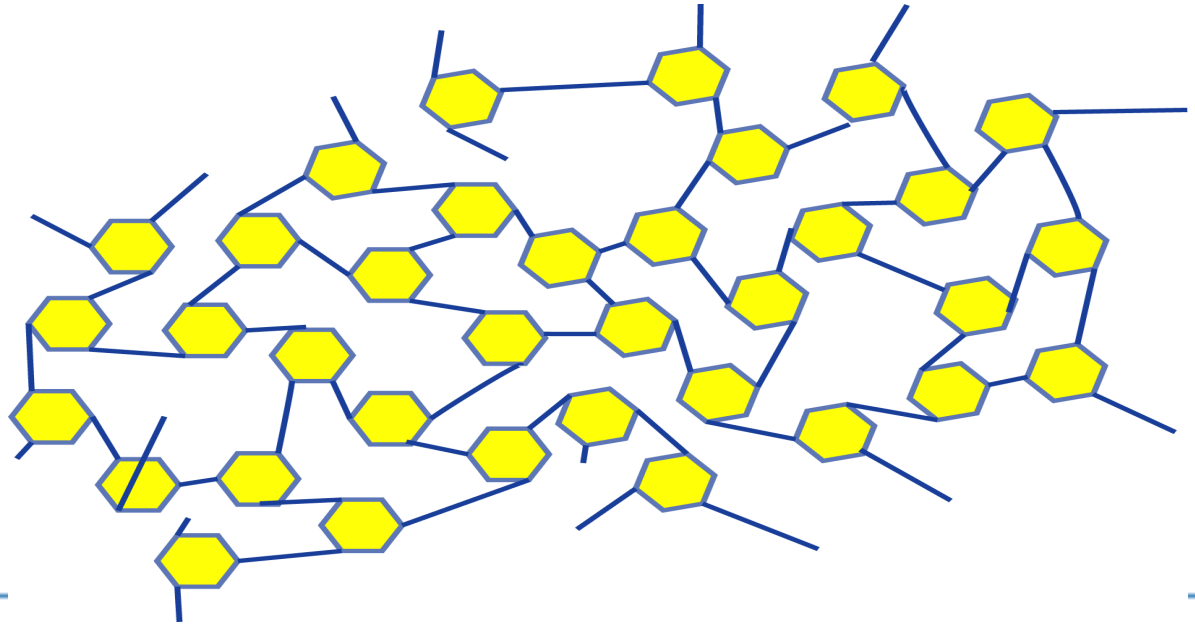
o-methylol phenol

p-methylol phenol

di methylol phenol

tri methylol phenol

Curing

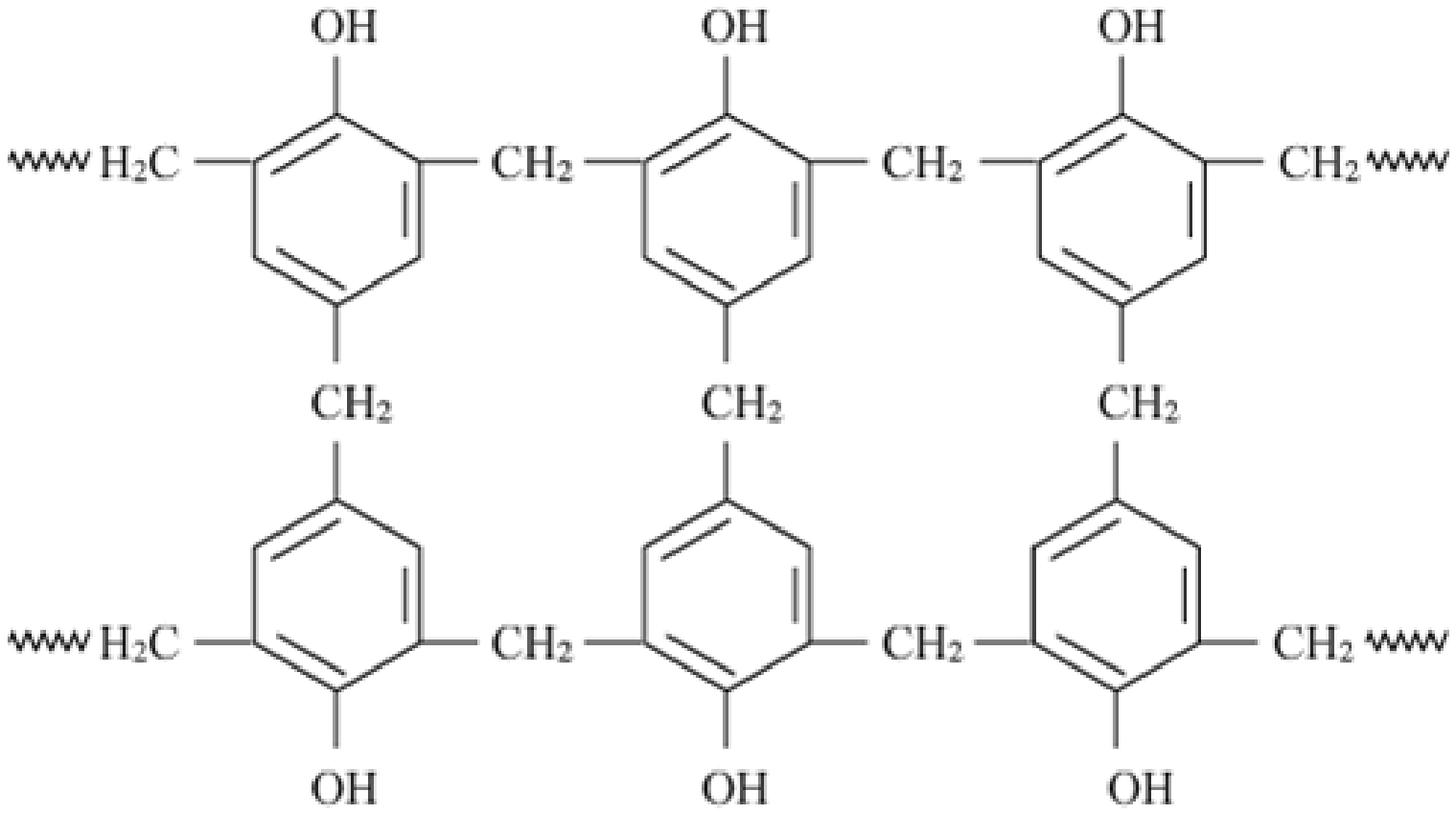


Properties of Bakelite:

- They are rigid, hard, scratch-resistant, infusible, water resistant, insoluble solid.
- Resistant to non-oxidizing acids, salts and many organic solvents.
- They are attacked by alkalis
- They possess excellent electrical insulting character

