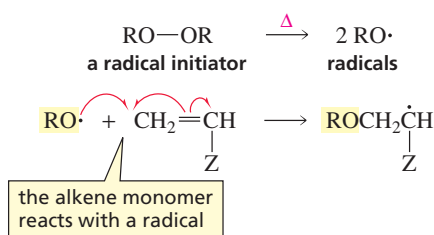


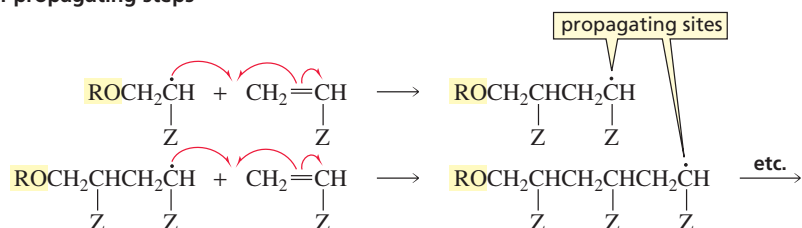
Radical Polymerization:

For chain-growth polymerization to occur by a radical mechanism, a radical initiator must be added to the monomer to convert some of the monomer molecules into radicals. The initiator breaks homolytically into radicals, and each radical adds to an alkene monomer, converting it into a radical. This radical reacts with another monomer, adding a new subunit that propagates the chain. The radical site is now at the end of the most recent unit added to the end of the chain. This is called the propagating site.

chain-initiating steps



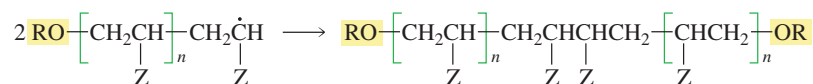
chain-propagating steps



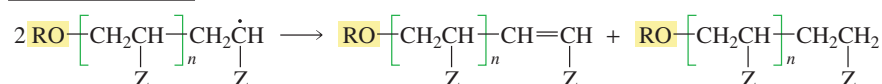
This process is repeated over and over. Hundreds or even thousands of alkene monomers can add one at a time to the growing chain. Eventually, the chain reaction stops because the propagating sites are destroyed. Propagating sites can be destroyed when two chains combine at their propagating sites; when two chains undergo *disproportionation*, with one chain being oxidized to an alkene and the other being reduced to an alkane; or when a chain reacts with an impurity that consumes the radical.

three ways to terminate the chain

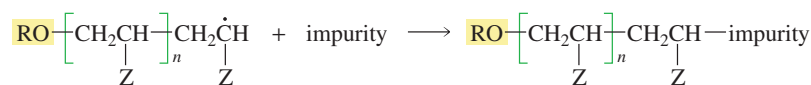
chain combination



disproportionation



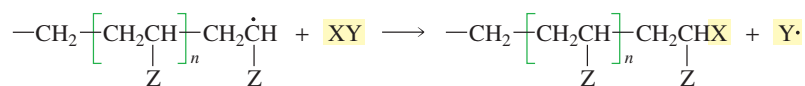
reaction with an impurity



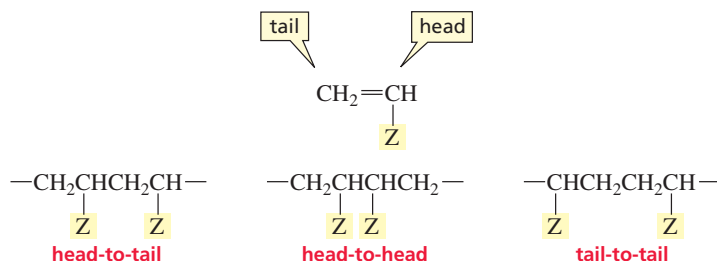
Thus, *radical polymerizations* have chain-initiating, chain-propagating, and chain-terminating steps similar to the steps that take place in the radical reactions discussed in Sections 4.10 and 9.2.

As long as the polymer has a high molecular weight, the groups at the ends of the polymer are relatively unimportant in determining its physical properties and are generally not even specified; it is the rest of the molecule that determines the properties of the polymer.

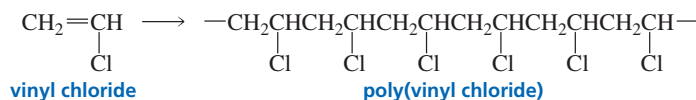
The molecular weight of the polymer can be controlled by a process known as **chain transfer**. In chain transfer, the growing chain reacts with a molecule XY in a manner that allows X• to terminate the chain, leaving behind Y• to initiate a new chain. XY can be a solvent, a radical initiator, or any molecule with a bond that can be cleaved homolytically.



