

Polymers L-4

weight average & o.Average molecular weight

mhttps://youtu.be/FyQCjD_1tx4

<https://youtu.be/T0rKGecWvdQ>

polymer

<https://www.slideshare.net/sagarsavale1/polymer-56240652>

mpf

GALGOTIAS
UNIVERSITY

School of Basic & Applied Sciences

Course Code : BSCC3004

Course Name: Organic Chemistry V

Introduction and classification including di-block, tri-block and amphiphilic polymers; Number average molecular weight, Weight average molecular weight, Degree of polymerization, Polydispersity Index.

Polymerisation reactions -Addition and condensation -Mechanism of cationic, anionic and free radical addition polymerization; Metallocene-based Ziegler-Natta polymerisation of alkenes; Preparation and applications of plastics – thermosetting (phenol-formaldehyde,

Polyurethanes) and thermosoftening (PVC, polythene); Fabrics – natural and synthetic (acrylic, polyamido, polyester); Rubbers – natural and synthetic:

Buna-S, Chloroprene and Neoprene; Vulcanization; Polymer additives ; Introduction to liquid crystal polymers; Biodegradable and conducting polymers with examples

[Polymer related Video links](#)

<https://youtu.be/D0I7ukw18FE>

<https://youtu.be/YduOEGBtNfo>

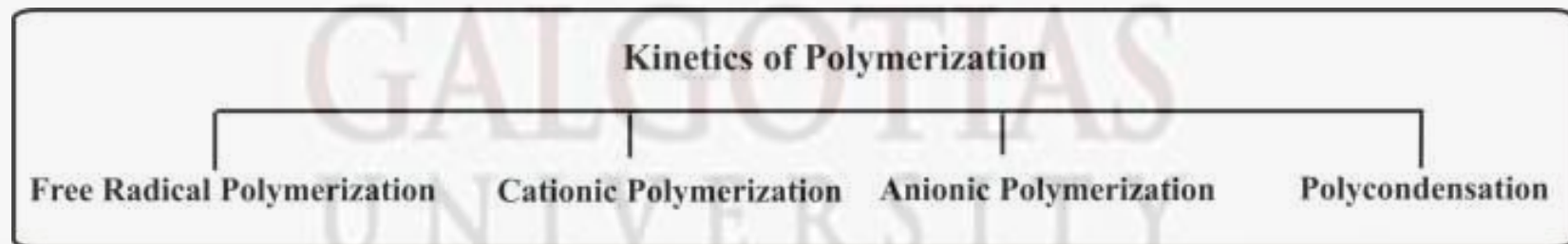
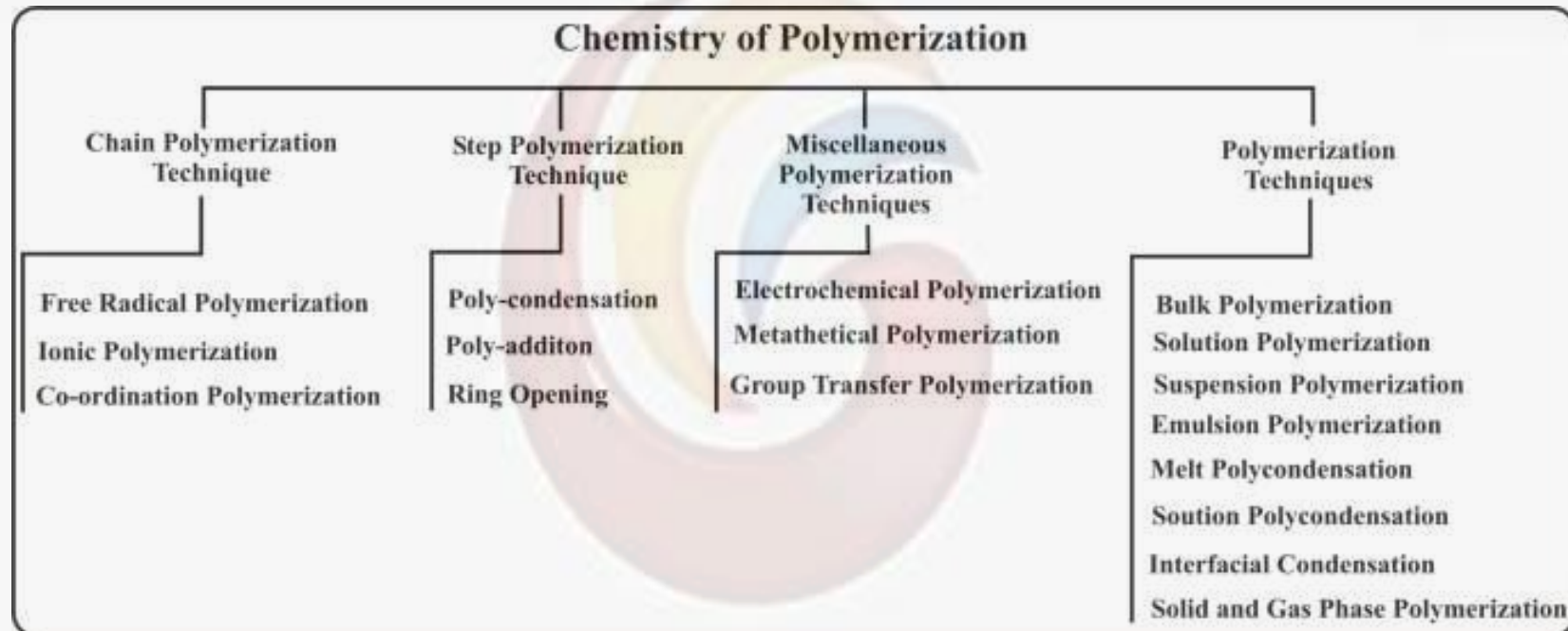
<https://web.mit.edu/8.334/www/grades/projects/projects10/AlexanderPapageorge/Page6.html>