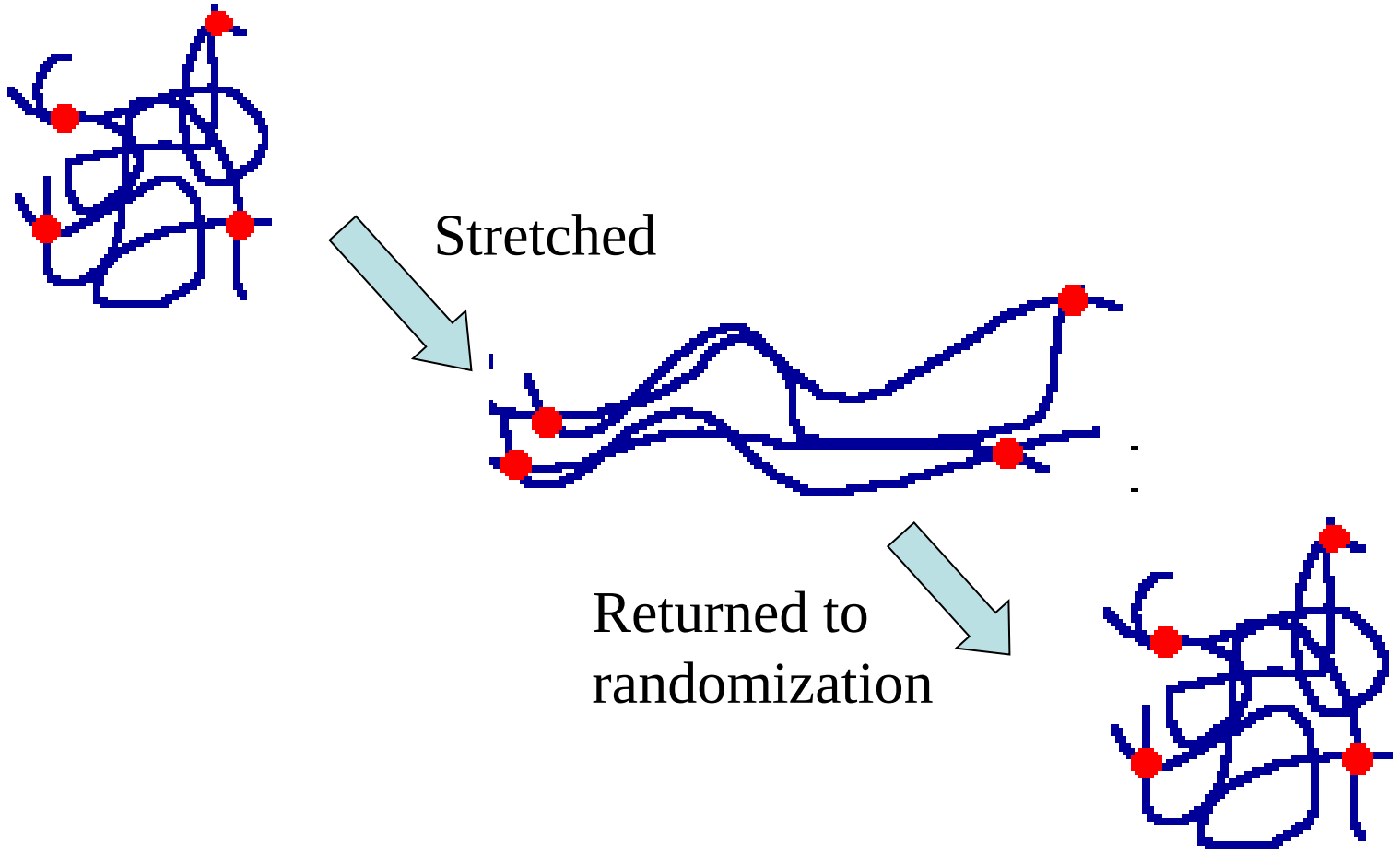
Uses

- For making electric insulators parts like switches, plugs, switch board, heater-handles etc.
- For making moulded articles like telephone parts, cabinets for radio and television.
- For impregnating fabrics, woods and paper
- As adhesives (binder) for grinding wheels.
- In paints and varnish
- As hydrogen exchanger resins in water softening



Bakelite

Elastomer is defined as a long chain polymer which under stress undergoes