N.B.-2 : To avoid incorrect classification, polymers are classified from a consideration of chemical structure of the groups present in the polymer chain. Condensation polymers are those polymers whose repeating unit are joint together by functional unit of one kind or another such as ester, amide, urethane, etc linkage.

$$-R-Z-R-Z-R-Z-R-$$

; [R = aliphatic or aromatic group
Z = Functional unit]

Addition polymers do not contain such functional group as part of the polymer chain.

▸ Based on polymerisation mechanism polymerisation is classified into step and chain polymerisation.

Step and chain polymerisation differ in several features, but the most important difference is in the identities of the species that can react with each other. Another difference is the manner in which polymer molecular size depends on the ~~ex~~ extend of conversion.

▸ Step polymerisation :

Step polymerisation proceed by the stepwise between the functional groups of reactants. The size of the polymer molecule increases at a relatively slow pace in such polymerisation. One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on until eventually large-sized polymer molecules have been formed.

Example :

Monomer + Monomer ⟶ dimer
dimer + Monomer ⟶ Trimer
Trimer + Monomer ⟶ Tetramer
Tetramer + Monomer ⟶ Pentamer.
Trimer + dimer ⟶ Pentamer etc.

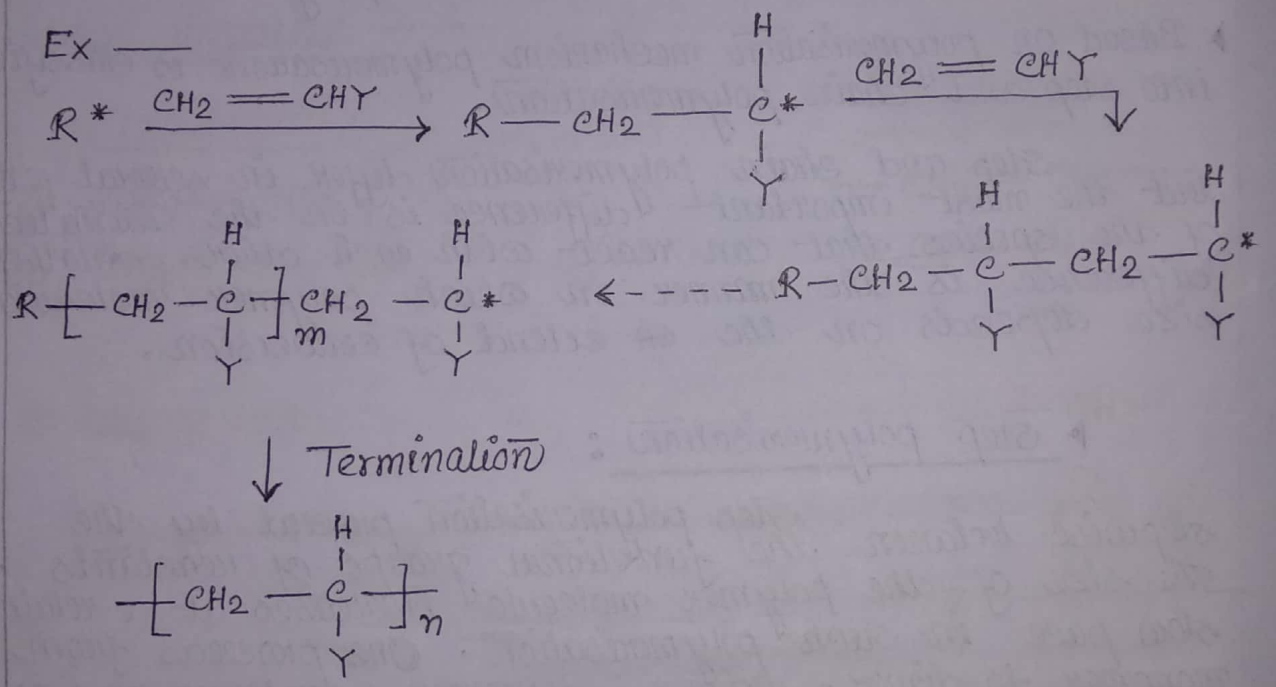
The characteristic of step polymerisation is that the reaction occurs between any of the different-sized species present in the reaction system.

Scanned with CamScanner

▸ Chain polymerisation :

In chain polymerisation, an initiator is used to produce an initiator-species R* with a reactive centre. The reactive centre may be either a free radical, cation or anion. Polymerisation occurs by the propagation of the reactive centre by the successive addition of large numbers of monomer molecules in a chain reaction. The distinguishing characteristic of chain polymerisation is that polymer growth takes place by monomer reacting only with the reactive centre. Monomer does not react with a monomer and the different-sized-species such as dimer, trimer etc. The growth of the polymer chain ceases when the reactive centre is destroyed by possible termination step.

