

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

**2. Synthetic Polymers**

**Coverage:**

- 8. (i) Cationic Polymerization: Mechanism and Examples  
(ii) Rearrangement of Carbocations in Cationic Polymerization**



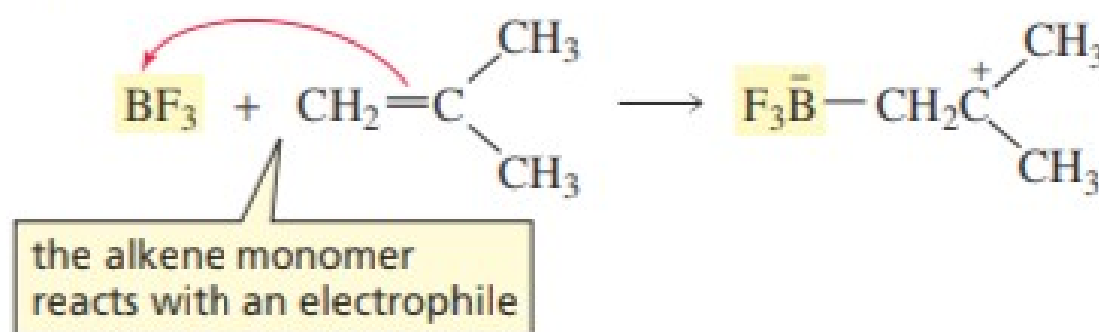
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## 8. (i) Cationic Polymerization

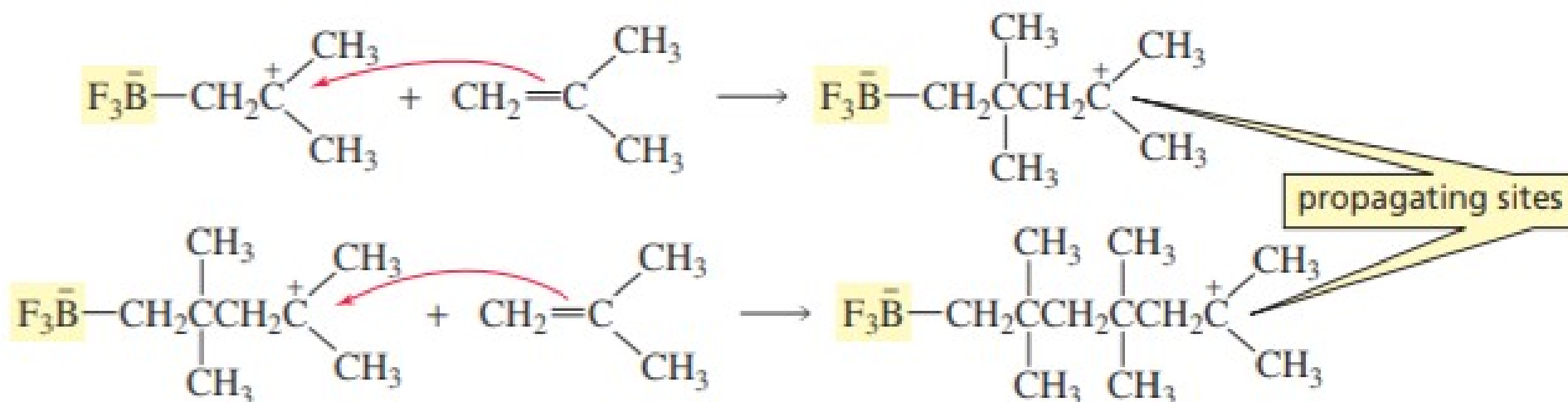
In cationic polymerization, the initiator is an electrophile that adds to the alkene, causing it to become a cation. The initiator most often used in cationic polymerization is a Lewis acid, such as  $\text{BF}_3$  or  $\text{AlCl}_3$ . The advantage of such an initiator is that it does not have an accompanying nucleophile that could act as a chain terminator, as would be the case with a proton-donating acid such as  $\text{HCl}$ . 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.