elongation by several times and regains its original shape when the stress is fully released



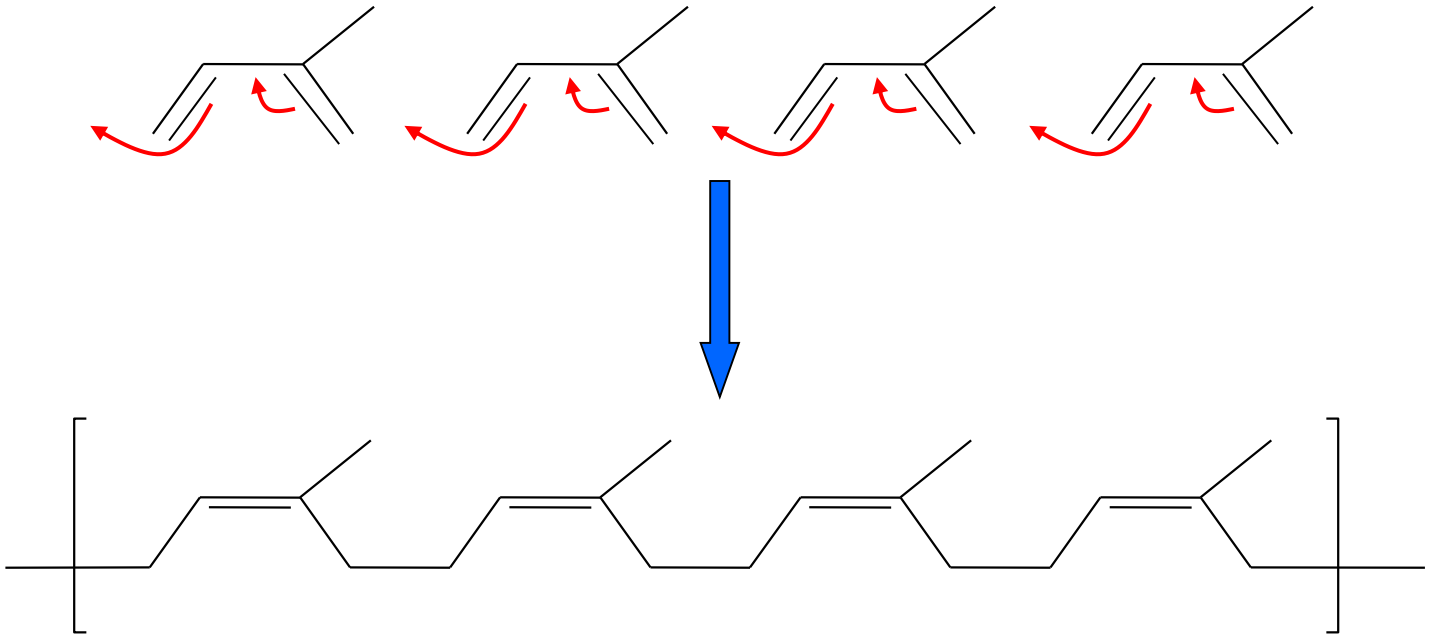
Natural rubber is obtained from the exudates of the rubber trees in the form of a milky colloidal solution called latex containing 25-45% of rubber dispersed in a watery medium with small amounts of protein and other materials. The latex is tapped by cutting through the bark of the tree and the liquid that comes out is collected in containers.

