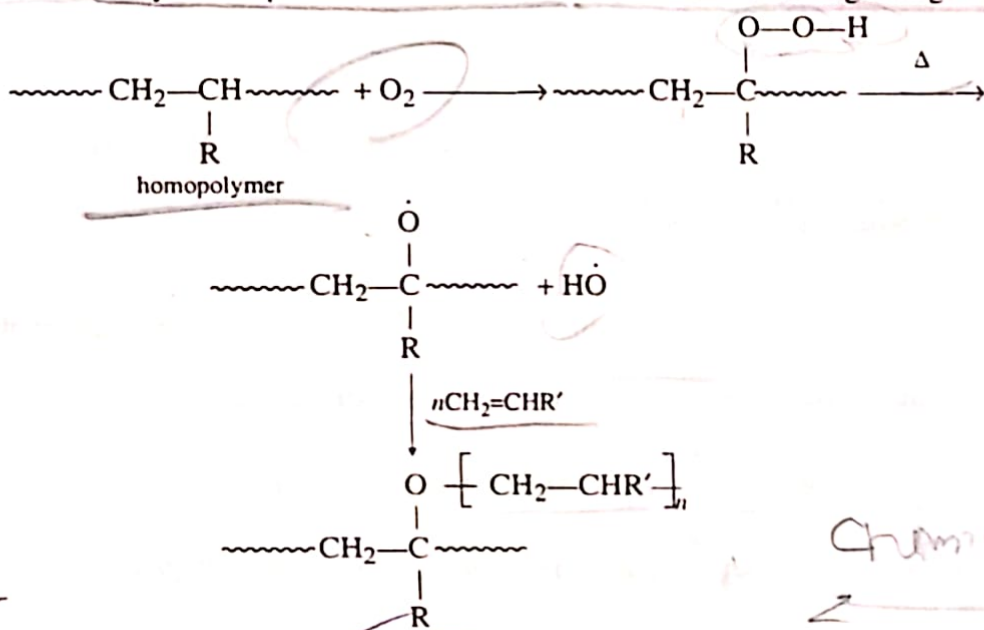


CH<sub>2</sub>—CHR' is grafted on the polymeric chain of ~~~~~CH<sub>2</sub>—CHR~~~~~. Grafting is invariably accompanied by formation of homopolymer of the monomer to be grafted. In irradiation grafting, an essentially similar process is involved except that the reactive sites on the polymeric substrate are created by irradiation with UV light.

In chemical grafting, reactive groups present along the polymer chain are used as sites for grafting. Both free radical and ionic reactions have been utilised in this technique. One method involves irradiation of the polymeric substrate in the presence of oxygen to produce peroxide groups which can be subsequently decomposed thermally in the presence of monomer to initiate free radical grafting. e.g.,



**1.4.4. Block Copolymer**

Block polymers have backbone consisting of fairly long sequences of different repeating units. These copolymers can be prepared by several techniques, of which anionic polymerisation offers the best possibilities for controlling the product. In this method the first step is to polymerise a single monomer, allowing reaction to proceed until, the monomer is exhausted. To the 'living polymer' is added a second monomer which then forms the second block. When the second monomer is exhausted a third monomer may be added, and so on. Many combinations of monomers have been investigated and a few block copolymers are now commercially available, e.g., the styrene-butadiene copolymer.

**1.5. POLYMER ISOMERISM**

Three types of isomerism are important in macromolecules. These involves constitutional, configurational and conformational isomerism.