School of Basic & Applied Sciences

Course Code : BSCC3004

Course Name: Organic Chemistry V

Chemistry of Polymerisations



Functionality

Compounds	Chemical Formula	Number of functional groups present per molecules				Functionality	
		-OH	-COOH	-NH ₂	-NCO		
<i>Carboxylic Groups</i>							
1	Acetic Acid	CH ₃ COOH	-	1	-	-	Monofunctional
	Benzoic Acid	C ₆ H ₅ COOH	-	1	-	-	Monofunctional
	Pthalic Acid	HOOC C ₆ H ₅ COOH	-	2	-	-	Bifunctional
<i>Alcohols</i>							
2	Ethyl Alcohol	CH ₃ CH ₂ OH	1	-	-	-	Monofunctional
	Ethylene Glycol	OH CH ₂ CH ₂ OH	2	-	-	-	Bifunctional
	Benzyl Alcohol	C ₆ H ₅ CH ₂ OH	1	-	-	-	Monofunctional
<i>Amines</i>							
3	Aniline	C ₆ H ₅ NH ₂	-	-	1	-	Monofunctional
	Hexyl Diamine	NH ₂ CH ₂ (CH ₂) ₄ CH ₂ NH ₂	-	-	2	-	Bifunctional
<i>Isocyanate</i>							
4	Methyl Isocyanate	CH ₃ NCO	-	-	-	1	Monofunctional
	Toluene Diisocyanate	CH ₃ C ₆ H ₅ (NCO) ₂	-	-	-	2	Bifunctional
<i>Amino Acids</i>							
5	Glycine	NH ₂ CH ₂ COOH	-	1	1	-	Bifunctional
<i>Hydroxy Acid</i>							
6	Lactic Acid	CH ₃ CH(OH)COOH	1	1	-	-	Bifunctional
	Malic Acid	HOOCCH ₂ CH(OH)COOH	1	2	-	-	Trifunctional

Chain Growth Polymerisation

1. The monomers contain at least a double bond that participates in the polymerisation reaction.
2. The initiators for chain polymerisation may be different depending upon the nature of initiation i.e. free radical, cation and anion.
3. The carbon-carbon double bond in vinyl monomers and the carbon-oxygen double bond in aldehydes and ketones are the two main types of linkages that undergo chain polymerisation.
4. Important characteristics of chain polymerisation
5. Once the initiation occurs, the polymer chains form very quickly i.e. in the time scale of 10^{-1} to 10^{-6} s,
6. The catalyst concentration needed is very low and that means during the course of polymerisation only monomers and polymer are present,
7. The process is exothermic
8. High polymers with molecular weights of 10,000 to 10 million can be obtained,)

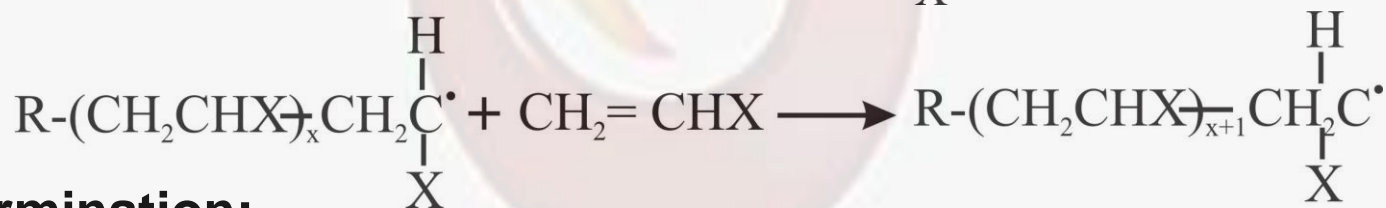
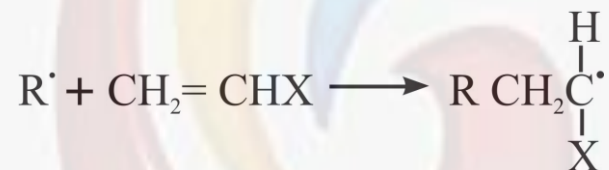
Free radical polymerisation

- The decomposition of peroxide type initiators in aqueous systems is generally accelerated in the presence of a reducing agent.

