

POLYMERS

Types of Polymerization :

(1) Addition Polymerization :

In addition polymerization, the polymer is formed from the monomer, without the loss of any material and the product is an exact multiple of the original monomeric molecules.

Addition polymerization reactions proceed by a chain reaction mechanism consisting of three important steps,

- (i) Initiation or the formation of an active centre,
- (ii) Propagation or the formation of a polymer having the active centre
- (iii) Termination or removal of the active centre.

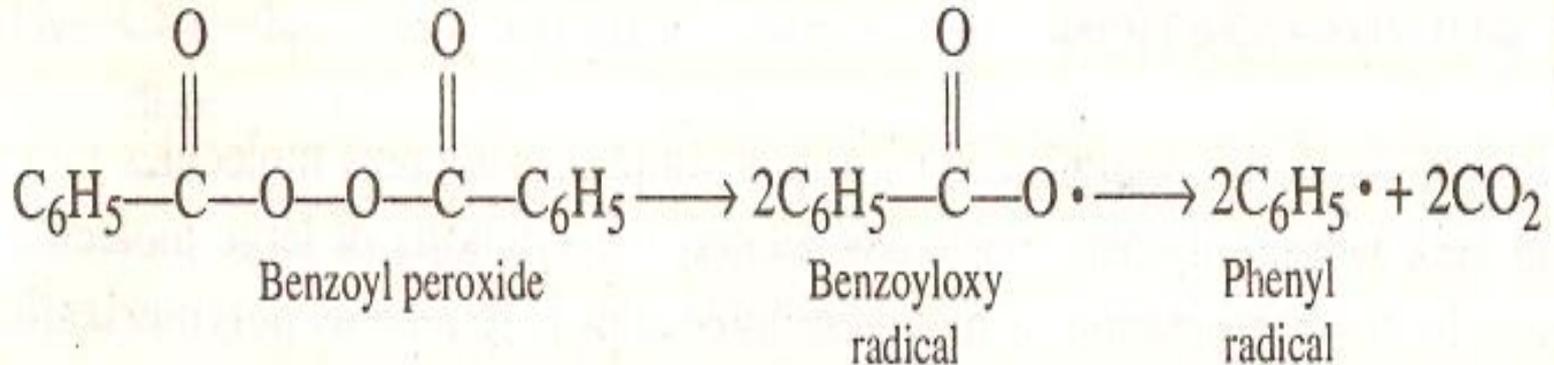
The three different types of active centres have been found to be formed during the addition polymerization, *viz.*, free radical, carbonium ion and carbanion. So the mechanisms involving these reactive species in polymerization constitute the mechanism of addition polymerization.

POLYMERS

(a) Free radical polymerization :

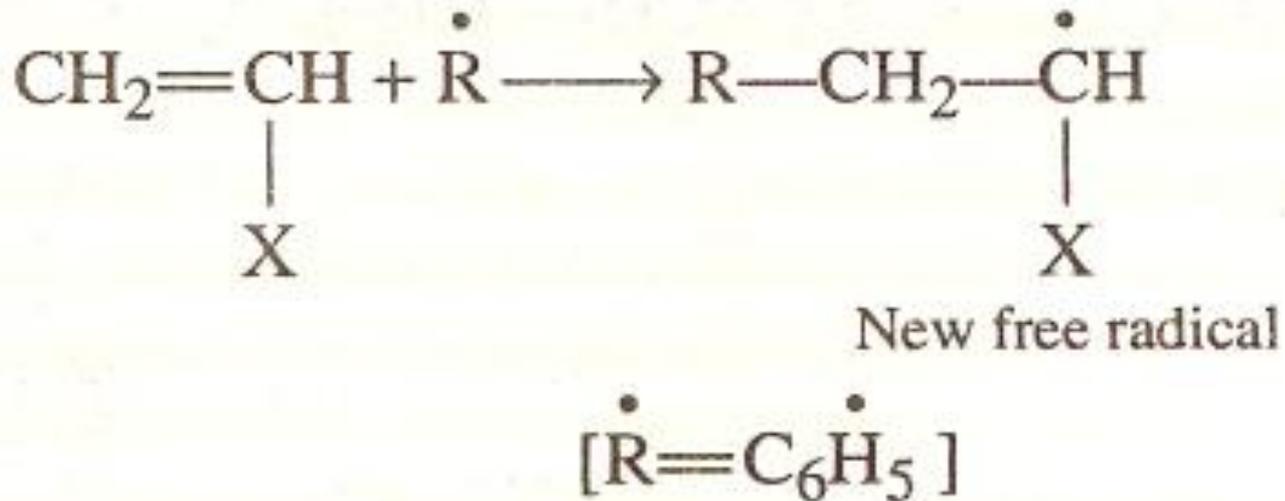
Free-radical polymerization form only linear molecules.

