The use of high resolution proton and ^{13}C NMR makes clear that the extent of rearrangement has previously not been fully understood. Five different repeating units, derived from carbenium ions **XV–XVIII**, are found in the polymer from 4-methyl-1-butene [46]. The first-formed carbenium ion **XIV** undergoes hydrogen shifts to form carbenium ions **XV**, **XVI**, and **XVIII**; **XVI** rearranges to **XVII** by a methyl shift. Carbenium ion **XVIII**, being the most-stable carbenium ion, is found in the greatest abundance. The other carbenium ions are of about equal stability
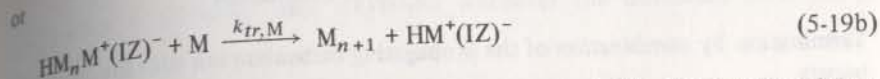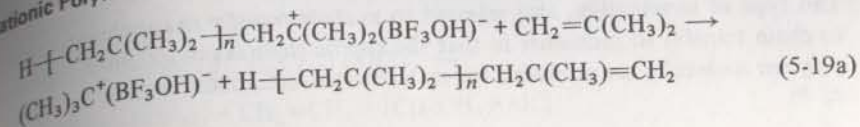

$$
\begin{array}{ccc}
CH_2{=}CH & & \\
\ \ \ \ \ | & & \\
\ \ CH_2CH(CH_3)_2 & &
\end{array}
$$

(5-18a)

(5-18b)

(5-18c)
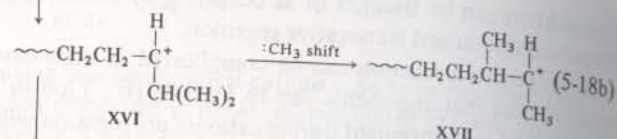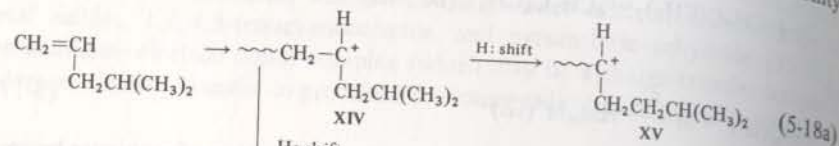
and the repeating units derived from them are found in comparable amounts. Other monomers which undergo isomerization–polymerization include 1-butene, 5-methyl-1-hexene, 6-methyl-1-heptene, 4,4-dimethyl-1-pentene, α- and β-pinene [47,48]. One generally finds that the first-formed carbenium ion undergoes hydrogen or methyl shifts whenever these lead to carbenium ions of equal or greater stability.

5-2c Termination

Various reactions lead to termination of chain growth in cationic polymerization [2–5,49]. Most reactions which terminate the growth of a propagating chain do not, however, terminate the kinetic chain because a new propagating species is formed in the process.
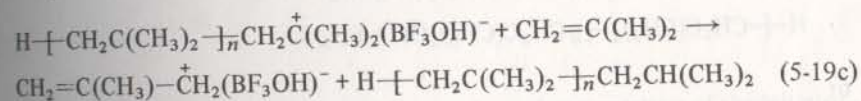
5-2c-1 Chain Transfer to Monomer

Chain transfer to monomer is one of the most common chain-breaking reactions for many monomers. There are few polymerizations where it does not occur. Transfer to monomer usually involves transfer of a proton to a monomer molecule with the formation of terminal unsaturation in the polymer molecule

$$H{-}[CH_2C(CH_3)_2{-}]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- + CH_2{=}C(CH_3)_2 \longrightarrow$$

$$(CH_3)_3C^+(BF_3OH)^- + H{-}[CH_2C(CH_3)_2{-}]_n CH_2C(CH_3){=}CH_2 \quad (5\text{-}19a)$$

or

$$HM_nM^+(IZ)^- + M \xrightarrow{\ k_{tr,M}\ } M_{n+1} + HM^+(IZ)^- \quad (5\text{-}19b)$$

