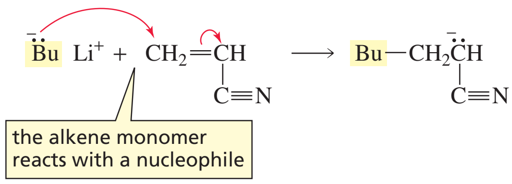
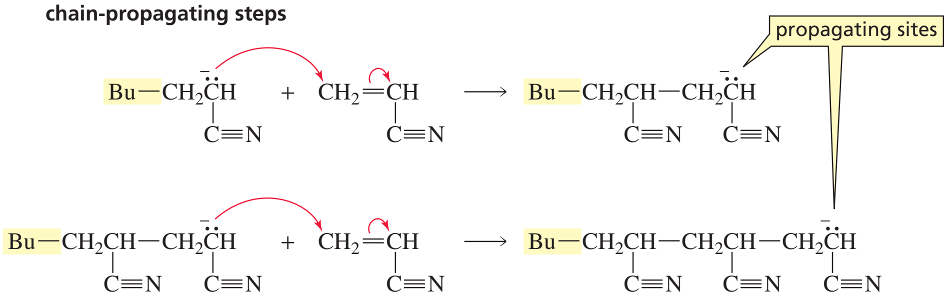
Anionic Polymerization

In anionic polymerization, the initiator is a nucleophile that reacts with the alkene to form a propagating site that is an anion. Nucleophilic attack on an alkene does not occur readily because alkenes are themselves electron rich. Therefore, the initiator must be a very good nucleophile, such as sodium amide or butyllithium, and the alkene must contain an electron-withdrawing substituent to decrease its electron density. Some alkenes that undergo polymerization by an anionic mechanism are shown in Table 28.5.

chain-initiating step



chain-propagating steps

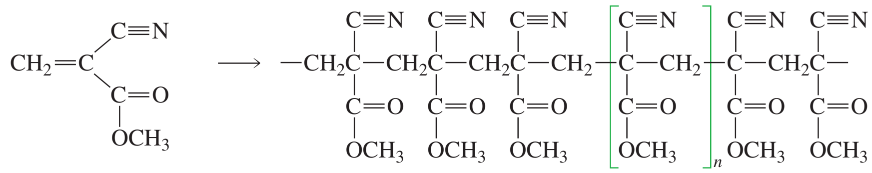


The chain can be terminated by a chain transfer reaction with the solvent or by reaction with an impurity in the reaction mixture. If the solvent cannot donate a proton to terminate the chain and if all impurities that can react with a carbanion are rigorously excluded, chain propagation will continue until all the monomer has been consumed. At this point, the propagating site will still be active, so the polymerization reaction will continue if more monomer is added to the system. Such nonterminated chains are called **living polymers** because the chains remain active until they are "killed." Living polymers usually result from anionic polymerization because the chains cannot be terminated by proton loss from the polymer, as they can in cationic polymerization, or by disproportionation or radical recombination, as they can in radical polymerization.

Super glue is a polymer of methyl α-cyanoacrylate. Because the monomer has two electron-withdrawing groups, it requires only a moderately good nucleophile to initiate anionic polymerization. An OH group of cellulose or a nucleophilic group of a protein can act as an initiator. You may well have experienced this reaction if you have ever spilled a drop of Super glue on your fingers. A nucleophilic group of the

Table 28.5 Examples of Alkenes That Undergo Anionic Polymerization

protein on the surface of the skin initiates the polymerization reaction, with the result that two fingers can become firmly glued together. The ability to form covalent bonds with groups on the surfaces of the objects to be glued together is what gives Super glue its amazing strength. Polymers similar to Super glue (they are butyl, isobutyl, or octyl esters rather than methyl esters) are used by surgeons to close wounds.

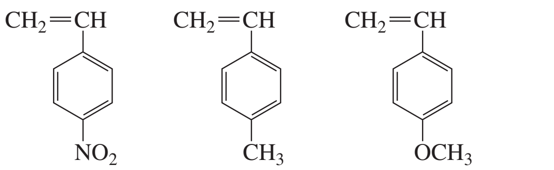


methyl α-cyanoacrylate **Super glue**

3-D Molecules:
Methyl α-cyanoacrylate;
Poly(methyl α-cyanoacrylate)

PROBLEM 8◆

List the following groups of monomers in order of decreasing ability to undergo anionic polymerization:

a. 

b. $CH_2{=}CHCH_3$ $CH_2{=}CHCl$ $CH_2{=}CHC{\equiv}N$

What Determines the Mechanism?

We have seen that the substituent on the alkene determines the best mechanism for chain-growth polymerization. Alkenes with substituents that can stabilize radicals readily undergo radical polymerization, alkenes with electron-donating substituents that can stabilize cations undergo cationic polymerization, and alkenes with electron-withdrawing substituents that can stabilize anions undergo anionic polymerizations.

Some alkenes undergo polymerization by more than one mechanism. For example, styrene can undergo polymerization by radical, cationic, and anionic mechanisms because the phenyl group can stabilize benzylic radicals, benzylic cations, and benzylic anions. The particular mechanism followed for the polymerization of styrene depends on the nature of the initiator chosen to start the reaction.