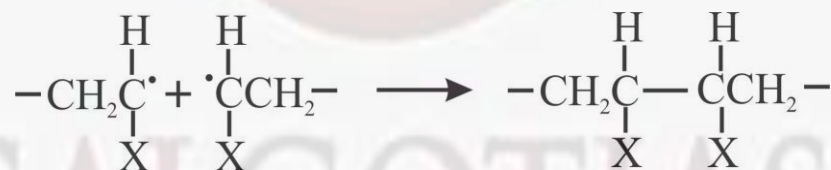
Initiation:



Proportion:



Termination:



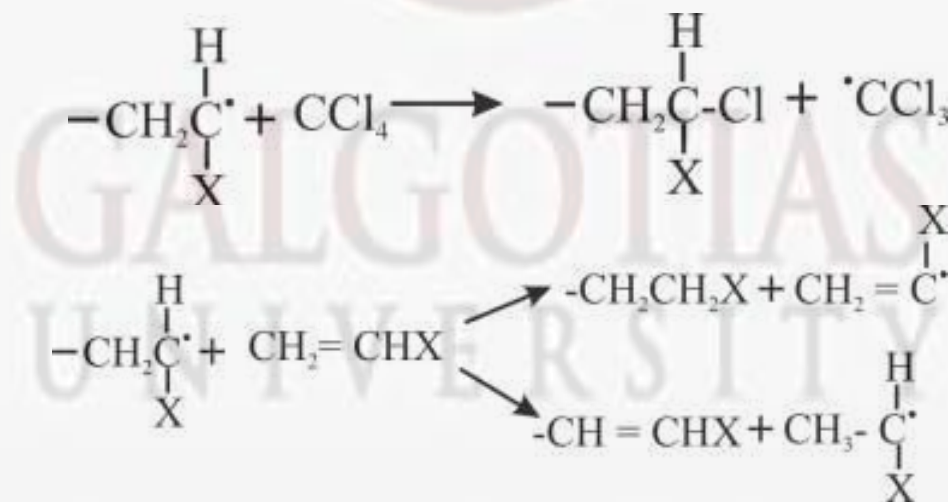
Or Disproportion



Radical Molecule Reaction (Chain Transfer)

Although the three steps of initiation, propagation, and termination are both necessary and sufficient for chain polymerisation, other steps 'also takes places during the polymerisation. As these often involve the reaction between a radical and a molecule, they are conveniently so classified Chain Transfer .

The reaction involves the transfer of an atom between the radical and the molecule. If the molecule is saturated, like a solvent or other additive, the atom must be transferred to the radical.



The major effect of chain transfer to a saturated small molecule (solvent, initiator, or deliberately added chain-transfer agent) is the formation of additional polymer molecules for each radical chain initiated.

Transfer to polymer and transfer to monomer with subsequent polymerization of the double bond lead to the formation of branched molecules.

The latter reaction has a pronounced effect on molecular-weight distribution and is important in the production of graft copolymers.

The efficiency of compounds as chain transfer agents varies widely with molecular structure. Aromatic hydrocarbons are rather unreactive unless they have benzylic hydrogens. Aliphatic hydrocarbons become more reactive when substituted with halogens.

Carbon tetrachloride and carbon tetrabromide are quite reactive. The reactivity of various polymer radicals to transfer varies widely.

Inhibition and Retardation

A retarder is defined as a substance that can react with a radical to form products incapable of adding monomer.

It both reduces the concentration of radicals and shortens their average lifetime and thus the length the polymer chain.

In the simplest case, the retarder may be a free radical, such as triphenylmethyl or diphenylpicrylhydrazyl, which is too unreactive to initiate a polymer chain.

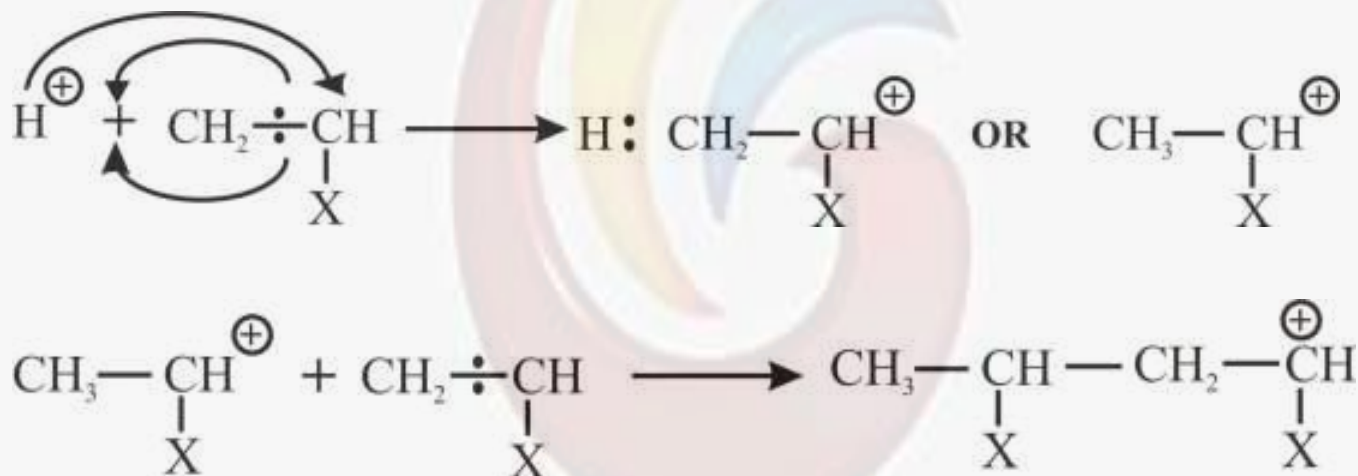
The mechanism of retardation is simply the combination or disproportionation of radicals.