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.

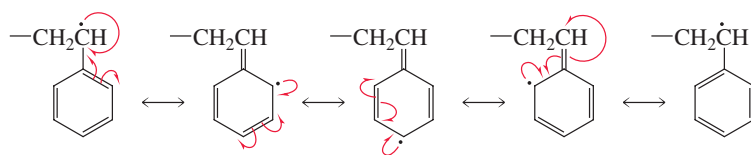


Head-to-tail addition of a substituted ethylene results in a polymer in which every other carbon bears a substituent.



3-D Molecules:
Vinyl chloride;
Poly(vinyl chloride)

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.

Monomers that most readily undergo chain-growth polymerization by a radical mechanism are those in which the substituent Z is able to stabilize the growing radical species by electron delocalization. Examples of monomers that undergo radical polymerization are shown in Table 28.2.

Table 28.2 Examples of Alkenes That Undergo Radical Polymerization

$\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CH}}$ styrene	$\text{CH}_2=\underset{\text{OCCH}_3}{\text{CH}}$ vinyl acetate	$\text{CH}_2=\underset{\text{COCH}_3}{\text{CCH}_3}$ methyl methacrylate
$\text{CH}_2=\underset{\text{Cl}}{\text{CH}}$ vinyl chloride	$\text{CH}_2=\underset{\text{C}\equiv\text{N}}{\text{CH}}$ acrylonitrile	$\text{CH}_2=\underset{\text{CH}=\text{CH}_2}{\text{CH}}$ 1,3-butadiene

PROBLEM 2 ♦

Which polymer would be more apt to contain abnormal head-to-head linkages: poly(vinyl chloride) or polystyrene?

PROBLEM 3

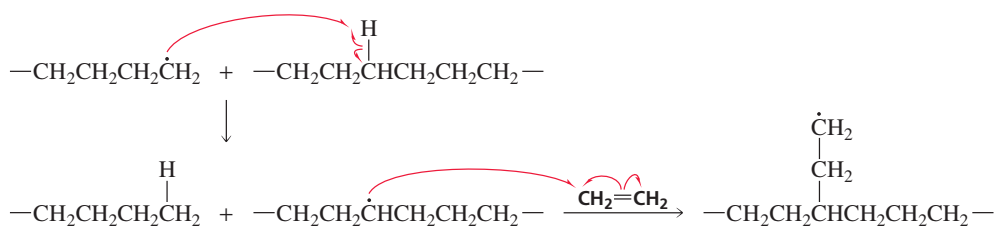
Draw a segment of polystyrene that contains abnormal head-to-head and tail-to-tail linkages.

PROBLEM 4

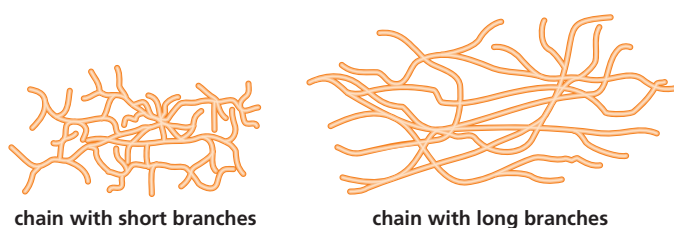
Show the mechanism for the formation of a segment of poly(vinyl chloride) containing three units of vinyl chloride and initiated by hydrogen peroxide.

Branching of the Polymer Chain

If the propagating site abstracts a hydrogen atom from a chain, a branch can grow off the chain at that point.



Abstraction of a hydrogen atom from a carbon near the end of a chain leads to short branches, whereas abstraction of a hydrogen atom from a carbon near the middle of a chain results in long branches. Short branches are more likely to be formed than long ones because the ends of the chain are more accessible.



Branching greatly affects the physical properties of the polymer. Linear unbranched chains can pack together more closely than branched chains can. Consequently, linear polyethylene (known as high-density polyethylene) is a relatively hard plastic, used for the production of such things as artificial hip joints, while branched polyethylene (low-density polyethylene) is a much more flexible polymer, used for trash bags and dry-cleaning bags.

Branched polymers are more flexible.

PROBLEM 5 ♦

Polyethylene can be used for the production of beach chairs and beach balls. Which of these items is made from more highly branched polyethylene?

PROBLEM 6

Draw a short segment of branched polystyrene that shows the linkages at the branch point.