(i) Initiation step: It involves the formation of a free-radical from a radical initiator such as benzoyl peroxides, and other materials that can generate free radicals.



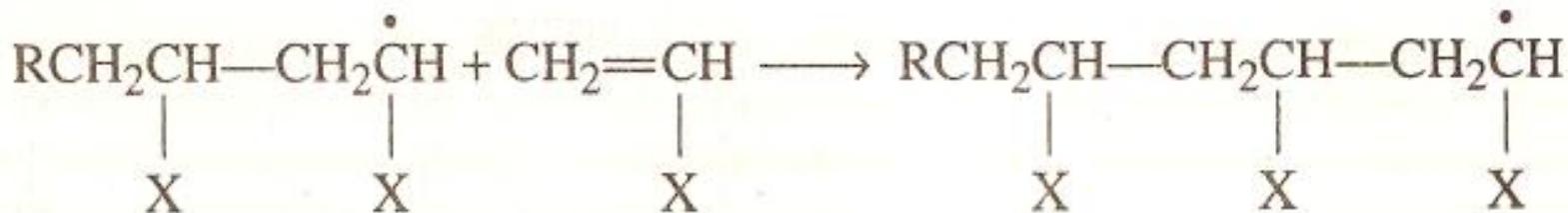
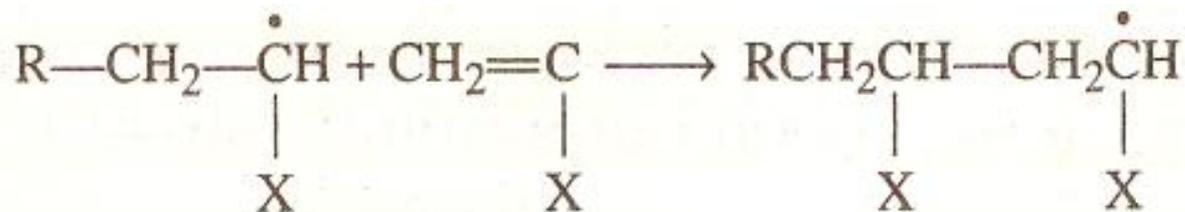
POLYMERS

The radical so formed then adds to the monomer to form a new free radical, e.g., it adds to vinyl monomer in the following way



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(ii) Propagation step: The new free radical now adds to another molecule of monomer to form another new free radical until a large free radical is formed .

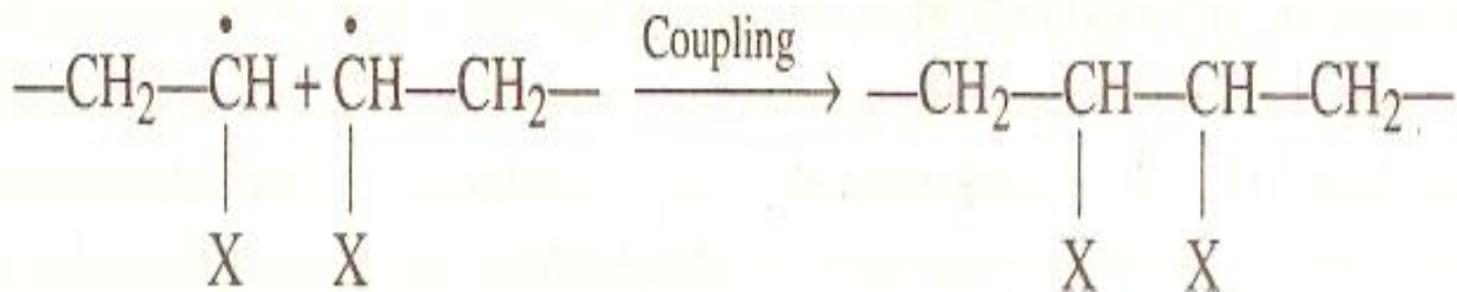


After the first few steps the addition of a monomer unit proceeds at a constant specific rate independent of the chain length of free radical formed.