It should be noted that the kinetic chain is not terminated by this reaction since a new propagating species is regenerated. Many polymer molecules are usually produced for each initiator–coinitiator species present. Chain transfer to monomer is on much more favorable terms with propagation in many cationic polymerizations compared to radical polymerization. Since it is kinetically indistinguishable from propagation, the relative rates of transfer and propagation are given by the ratio $k_{tr,M}/k_p$, which is the chain transfer constant for monomer C_M. The value of C_M determines the molecular weight of the polymer if other chain-breaking processes are not significant. The larger the value of C_M the lower will be the molecular weight.
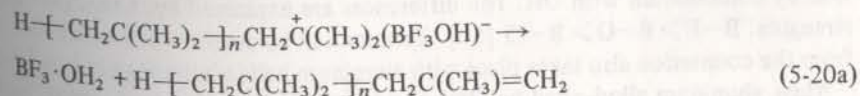
Another type of chain transfer to monomer reaction that may be important is that involving a hydride ion abstraction from the monomer by the propagating species [50]

$$H{-}[CH_2C(CH_3)_2{-}]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- + CH_2{=}C(CH_3)_2 \longrightarrow$$

$$CH_2{=}C(CH_3){-}\overset{+}{C}H_2(BF_3OH)^- + H{-}[CH_2C(CH_3)_2{-}]_n CH_2CH(CH_3)_2 \quad (5\text{-}19c)$$
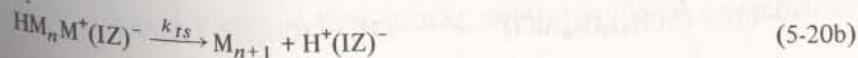
Hydride abstraction by monomer is less likely a mode of termination compared to proton transfer to monomer, since the carbenium ion in the latter case is the more stable one. The two types of chain transfer to monomer reactions are kinetically indistinguishable but one (Eq. 5-19a) yields an unsaturated end group, while the other (Eq. 5-19c) yields a saturated end group.

5-2c-2 Spontaneous Termination

Termination can also take place by rearrangement of the propagating ion pair. *Spontaneous termination* involves regeneration of the initiator–coinitiator complex by expulsion from the propagating ion pair with the polymer molecule left with terminal unsaturation.

$$H{-}[CH_2C(CH_3)_2{-}]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- \longrightarrow$$

$$BF_3\cdot OH_2 + H{-}[CH_2C(CH_3)_2{-}]_n CH_2C(CH_3){=}CH_2 \quad (5\text{-}20a)$$

or, in more general terms,

$$HM_nM^+(IZ)^- \xrightarrow{\ k_{ts}\ } M_{n+1} + H^+(IZ)^- \quad (5\text{-}20b)$$
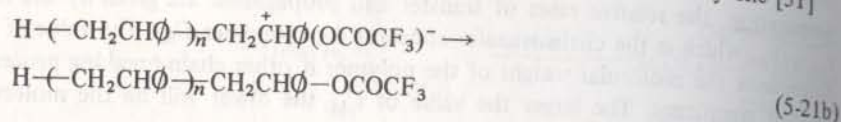
This type of termination, also referred to as *chain transfer to counterion*, is similar to chain transfer to monomer in that the kinetic chain is not terminated and many polymer molecules are produced for each initiator-coinitiator species.
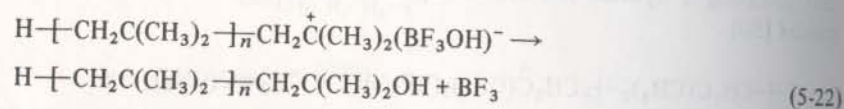
5-2c-3 Combination with Counterion

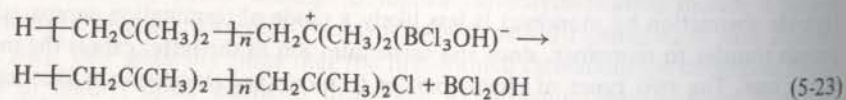Termination by *combination* of the propagating carbenium ion with the counterion occurs

$$HM_nM^+(IZ)^- \xrightarrow{k_t} HM_nMIZ \tag{5-21a}$$

for example, in the trifluoroacetic acid catalyzed polymerization of styrene [51]

$$H \text{---}(CH_2CH\phi)_{\overline{n}} CH_2\overset{+}{C}H\phi(OCOCF_3)^- \longrightarrow$$

$$H \text{---}(CH_2CH\phi)_{\overline{n}} CH_2CH\phi\text{---}OCOCF_3 \tag{5-21b}$$

Alternately, the propagating ion may combine with an anionic fragment from the gegenion, for example

$$H \text{---}(CH_2C(CH_3)_2)_{\overline{n}} CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- \longrightarrow$$

$$H \text{---}(CH_2C(CH_3)_2)_{\overline{n}} CH_2C(CH_3)_2OH + BF_3 \tag{5-22}$$

or

$$H \text{---}(CH_2C(CH_3)_2)_{\overline{n}} CH_2\overset{+}{C}(CH_3)_2(BCl_3OH)^- \longrightarrow$$