Inhibitors are useful in determining initiation rates; since their reaction with radicals is so rapid that the decomposition of inhibitor is independent of its concentration but gives directly the rate of generation of radicals.

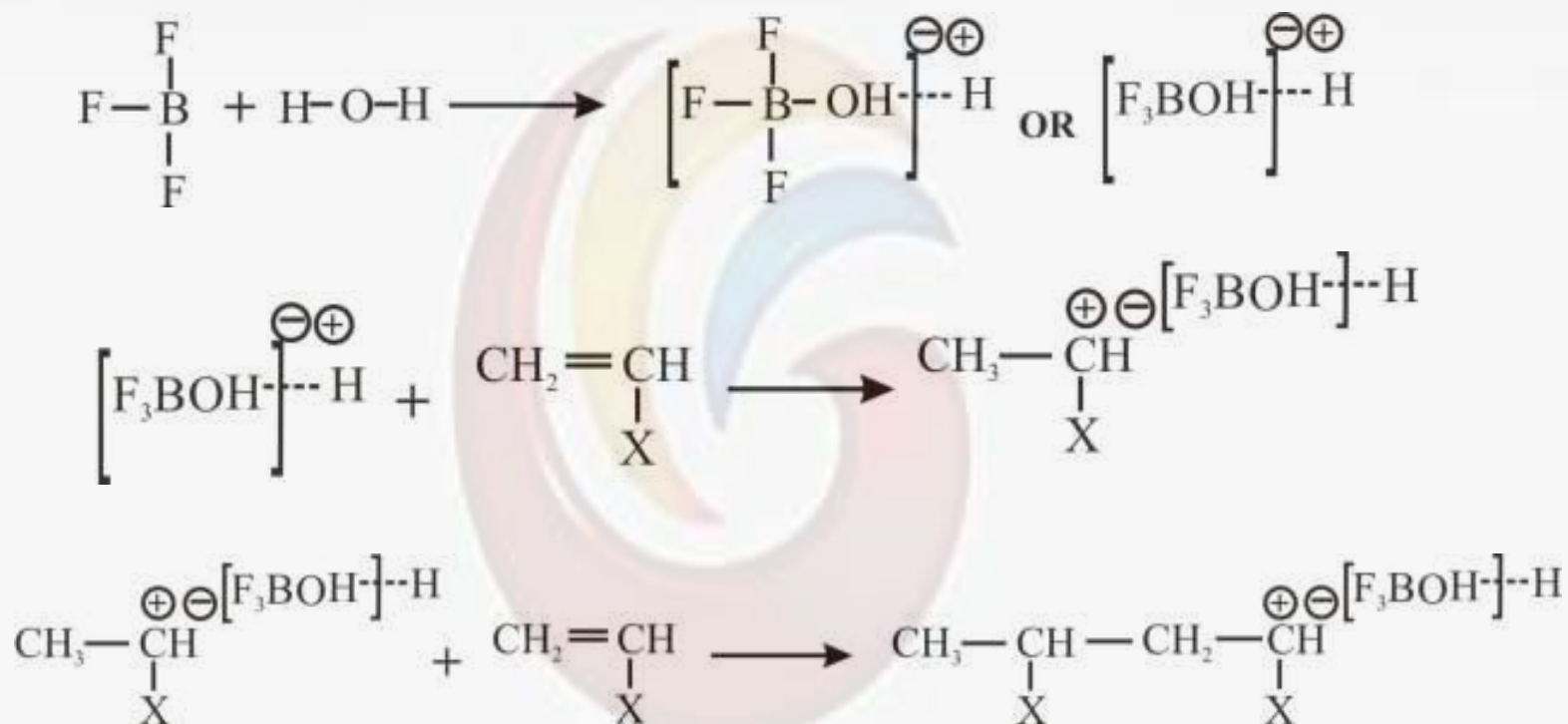
As a result, the length of the induction period before polymerization starts is directly proportional to the number of inhibitor molecules initially present. to one radical.

Cationic Polymerisation

The ionic mechanism of chain polymerisation also involves an attack on the π electron pair of the monomer.



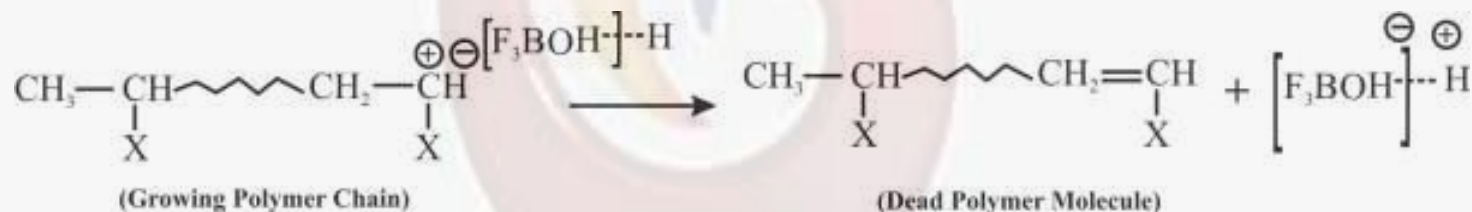
chain reaction initiated and propagated. Strong Lewis acids such as -BF_3 (generally called the 'catalysts' in ionic polymerisation), in the presence of small amounts of water or methanol (known as the 'co-catalysts'), form hydrates, which exist as ion pairs:



The initiators used for this purpose, in addition to BF_3 , AlCl_3 , SnCl_4 and TiCl_4 . Examples of monomers that can undergo cationic polymerisation are isobutylene, styrene, methyl styrene and many vinyl ethers.