The latex is processed either by i) coagulation by acid or by heat and processed further or ii) mixed with compounding materials and precipitated directly from the solution.

Natural rubber is an addition polymer formed from the monomer called isoprene
i.e., 2-methyl-1,3-butadiene

The average D.P. (n) of rubber is around 5000

Addition between molecules of isoprene takes place by 1,4 addition and one double bond shifts between 2nd and 3rd positions



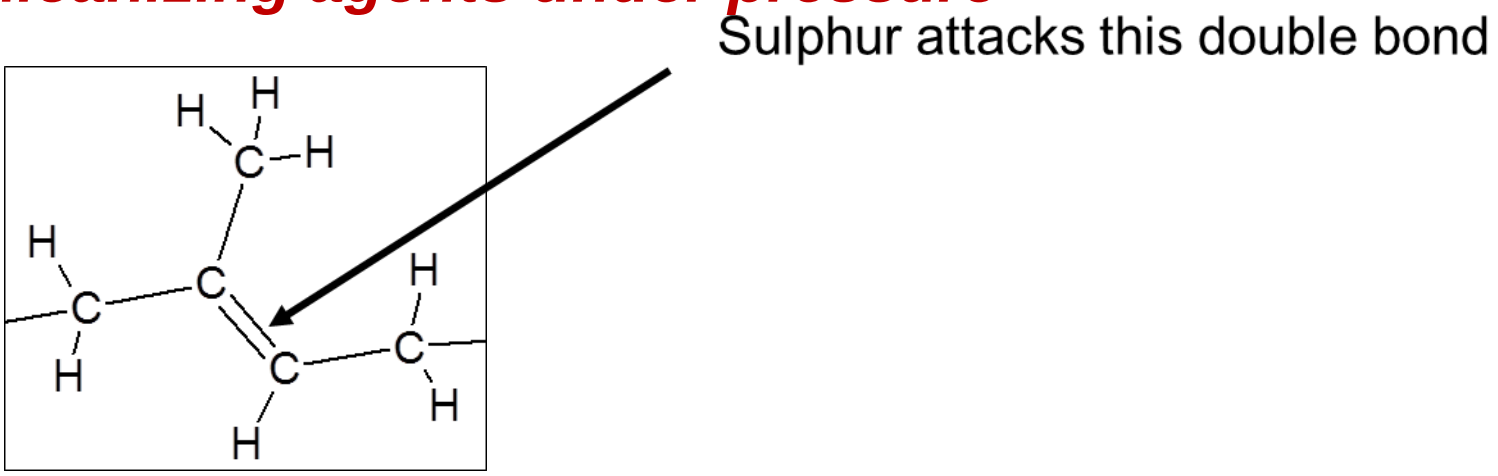
Drawback of raw rubber

- It is plastic in nature: It becomes soft at high temperature and is too brittle at low temperature. So it can be used in temperature range between 10 to 60˚C only
- It is weak: tensile strength is only 200kg/cm^2
- It has large water absorption capacity
- It is non-resistant to non-polar solvents like vegetable and mineral oil
- It is attacked by oxidizing agent
- It swells in organic solvent and gradually degrade
- It has little durability

Vulcanization

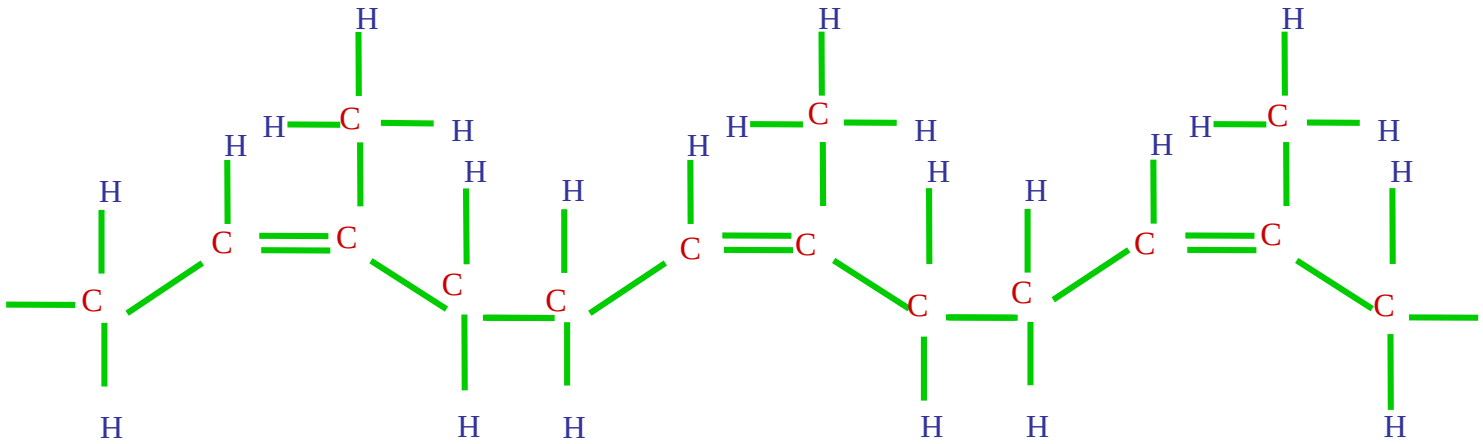
Vulcanization is a process, through which elasticity of the rubbers increases and reduces plasticity(ability to flow) by the formation of a crosslinked molecular network.