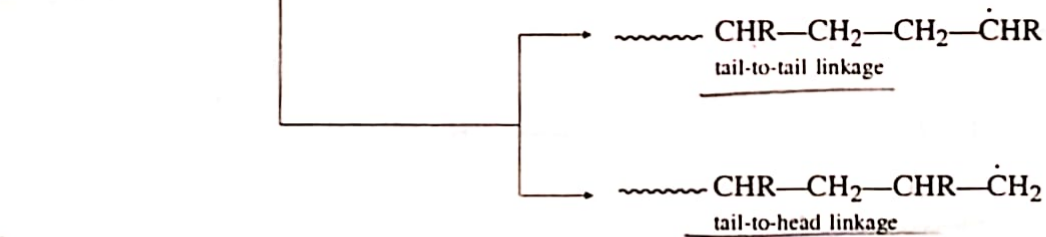
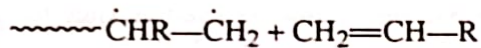
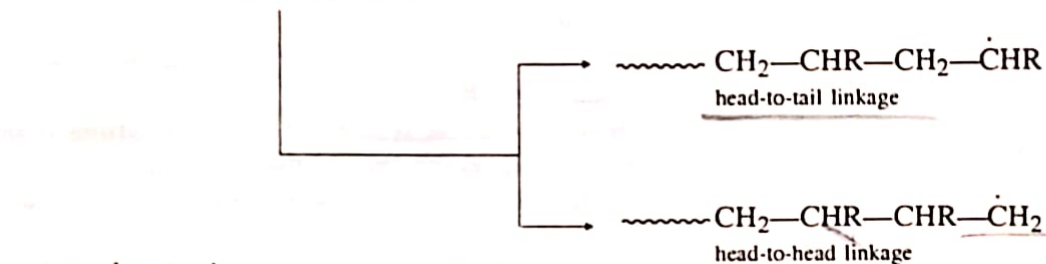


## Constitutional Isomerism

Positional isomerism and branching are the most important constitutional isomerism in macromolecules.

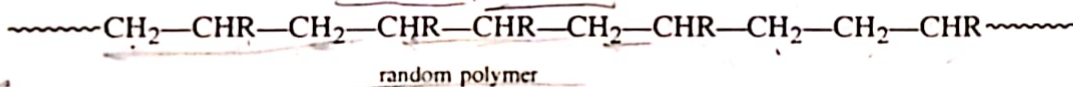
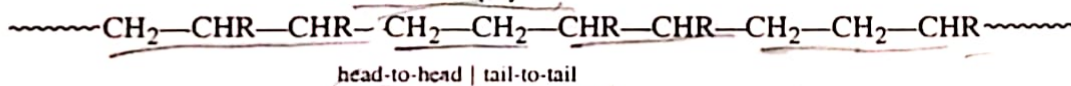
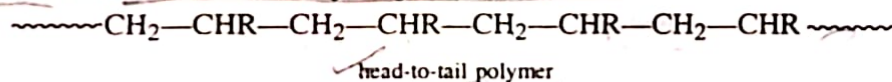
### 1.5.1. Positional Isomerism (Head-to-tail and head-to-head isomerism)

In vinyl polymerisations, the vinyl monomers are basically unsymmetrical because the two doubly bonded carbons are distinguishable. The more substituted doubly bonded carbon is known as head and the less substituted doubly bonded carbon is known as tail.



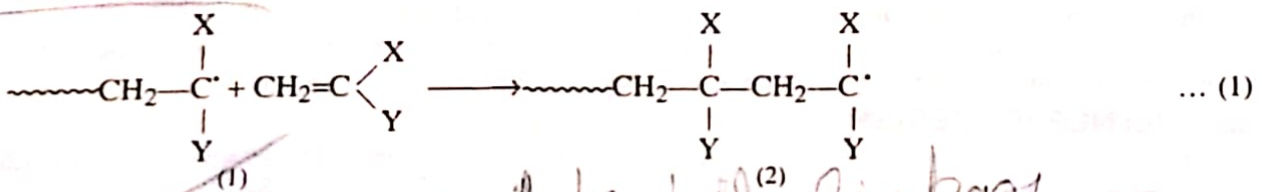
In principle, the monomers can be enchainment by head-to-tail, head-to-head, tail-to-tail or tail-to-head linkages.

In the above scheme, the tail-to-head linkage is equivalent to the head-to-tail linkage. Thus in theory, three arrangements are possible in the polymer, the linkage may be all head-to-tail, they may be alternately head-to-head and tail-to-tail or they may be mixed:



It follows that a polymer which contains head-to-head linkages must also contain tail-to-tail linkages and vice versa. All the vinyl polymers are mostly head-to-tail in their orientation because of the influence of resonance and steric effects.

Vinyl monomers polymerise by attack of an active center on the double bond. Equation (1) represents head-to-tail enchainment:



head to tail linkage