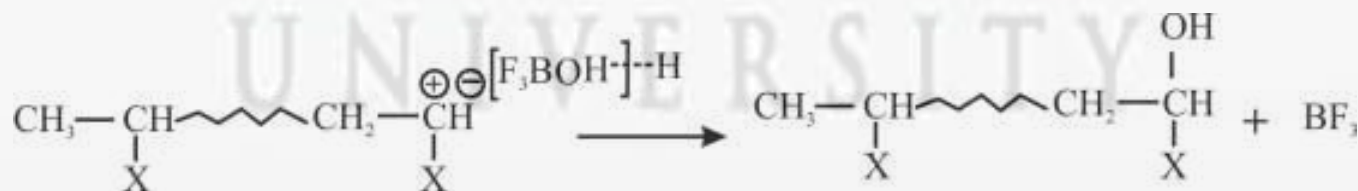
It involves further two steps:

(i) Donation of a proton to the counter-ion (which is, in fact, the reversal of the initiation step), resulting in the formation of a double bond at the end of the growing polymer molecule and the resultant arrest of the chain growth:



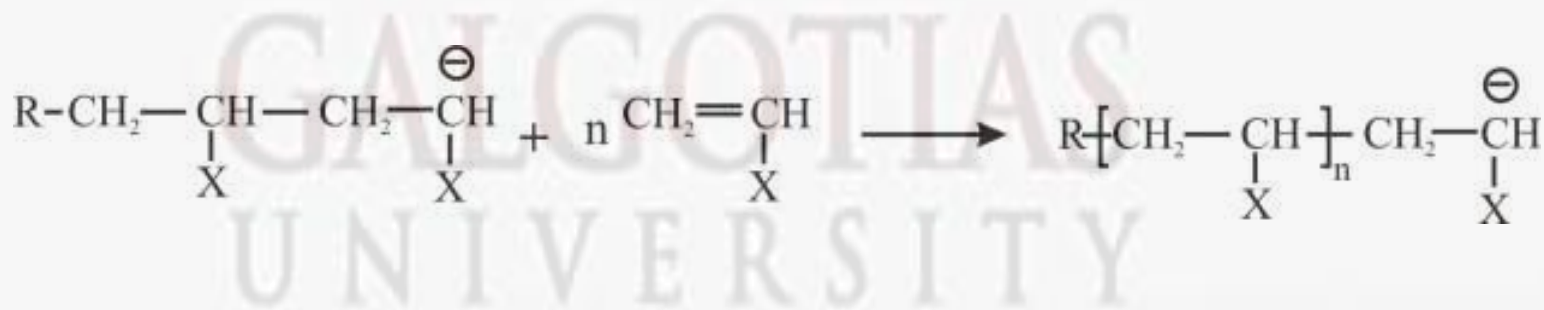
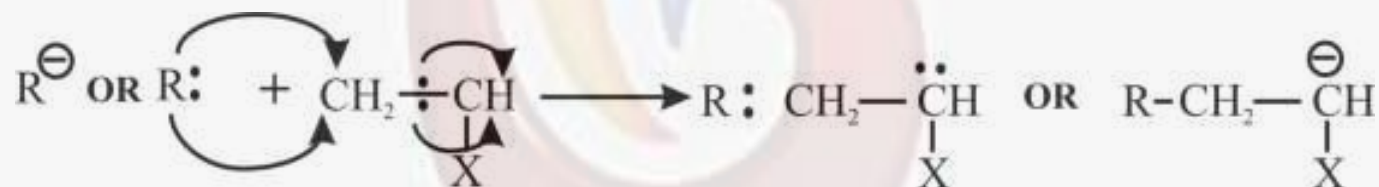
This process of donation of a proton and the re-formation of the BF_3 hydrate is called 'ion-pair precipitation'.

Formation of a covalent bond between the carbonium ion and the counter-ion when the termination occurs by simple 'coupling'



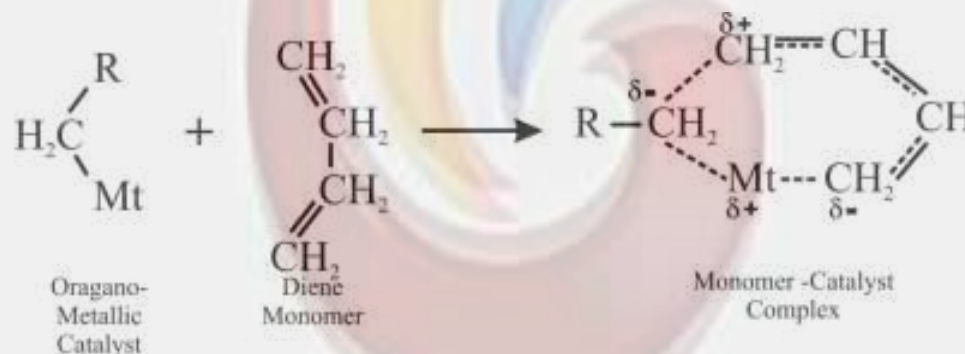
Anionic Polymerisation

The attack on the π electron pair of the monomer is done by a negatively charged ion (an anion). Such a system has extra electrons and the resultant negative charge attacks the π electron pair away from end of the molecule.