Vulcanization is done by heating the rubber with sulfur or other vulcanizing agents under pressure



Charles Goodyear (December 29, 1800 – July 1, 1860) was an American inventor who developed a process to vulcanize rubber in 1839—a method that he perfected while living and working in Springfield, Massachusetts in 1844, and for which he received patent number 3633 from the United States Patent Office.

e.g., a tyre rubber may contain 3 to 5% sulphur, but a battery case rubber may contain as much as 30% sulphur



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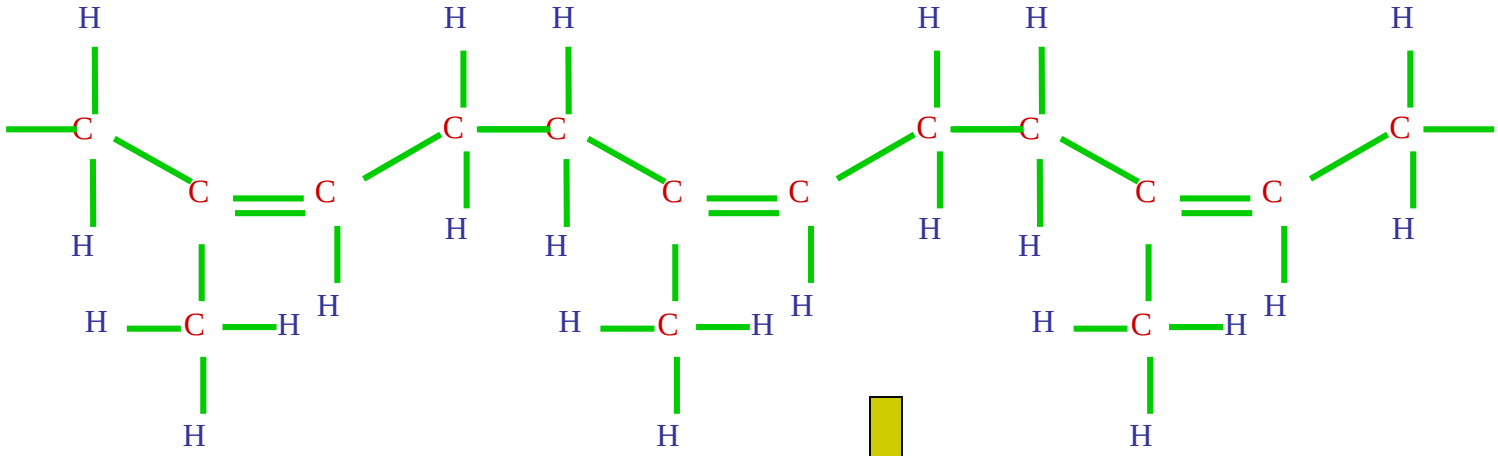