POLYMERS

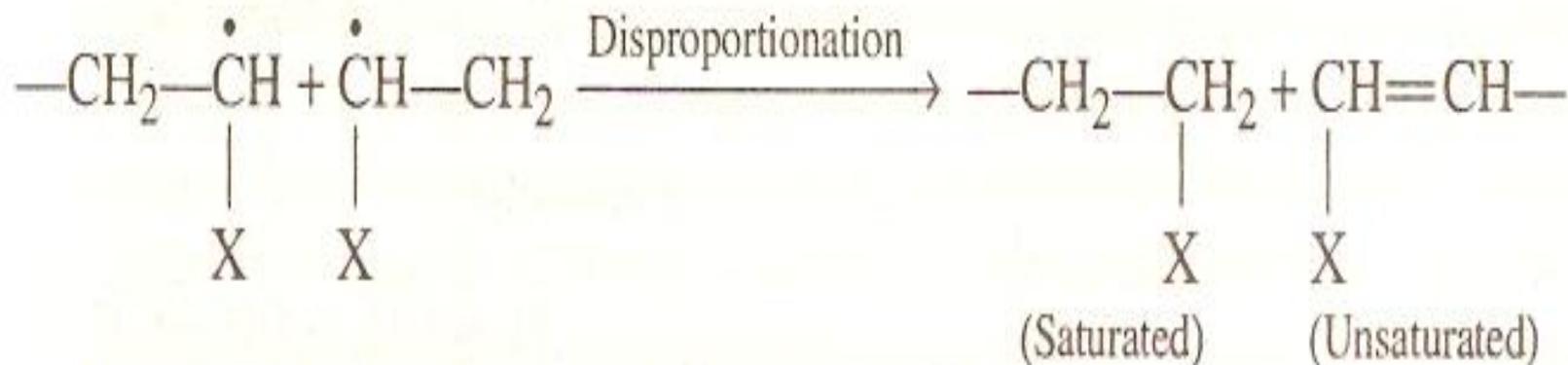
(iii) Termination step: Termination of chains usually occurs by radical coupling or disproportionation reactions.

By coupling or combination, e.g.,



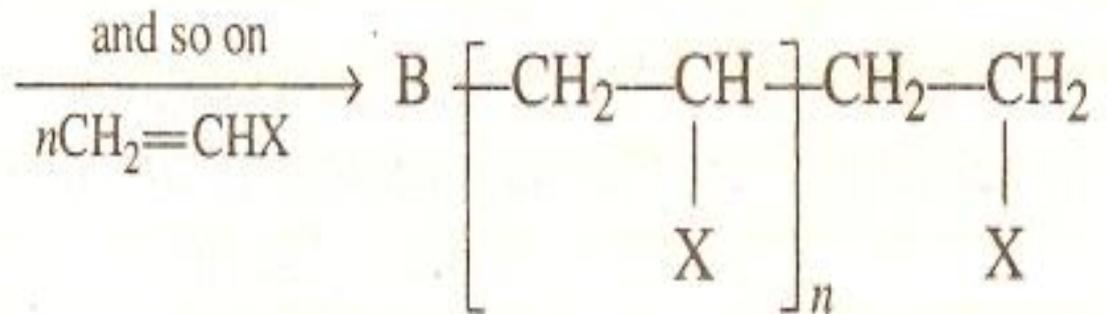
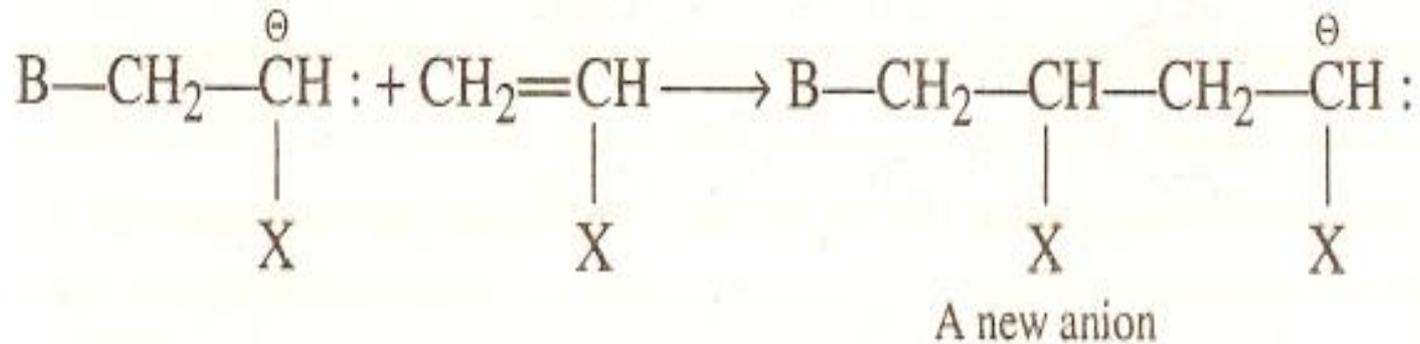
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Disproportionation: In which a hydrogen atom of one radical centre is transferred to another radical centre. This results in the formation of two polymer molecules, **one saturated and other unsaturated**, e.g.,