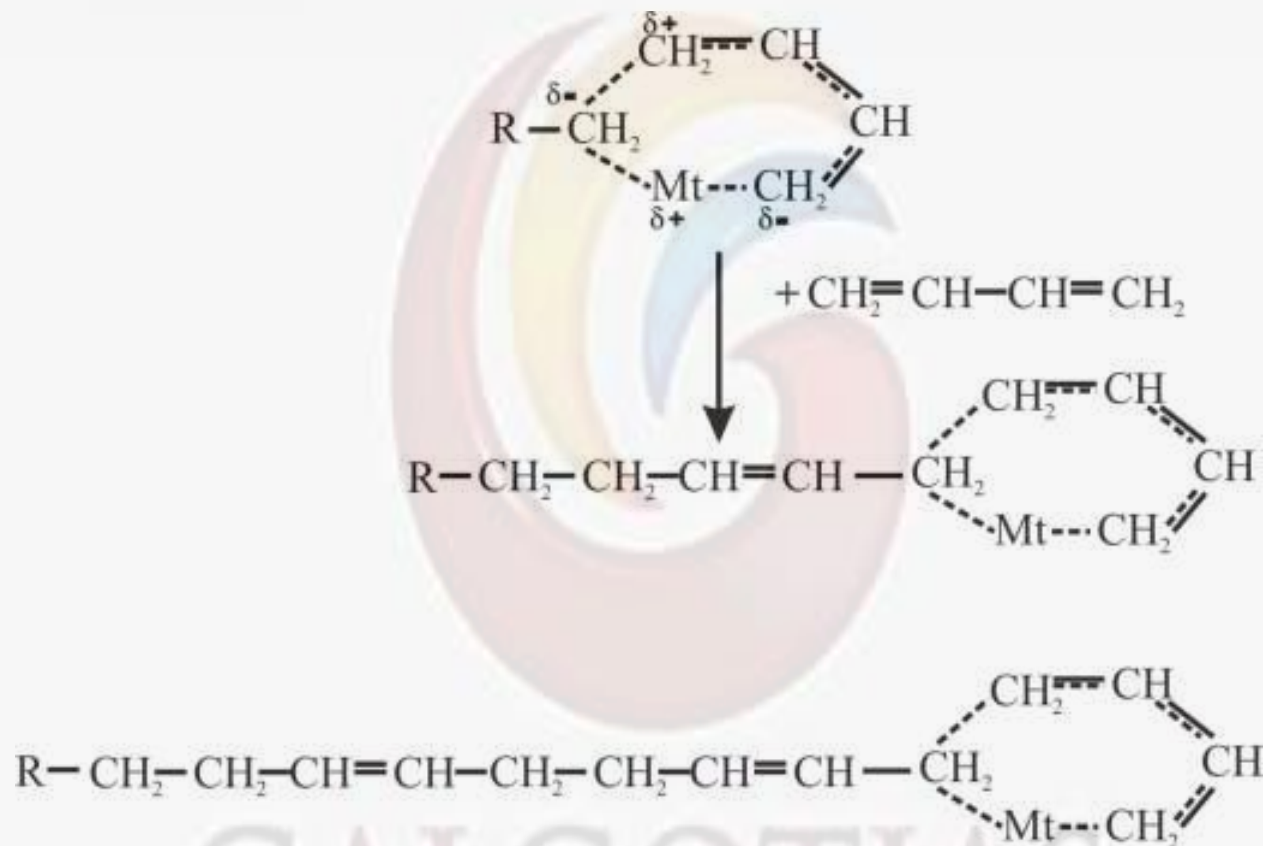
Co-ordination Polymerisation

Polymerisation reactions, especially of olefins and Dienes, catalysed by Organo-metallic compounds, fall under the category of coordination polymerisation.



Where Mt represents transition metals such as Ti, Mo, Cr, V, Ni or Rh.

The coordinated metal-carbon bond formed in the monomer-catalyst complex acts as the active center from where propagation starts.

