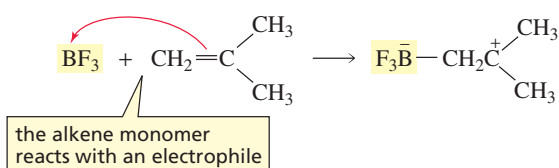


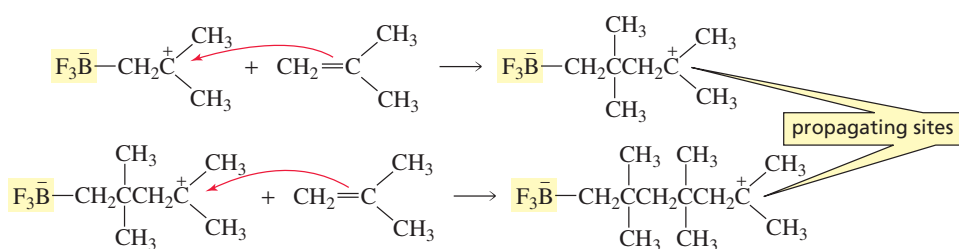
Cationic Polymerization

In cationic polymerization, the initiator is an electrophile that adds to the alkene, causing it to become a cation. The initiator most often used in cationic polymerization is a Lewis acid, such as BF_3 or AlCl_3 . The advantage of such an initiator is that it does not have an accompanying nucleophile that could act as a chain terminator, as would be the case with a proton-donating acid such as HCl . The cation formed in the initiation step reacts with a second monomer, forming a new cation that reacts in turn with a third monomer. As each subsequent monomer adds to the chain, the positively charged propagating site always ends up on the last unit added.

chain-initiating step



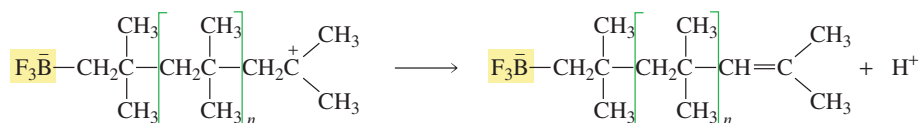
chain-propagating steps



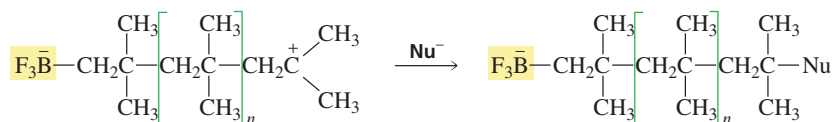
Cationic polymerization can be terminated by loss of a proton or by addition of a nucleophile that reacts with the propagating site. The chain can also be terminated by a chain-transfer reaction with the solvent (XY).

three ways to terminate the chain

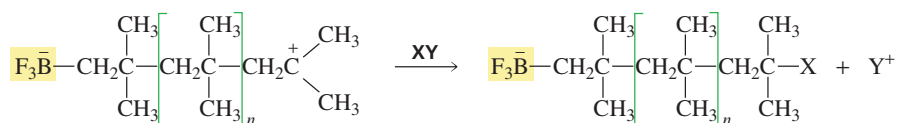
loss of a proton



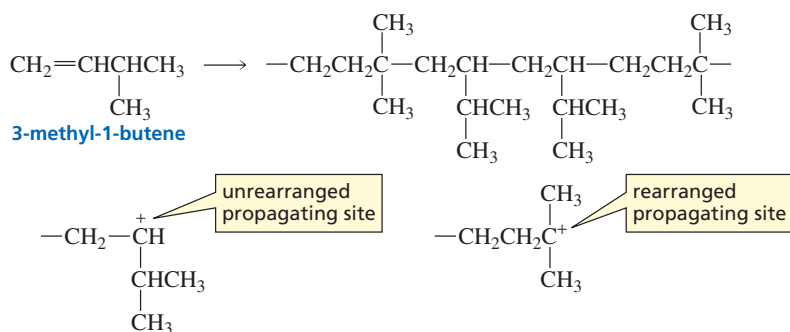
reaction with a nucleophile



chain-transfer reaction with the solvent



The carbocation intermediates formed during cationic polymerization, like any other carbocations, can undergo rearrangement by either a 1,2-hydride shift or a 1,2-methyl shift if rearrangement leads to a more stable carbocation (Section 4.6). For example, the polymer formed from the cationic polymerization of 3-methyl-1-butene contains both unrearranged and rearranged units. The unrearranged propagating site is a secondary carbocation, whereas the rearranged propagating site—obtained by a 1,2-hydride shift—is a more stable tertiary carbocation. The extent of rearrangement depends on the reaction temperature.



Monomers that are best able to undergo polymerization by a cationic mechanism are those with substituents that can stabilize the positive charge at the propagating site by donating electrons inductively or by resonance. Examples of monomers that undergo cationic polymerization are given in Table 28.4.

Table 28.4 Examples of Alkenes That Undergo Cationic Polymerization

$\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}$ <p>propylene</p>	$\text{CH}_2=\underset{\text{CH}_3}{\text{CCH}_3}$ <p>isobutylene</p>	$\text{CH}_2=\underset{\text{OCCH}_3}{\text{CH}}$ <p>vinyl acetate</p>	$\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CH}}$ <p>styrene</p>
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PROBLEM 7 ♦

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

- a. $\text{CH}_2=\underset{\text{NO}_2}{\text{CH}}$ $\text{CH}_2=\underset{\text{CH}_3}{\text{CH}}$ $\text{CH}_2=\underset{\text{OCH}_3}{\text{CH}}$
- b. $\text{CH}_2=\text{CHCH}_3$ $\text{CH}_2=\underset{\text{O}}{\text{CHO}}\text{CCH}_3$ $\text{CH}_2=\underset{\text{O}}{\text{CHCO}}\text{CH}_3$
- c. $\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CH}}$ $\text{CH}_2=\underset{\text{C}_6\text{H}_5}{\text{CCH}_3}$