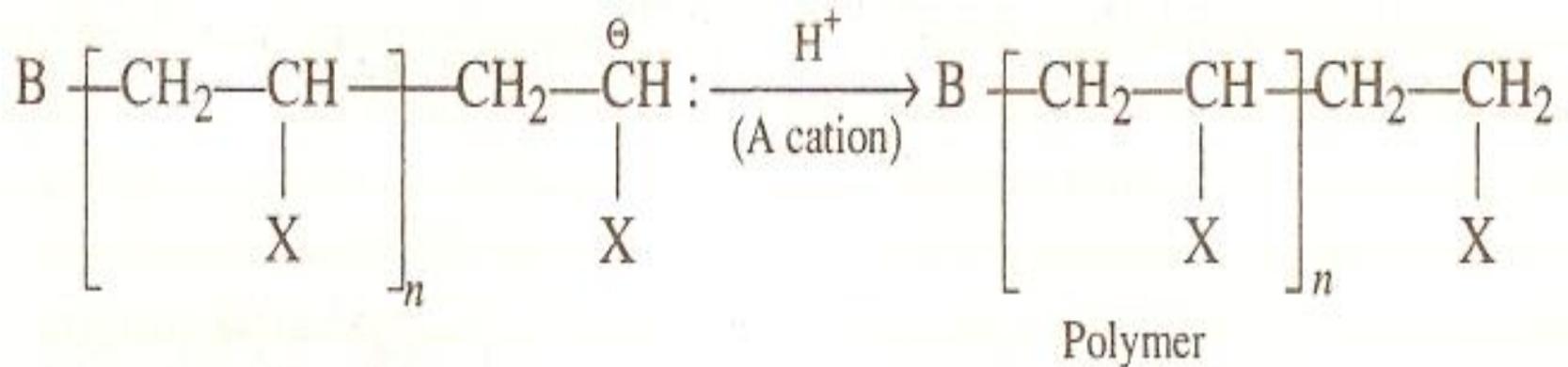
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Propagation :