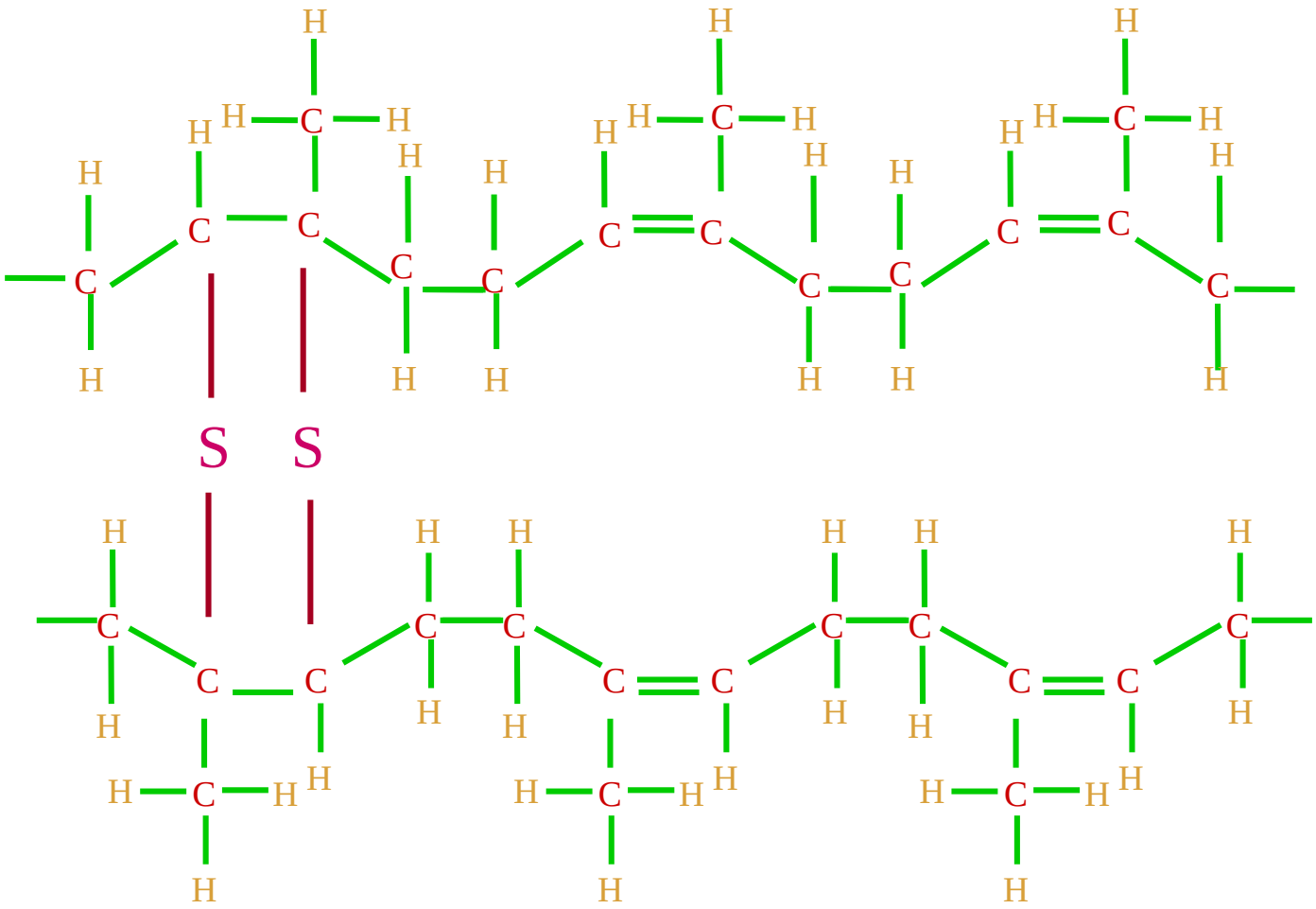
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Compounding of Rubber

Compounding is mixing of the raw rubber (synthetic or natural) with other substances so as to impart the product specific properties suitable for particular job.

(1) Softener and plasticizers are added to give the rubber greater tenacity and adhesion. For e.g. vegetable oil, waxes, stearic acid.

(2) **Vulcanizing agents**: sulfur, sulfur monochloride, benzoyl chloride etc.

(3) **Accelerators**: These materials drastically shorten the time required for vulcanization. 2-mercaptol, Benzothiazole *etc*.

(4) **Antioxidants**: Natural rubbers has a tendency to perish due to the oxidation. For this reason antioxidants are required, such as complex amine, phosphites etc.