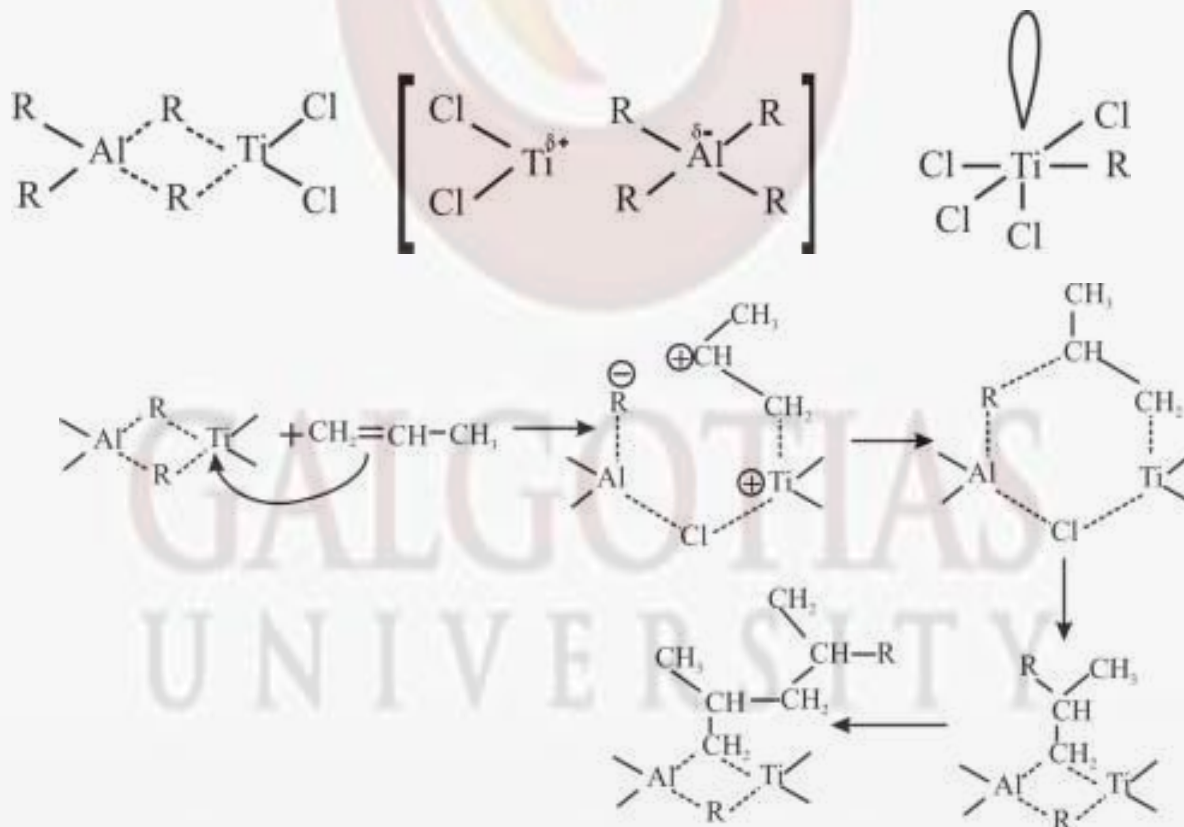


coordination polymerisation is also known as insertion polymerisation. The well-known Ziegler Natta Catalyst belongs to this category for the polymerisation.

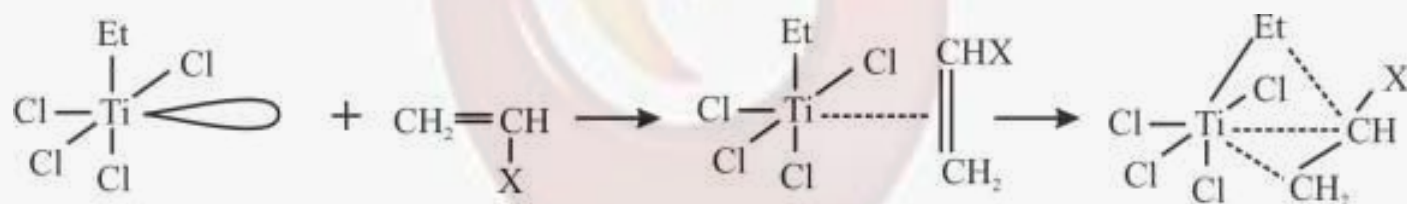
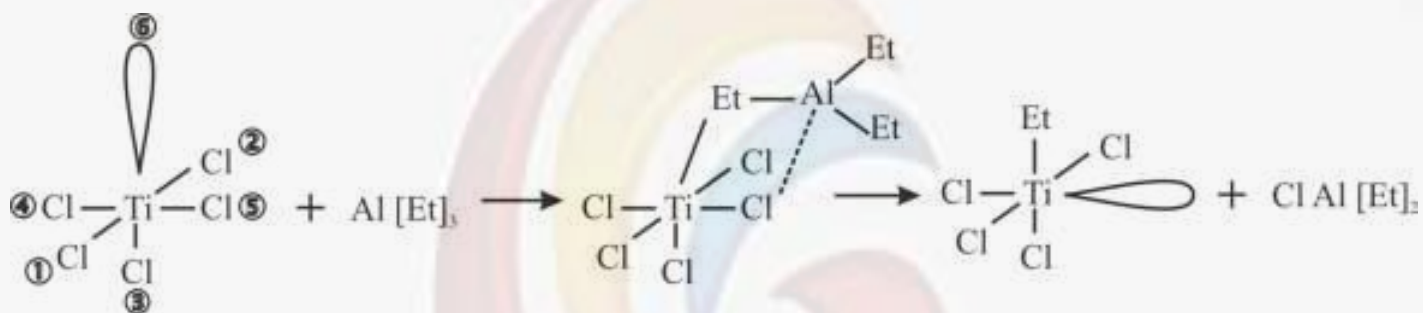
Ziegler-Natta Catalysts

The catalyst component consists of halides of IV-VIII group elements having transition valence and the co-catalysts are organo-metallic compounds such as alkyls, aryls and hydrides of group I-IV metals.

