

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

2. Synthetic Polymers

Coverage:

9. Anionic Polymerization: Mechanism and Examples



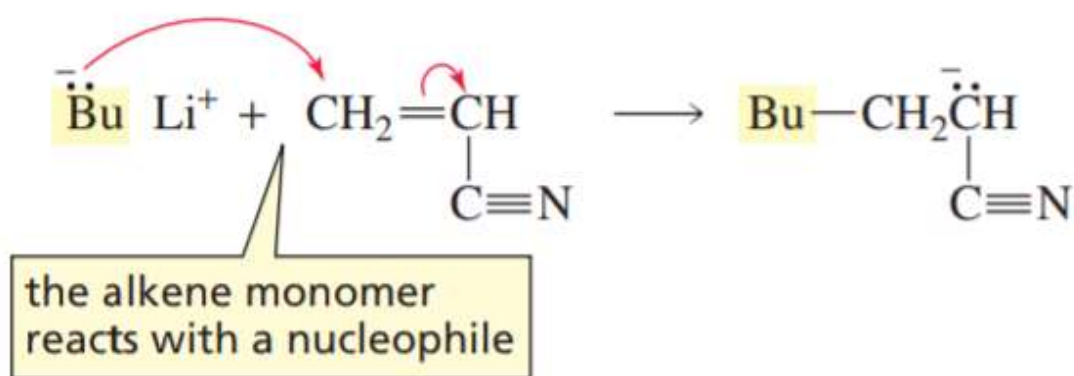
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9. Anionic Polymerization

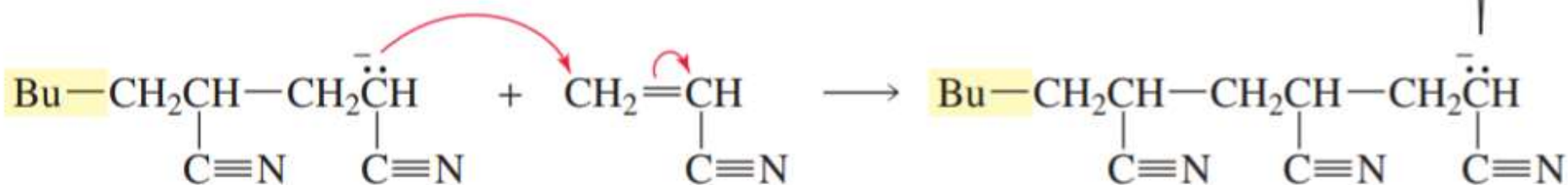
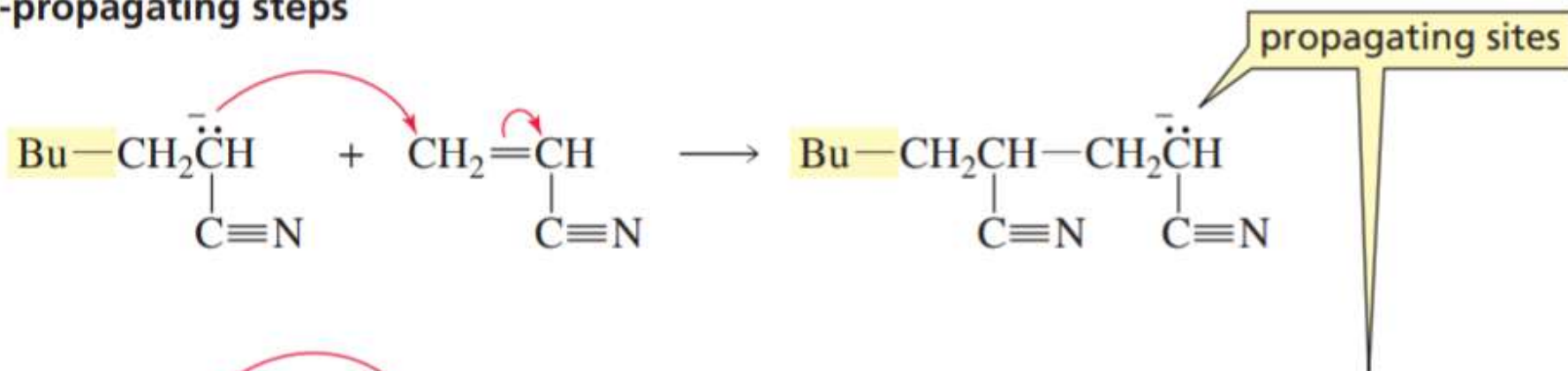
In anionic polymerization, the initiator is a nucleophile that reacts with the alkene to form a propagating site that is an anion. Nucleophilic attack on an alkene does not occur readily because alkenes are themselves electron rich. Therefore, the initiator must be a very good nucleophile, such as sodium 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 4.

Mechanism:

chain-initiating step



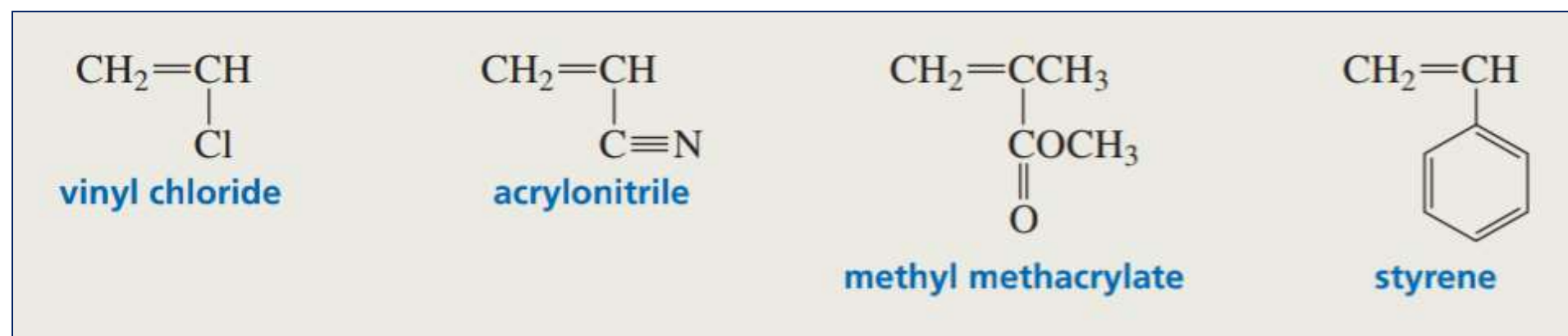
chain-propagating steps



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 4: 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.