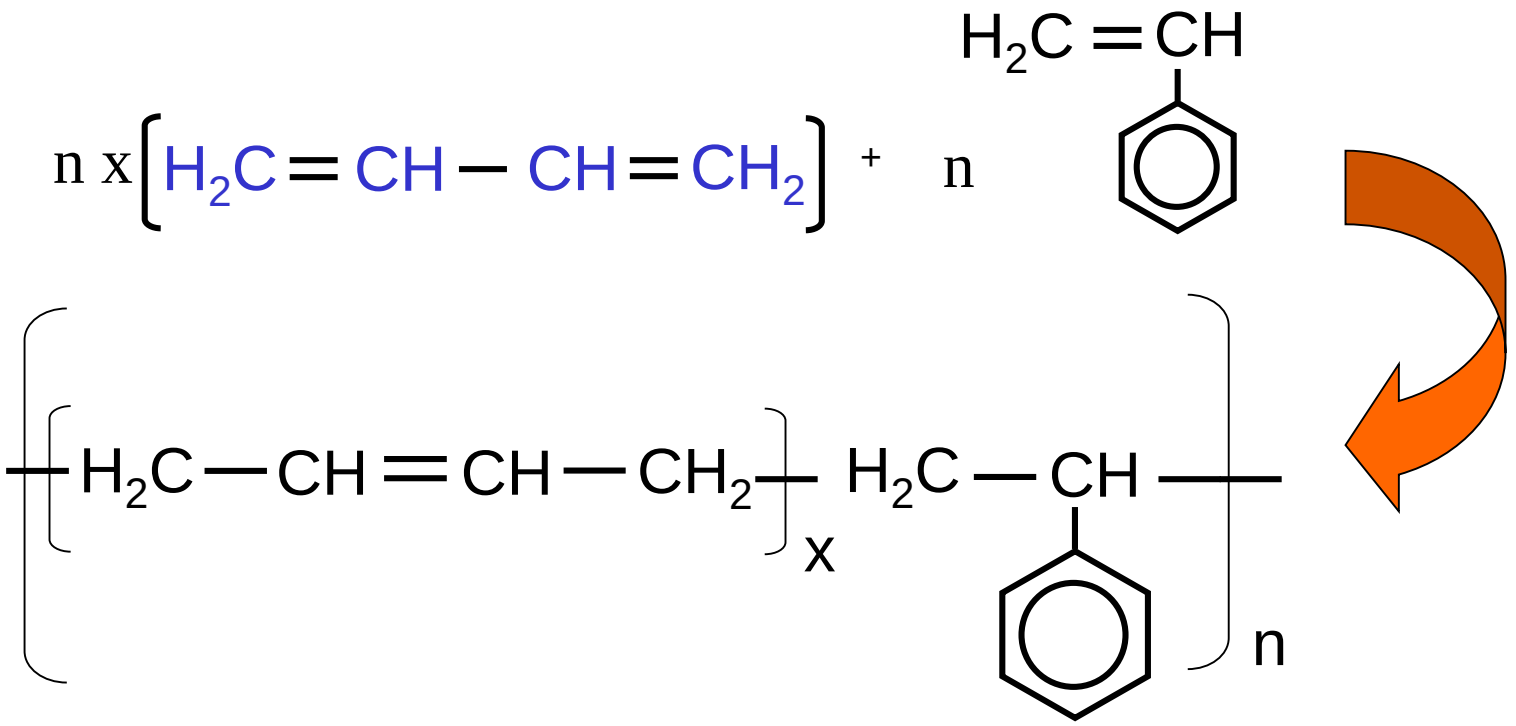
(5) **Reinforcing fillers**: theses materials gives strength and rigidity to the rubber products. For e.g. $CaCO_3$, ZnO etc.

(6) **Colouring agents**

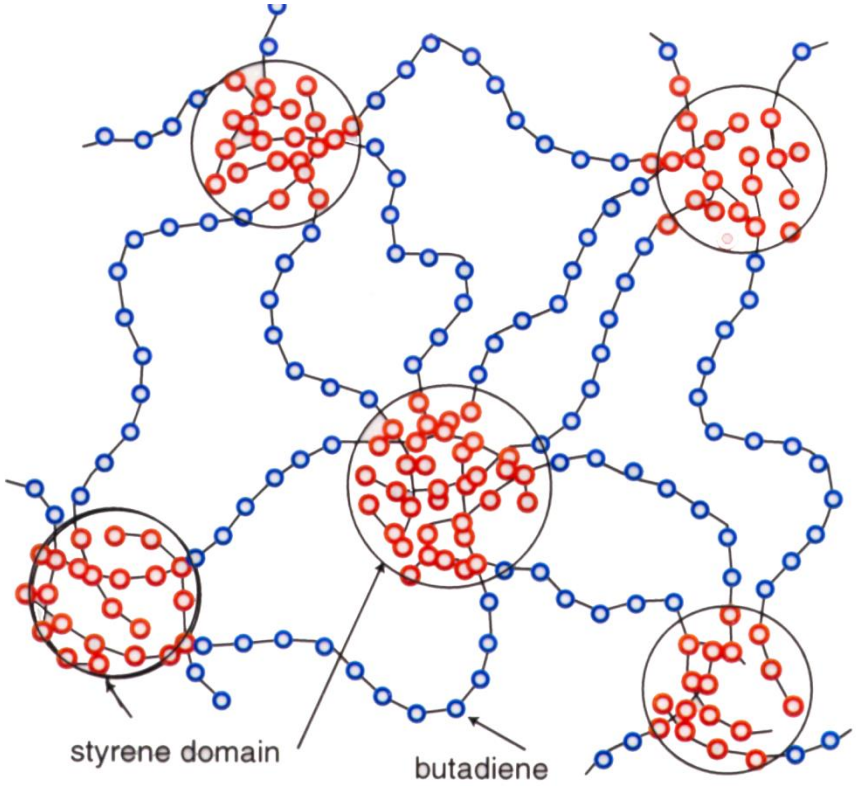
Styrene rubber (GR-S or Buna-S or SBR)

Preparation

This is produced by copolymerization of butadiene (about 75% by wt.) and styrene (about 25% by wt.)