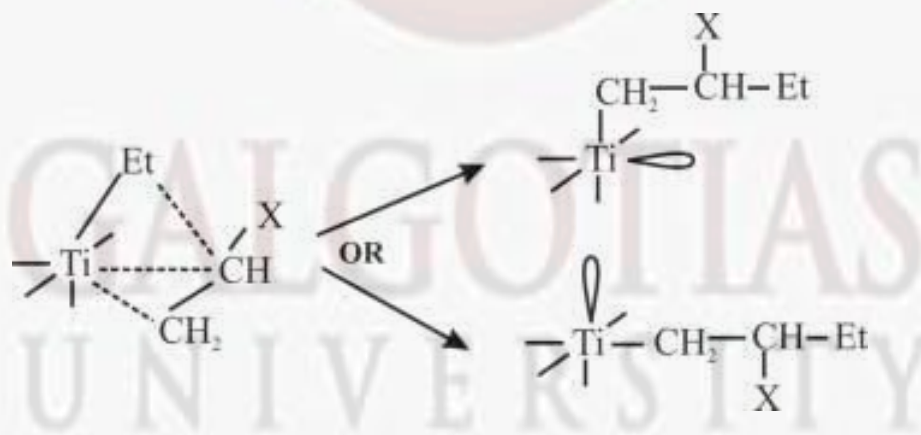
Natta Monometallic Mechanism:



Cossee Mechanism



Transition State

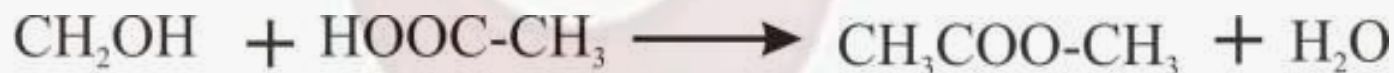
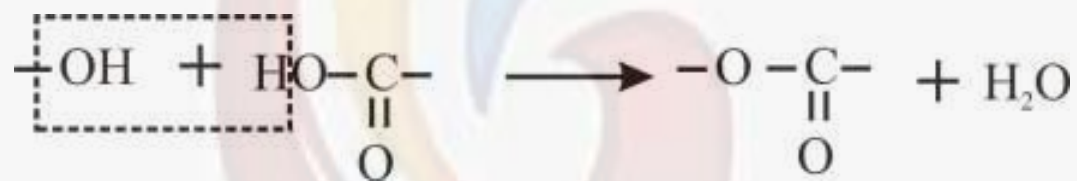


Step Polymerization

- The polymer build-up proceeds through a reaction between functional groups of the monomers.
- The reaction takes place in a step-wise manner (i.e., one after another), and the polymer build-up is, therefore, slow (unlike in chain polymerisation where the chain growth is very rapid).
- Although many known reactions with organic functional groups can be made use of in step polymerisation, condensation, addition, ring opening, amidation and ester-interchange reactions are the most commonly used ones. In step polymerisation reactions are accompanied by the elimination of small molecules.

Polycondensation

Polycondensation is brought about by monomers containing two or more reactive functional groups (such as hydroxyl, carboxyl and amino) condensing with each other



GALGOTIAS
UNIVERSITY

For polycondensation the monomer should have:

- 1. Those monomers should have two reactive functional groups for polymerisation to proceed.
- 2. That polymerisation proceeds by stop-wise reaction between reactive functional groups.
- 3. That only one type of reaction (i.e., condensation reaction, in this case) between two functional groups is involved in polymer formation.
- 4. That the polymer formed still contains both the reactive functional groups at its chain ends (as end group) and, hence, is 'active' and not 'dead', as in chain polymerization.

GALGOTIAS
UNIVERSITY

References

Painter, Paul C.; Coleman, Michael M. (1997). *Fundamentals of polymer science: an introductory text*. Lancaster, Pa.: Technomic Pub. Co. p. 1. [ISBN 978-1-56676-559-6](#).

^ McCrum, N. G.; Buckley, C. P.; Bucknall, C. B. (1997). *Principles of polymer engineering*. Oxford; New York: Oxford University Press. p. 1. [ISBN 978-0-19-856526-0](#).

^ Jensen, William B. (2008). "[Ask the Historian: The origin of the polymer concept](#)"(PDF). *Journal of Chemical Education*. **85** (5): 624–625. [Bibcode:2008JChEd..85..624J](#). [doi:10.1021/ed085p624](#).

^ Staudinger, H (1920). "[Über Polymerisation](#)" [On polymerization]. *Berichte der Deutschen Chemischen Gesellschaft (in German)*. **53** (6): 1073–1085. [doi:10.1002/cber.19200530627](#).

^ Allcock, Harry R.; Lampe, Frederick W.; Mark, James E. (2003). *Contemporary Polymer Chemistry (3 ed.)*. Pearson Education. p. 21. [ISBN 978-0-13-065056-6](#).

^

GALGOTIAS
UNIVERSITY

School of Basic & Applied Sciences

Course Code : BSCC3004

Course Name: Organic Chemistry V



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley

2. Polymer Chemistry by Charles E Carragher, Jr., Marcel Dekker, Inc.

3. Principle of Polymerization by George Odian, Wiley

GALGOTIAS
UNIVERSITY