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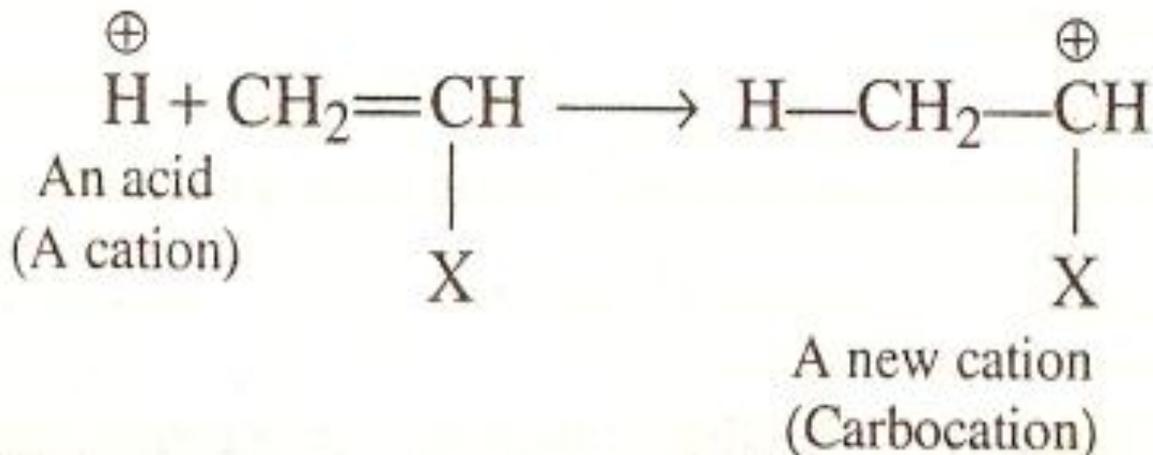
Termination: Termination occurs by a hydride transfer or by the action of reactive centres with solvent or with a functional group of the monomer,



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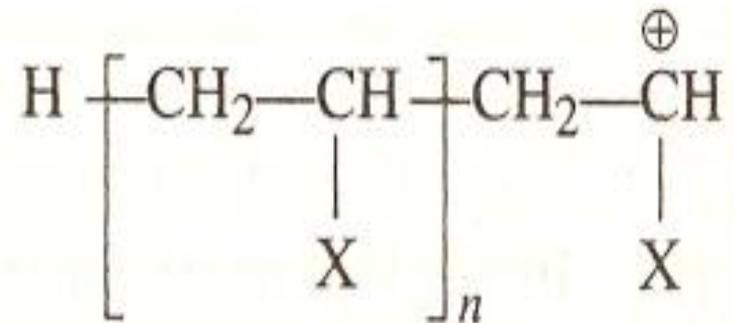
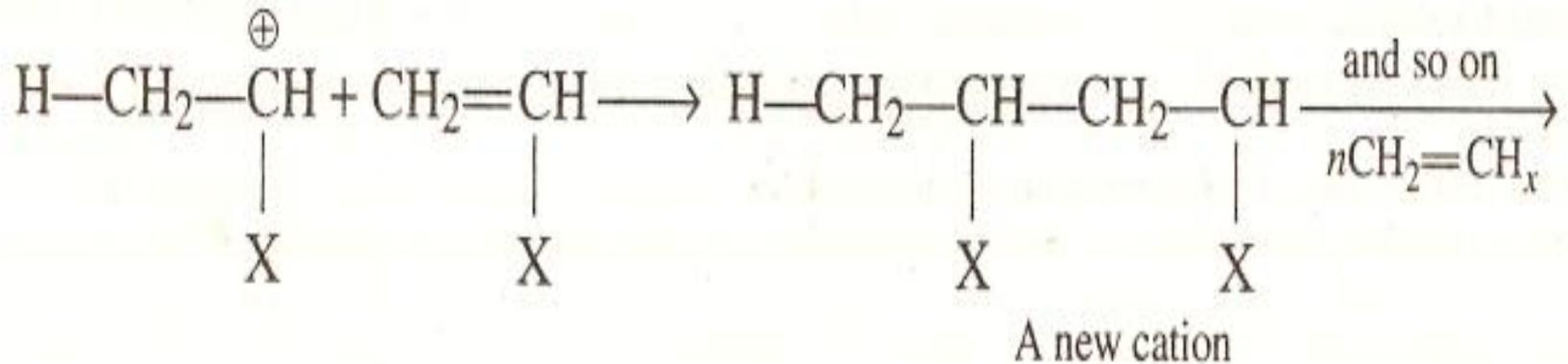
(ii) Cationic Polymerization: Cationic polymerization is initiated by acids and involves carbocationic centres. Monomers with electron-releasing substituents such as alkoxy or phenyl groups readily undergo this type of polymerization. The mechanism is as follows:

Initiation:



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Propagation :



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Termination :