### Mechanism:

#### chain-initiating step



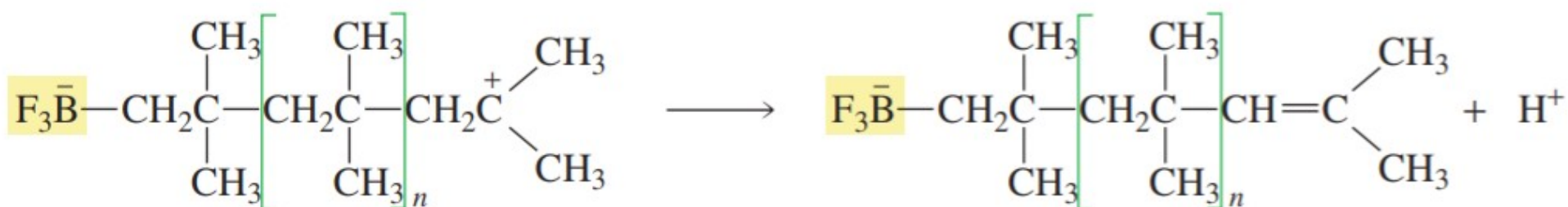
#### chain-propagating steps



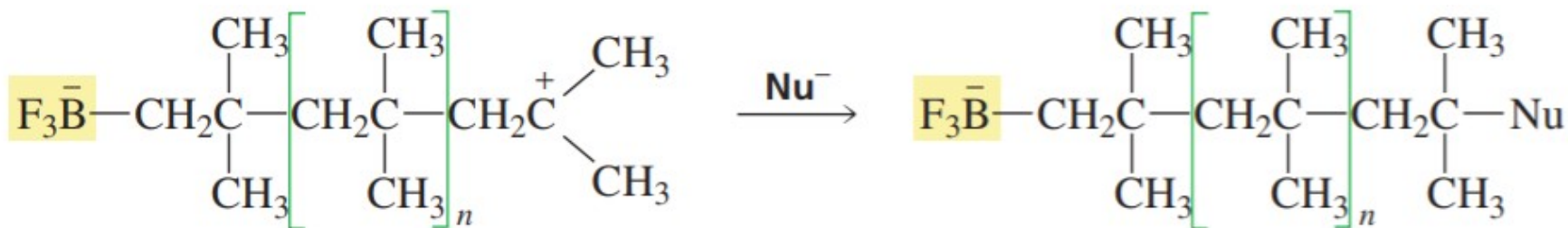
Cationic polymerization can be terminated by loss of a proton or by addition of a nucleophile that reacts with the propagating site. The chain can also be terminated by a chain-transfer reaction with the solvent (XY).

### three ways to terminate the chain

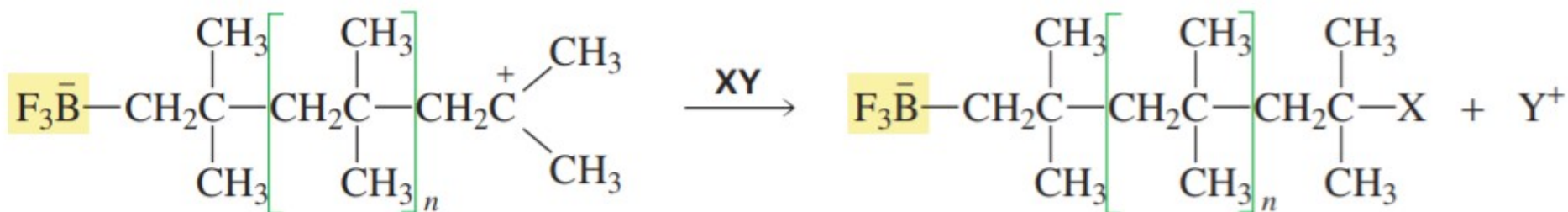
loss of a proton



reaction with a nucleophile



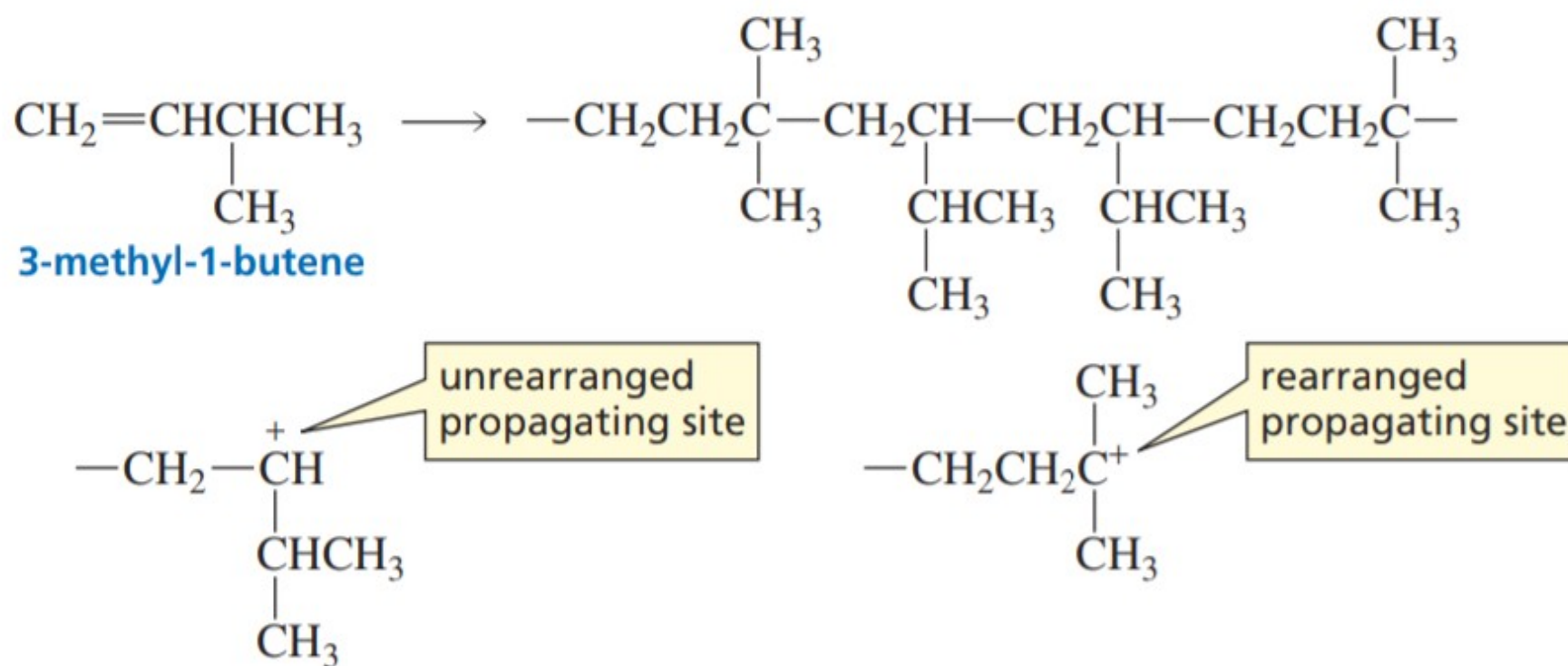
chain-transfer reaction with the solvent





## 8. (ii) Rearrangement of Carbocations in Cationic Polymerization

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 3.

**Table 3: Examples of Alkenes That Undergo Cationic Polymerization**