Styrene-butadiene copolymer



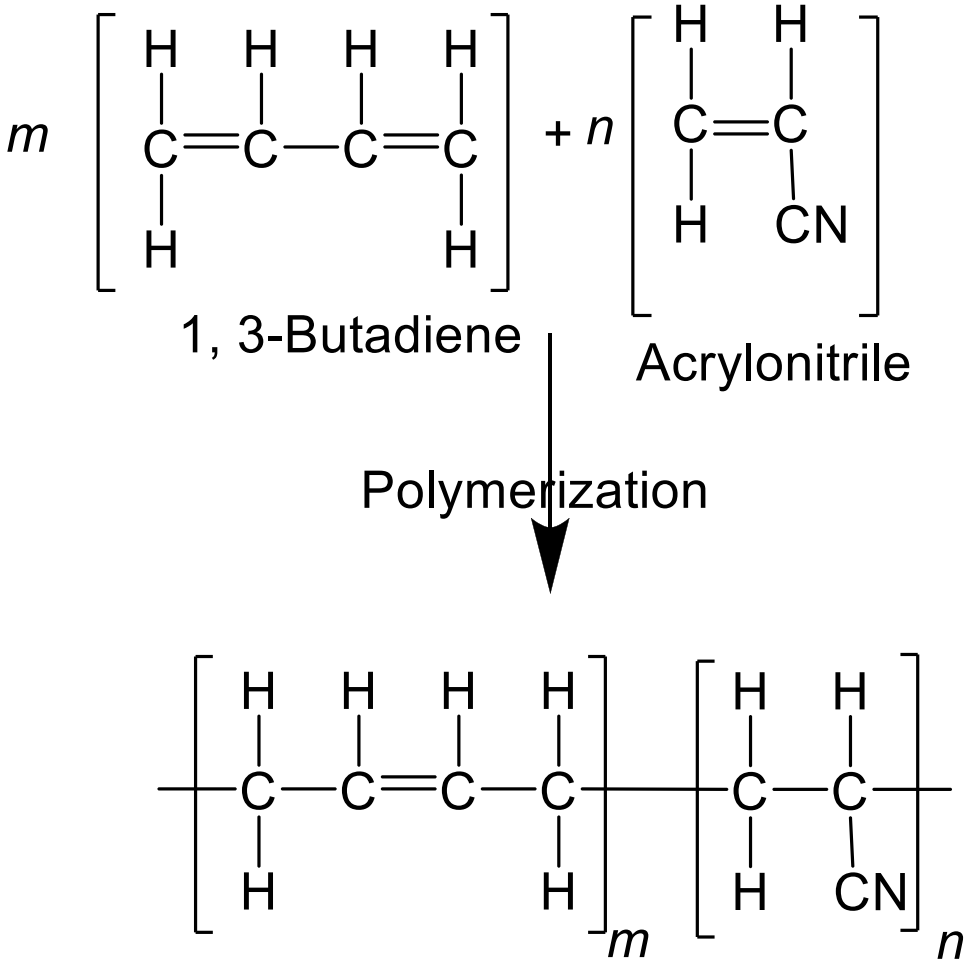
Styrene domains act as anchors or junctions

Butadienes provide flexible linkages

The desire to maximize the ways you can arrange the flexible links is what causes rubbers to return to given shapes

Buna-N(Nitrile rubber)

Buna –N is copolymer of butadiene and acrylonitrile rubber.



Nitrile rubber *or* Buna-N

Properties of Buna-N

It possesses excellent resistance to heat, sunlight, oils, acids and salts, but less resistant to alkalis than natural rubber, because of presence of cyano (-CN) groups. As the proportion of acrylonitrile is increased, the resistance to acids, salts, oils, solvents increases but the low temperature resilience suffers. Vulcanized nitrile rubber is more resistant to heat and ageing than natural rubber.

Uses:

For making conveyer belts, high altitude aircraft components, tank lining, hoses, gaskets, printing rollers, adhesives, oil resistant foams and automobile parts.

Properties:

1. PET can exist both in amorphous and semi-crystalline form
2. It has high mechanical strength and dimension stability and is stable over temperature range of -40 ^{o}C to 100 ^{o}C.
3. It shows creep and abrasion resistance and good electrical insulating properties.
4. At room temperature, it is resistant to water, dilute acids, salts, aromatic and aliphatic hydrocarbons and alcohols.

Applications:

1. It is used for making video and audio tapes.
2. It is commonly used in making clear bottles for foods and beverages.
3. It is used to make films for shrink packaging.
4. As an electrical insulator, it is used for making molds for electrical appliances.
5. The synthetic fibers can be woven to make fabrics, upholstery, artificial grass etc.
6. The fiber may be blended with wool and other natural fibers.
7. The films may be combined with paper or other polymeric films to form multilayer materials.
8. It can be used to produce injection molded articles, such as switches, valves etc.