Kinetics and mechanism of Polymerization

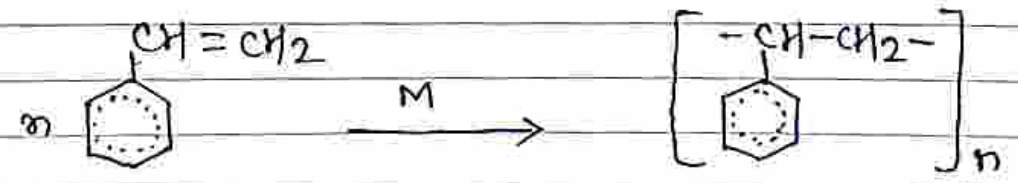
The polymerization reactions are classified into two categories

1. Addition Polymerization OR Chain Growth Polymerization.
2. Condensation Polymerization OR Step Growth Polymerization.

1. Addition Polymerization

A polymerization reaction in which monomers containing one or more double bonds are linked to each other without the elimination of any byproducts, usually in the presence of free radical initiator is called Addition polymerization.

Consider the Addition polymerization of Styrene in the presence of a suitable catalyst M.

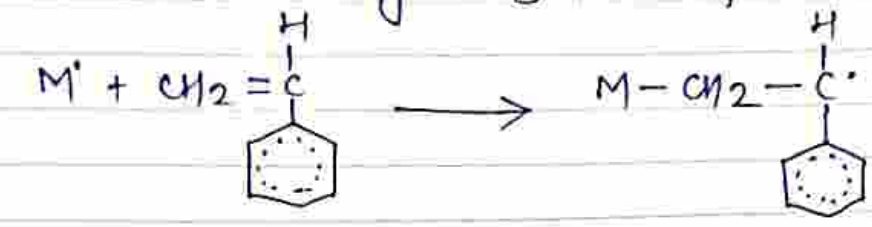


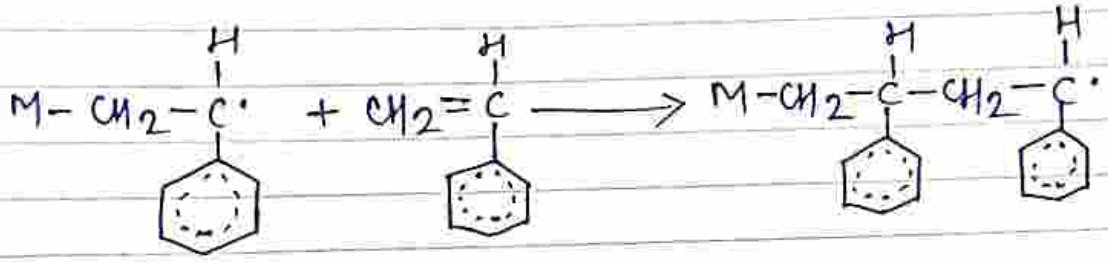
The mechanism of addition polymerization involves the production of a 'growth centre' which may be a free radical, a carbonium ion or a carbanion.

The step by step addition of monomeric molecules to a growth centre leads to a polymeric chain in which the length of the growth centre is

increased.

The following mechanism is suggested for the free radical polymerization of styrene.





and so on.

2. Condensation Polymerization.

A polymerization reaction in which bifunctional or polyfunctional monomers undergo intermolecular condensation leading to the formation of high molecular mass polymers with continuous elimination of byproducts, such as H_2O, HCl, NH_3 etc. is called condensation polymerization.

Nylons and Polyesters are the products of condensation polymerization. The former are polyamides having $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$ linkage where as the latter are polyesters having $-\overset{O}{\overset{\|}{C}}-O-$ linkage.

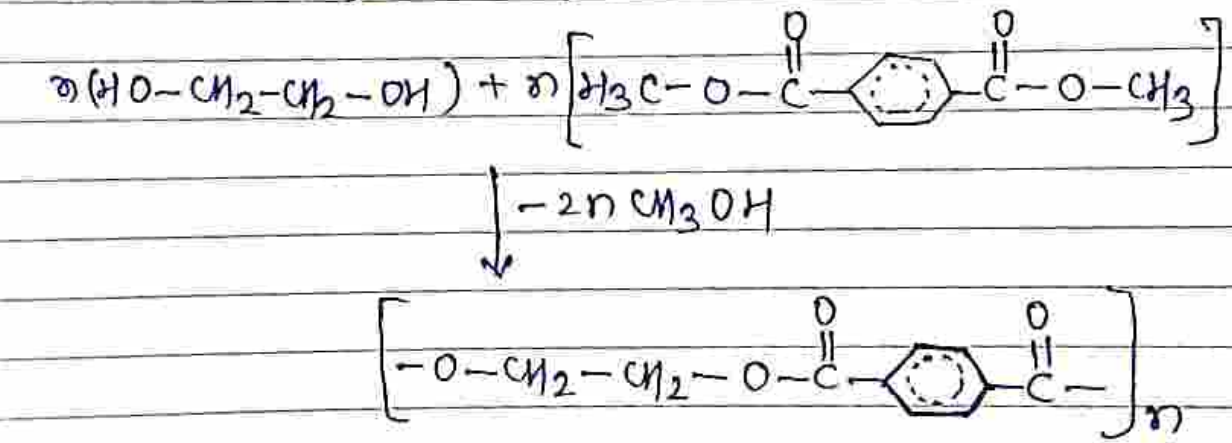
Nylon 6,6 is obtained by the polymerization of adipic acid and hexamethylene diamine.

$$n\left[NH_2-(CH_2)_6-NH_2\right] + n\left[HOOC-(CH_2)_4-COOH\right]$$

$$\Big\downarrow -2nH_2O$$

$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

The common variety of Polyester is called PET (Polyethylene terephthalate), terylene or dacron is synthesized by polymerizing ethylene glycol with dimethyl terephthalate.



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