Ex —



▸ Characteristics of step and chain polymerisation :

The typical step and chain polymerisation differ significantly in the relationship between polymer-molecular-weight and the percent conversion of monomer. The chain polymerisation will show the presence of high-molecular-weight polymer molecules at all percents of conversion. There are no intermidiate-sized molecules in the reaction mixture - only monomer, high-polymer and initiator present. The only change that occure with conversion (i.e reaction time) is the continuous increase in the number of polymer molecules (Fig-1a)

Scanned with CamScanner

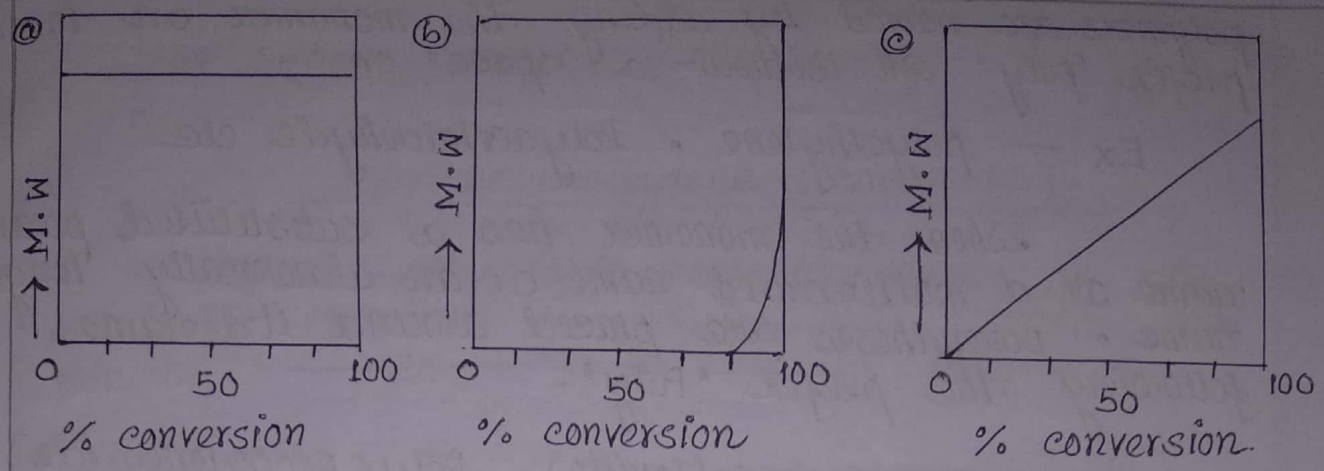
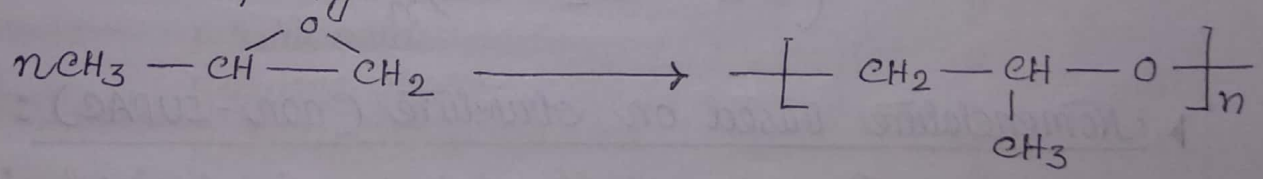


Figure – 1

On the otherhand, high-molecular-weight-polymer is obtained in the step polymerisation only near the very end on the reaction (>90% conversion) (Fig – 1ⓑ). Thus both polymer-size and the amount of polymer are dependent on conversion in step-polymerisation.

Certain polymerisation show a linear increase of molecular weight (M.W) with conversion (Fig – 1ⓒ) when the polymerisation mechanism departs from the normal chain pathway. This is observed in case of fast initiation & process coupled with the absence of termination reaction. Such behavior can be seen in the ring opening polymerisation of cyclic monomers such as propylene oxide.



▸ Nomenclature :

It is not unusual for a polymer to have several names because of the use of different nomenclature systems. The nomenclature systems are based on either the structure of the polymer or the source of the polymer (i.e monomer) or trade names.

▸ Nomenclature based on source :

This system is applicable primarily to polymers synthesized from a single monomer as in addition and ring opening polymerisations. Such

Scanned with CamScanner

polymers are named by adding the monomer on to the prefix 'poly' ~~ah~~ without a 'space' or '-'.

