

**B.Sc. Semester-VI  
Organic Chemistry  
Paper-XIV**

**2. Synthetic Polymers**

Coverage:

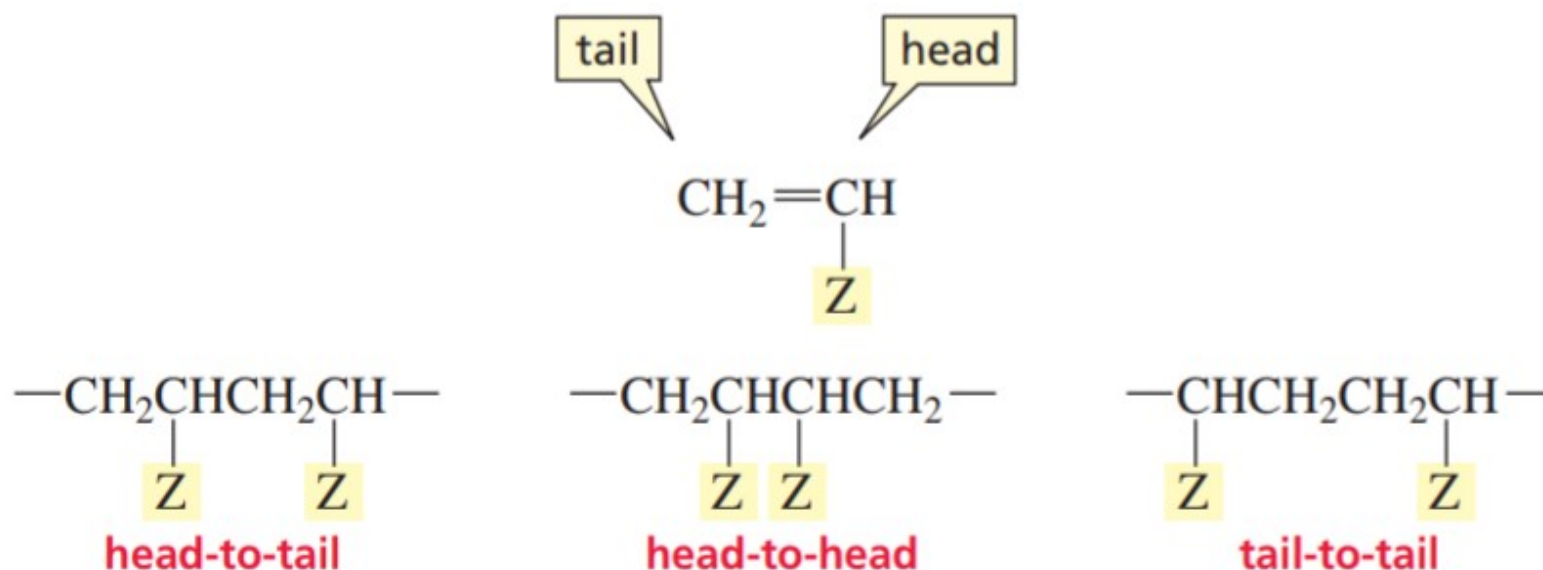
**6. Head-To-Tail Addition in Chain-Growth Polymerization**



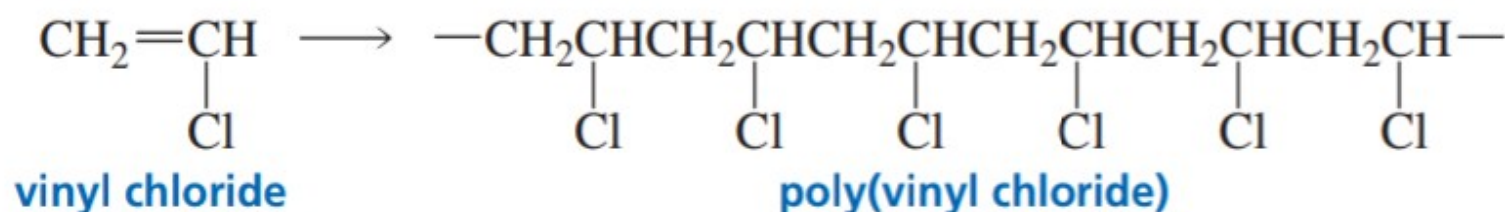
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## 6. Head-To-Tail Addition in Chain-Growth Polymerization

Chain-growth polymerization of monosubstituted ethylenes exhibits a marked preference for **head-to-tail addition**, where the head of one monomer is attached to the tail of another.

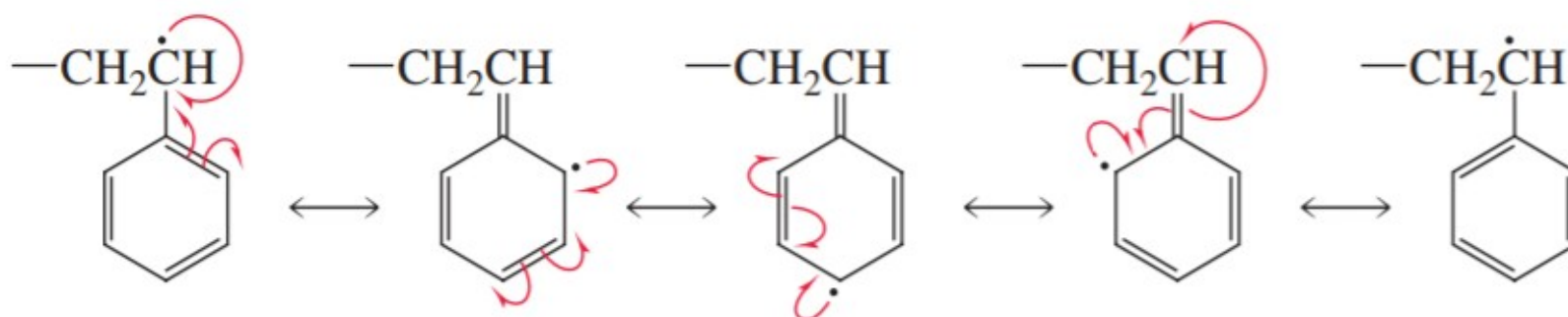


Head-to-tail addition of a substituted ethylene results in a polymer in which every other carbon bears a substituent.



Head-to-tail addition is favored for steric reasons because the propagating site preferentially attacks the less sterically hindered unsubstituted  $sp^2$  carbon of the alkene. Groups that stabilize radicals also favor head-to-tail addition. For example, when Z is a phenyl substituent, the benzene ring stabilizes the radical by electron delocalization, so the propagating site is the carbon that bears the phenyl substituent.





In cases where Z is small—which makes steric considerations less important—and is less able to stabilize the growing end of the chain by electron delocalization, some head-to-head addition and some tail-to-tail addition also occur. This has been observed primarily in situations where Z is fluorine. Abnormal addition, however, has never been found to constitute more than 10% of the overall chain.

A common feature of all radical initiators is a relatively weak bond that readily undergoes homolytic cleavage. In all but one of the radical initiators shown in Table 2, the weak bond is an oxygen–oxygen bond. Two factors enter into the choice of radical initiator for a particular chain-growth polymerization. The first is the desired solubility of the initiator. For example, potassium persulfate is often used if the initiator needs to be soluble in water, whereas an initiator with several carbons is chosen if the initiator must be soluble in a nonpolar solvent. The second factor is the temperature at which the polymerization reaction is to be carried out. For example, a *tert*-butoxy radical is relatively stable, so an initiator that forms a *tert*-butoxy radical is used for polymerizations carried out at relatively high temperatures.