Ex — polyethylene, Polyacetaldehyde etc.

When the monomer has a substituted parent name or a multiworded name or an abnormally long name, parentheses are placed around it's name following the prefix 'Poly'.

Ex — Poly (vinylchloride), Poly (propyleneoxide), Poly (ε-caprolactam), Poly (3-methyl-1-pentene), Poly (chlorotrifluoroethylene).

In case of condensation polymer — polyamide, polyester.

N.B: In some cases the omission of parentheses can lead to uncertainly to the structure of the polymer. For example, polyethyleneoxide lead to the following structure.

$$-(CH_2-CH_2)_n-O-(CH_2-CH_2)_n- \quad \text{or} \quad -(CH_2-CH_2)_n-O-$$

Instead of poly(ethyleneoxide) as,

$$-(CH_2-CH_2-O)_n-$$

▸ Nomenclature based on structure (non-IUPAC):

The name of the polymer is obtained by following the prefix 'Poly' without a 'space' or '-' with parentheses enclosing the name of the structural grouping attached to the parent compound. The parent compound is the members of ester, amide, urethane etc.

Example —

$$H_2N-(CH_2)_6-NH_2 + HO_2C-(CH_2)_8-CO_2H \longrightarrow$$

Sebacic acid

Scanned with CamScanner

$$\left[NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}} \right]_n$$

Poly(hexamethylene sebacamide)

Another way is to keep the names of the two reactants involved in condensation reaction and use of "—Co—" to seperate them.

▸ Example : Poly (Phenol—Co—formaldehyde)

But this method did not get much acceptance.

▸ Chemistry of polymerisation :

Polymerisation is a process which allows simple low-molecular-weight compound to combine and form a complex, high M.W compound. For this, each molecule of the compound should have the capability to react atleast with two other molecules of the same or some other compounds. In otherwords, they should have a ~~fund~~ functionality of atleast two. The functionality of a compound depends on the number of reacting site it has.

	Compound	Functionality
Example	CH_3COOH	1
	$COOH-CH_2-COOH$	2
	Pthalic acid	2
	Ethylene glycol	2
	Hexamethylene diamine	2
	Glutamic acid	3
	Lycine	3
	Lactic acid	2
	Tartaric acid	4
	$CH_2=CH_2$	2
	$CH\equiv CH$	4

Depending on the functionality of the monomers used, we get linear, branched or three-dimensional cross-linked polymers.

Scanned with CamScanner

Ex —

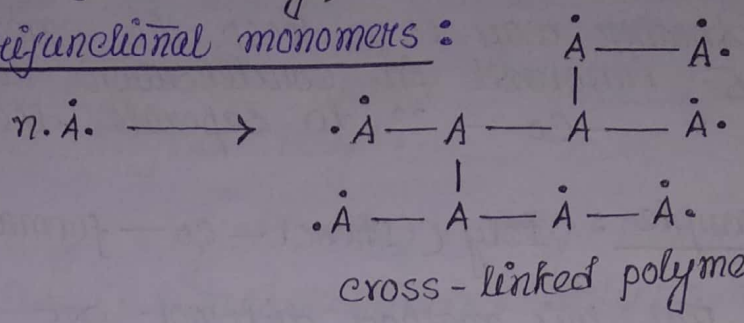
1. Bifunctional monomers :

$$n.A. \longrightarrow \cdot A - A - A - A - A \cdot$$

Linear polymer

(• represent functionality)

2. Trifunctional monomers :



cross-linked polymer

If we take a mixture of bifunctional and trifunctional monomers, their ratio decides whether the polymer shall be branched or cross-linked.

A. ▸ Chain polymerisation :

Chain polymerisation is characterised by a self-addition of the monomer molecules to each other very rapidly through a chain reaction. No byproduct is formed. compounds containing reactive double bonds can therefore, undergoes a chain polymerisation reaction. Typical examples are —

Vinyl ($CH_2 = CHX$), allyl ($CH_2 = CH - CH_2X$),
Olefin ($CH_2 = CHR$), diene ($CH_2 = CR - CH = CH_2$)

Since a majority of this monomers fall under the 'vinyl' category, chain polymerisation is also termed "Vinyl polymerisation".

chain polymerisation consists of three major steps : Initiation, propagation & termination. The process can be brought ~~ar~~ about by a free radical, ionic or coordination mechanism. Depending on the mechanism, we have three types of chain polymerisation —

1) Free-radical polymerisation :

The initiation of the polymer chain growth is brought about by free-radicals produced by compounds, called initiator. The term chain growth represents a process involving a continuous and very rapid addition of monomer unit to form polymer molecule.

Scanned with CamScanner