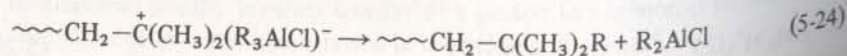$$H \text{---}(CH_2C(CH_3)_2)_{\overline{n}} CH_2C(CH_3)_2Cl + BCl_2OH \tag{5-23}$$
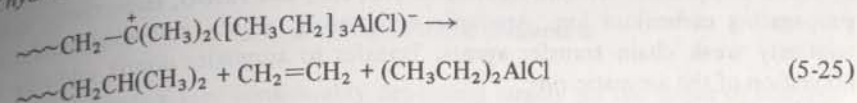
Termination by combination differs from the other modes of termination in that the kinetic chain is usually terminated (as well as the degree of polymerization), since the concentration of the initiator-coinitiator complex decreases.

Equations 5-22 and 5-23 indicate the complexity of cationic polymerization even when seemingly similar initiators such as BCl₃ and BF₃ are used. Termination in the BCl₃-initiated polymerizations of isobutylene and styrene occurs almost exclusively by combination with chloride [9]. For BF₃-initiated polymerization, chain transfer to monomer is the major mode of termination with a minor contribution by combination with OH. The differences are explained by the order of bond strengths: B—F > B—O > B—Cl [52]. Termination by combination with halide ion from the counterion also takes place with aluminum halide-initiating systems [10]. When aluminum alkyl-alkyl halide initiator-coinitiators systems are used, termination occurs by combination [10,11,15], either by *alkylation*,

$$\sim\sim\sim CH_2\text{---}\overset{+}{C}(CH_3)_2(R_3AlCl)^- \longrightarrow \sim\sim CH_2\text{---}C(CH_3)_2R + R_2AlCl \tag{5-24}$$

or *hydridation*,

$$\sim\sim\sim CH_2\text{---}\overset{+}{C}(CH_3)_2([CH_3CH_2]_3AlCl)^- \longrightarrow$$

$$\sim\sim\sim CH_2CH(CH_3)_2 + CH_2{=}CH_2 + (CH_3CH_2)_2AlCl \tag{5-25}$$

Hydridation is preferred over alkylation whenever the aluminum alkyl has β-hydrogens.

5-2c-4 Backbiting

Intramolecular electrophilic aromatic substitution by a *backbiting* mechanism occurs in the polymerization of styrene and most other aromatic monomers


$$\tag{5-26}$$
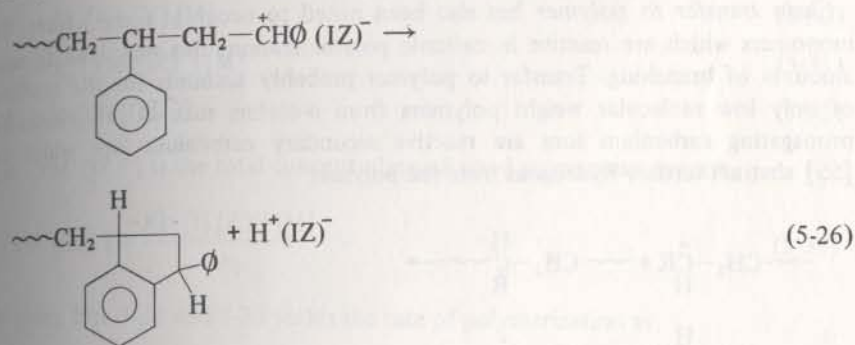
with the formation of a terminal indanyl structure and regeneration of the initiator-coinitiator complex [23,53].

Some branching (and, possibly, crosslinking) has been detected in the polymerization of anethole (β-methyl-p-methoxystyrene), indicating intermolecular substitution by a propagating carbenium ion on the aromatic ring of another polymer chain [23].

5-2c-5 Other Chain Transfer Reactions

In addition to chain transfer to monomer, one or more of other transfer reactions may be important in any specific polymerization system. Various transfer agents (denoted by S or XA as in Chap. 3), present as a solvent, impurity or deliberately added to the system, can terminate the growing polymer chain by transfer of a negative fragment A⁻

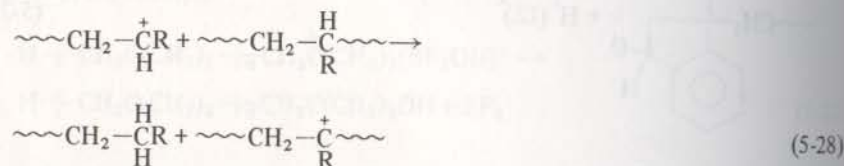$$HM_nM^+(IZ)^- + XA \xrightarrow{k_{tr,S}} HM_nMA + X^+(IZ)^- \tag{5-27}$$
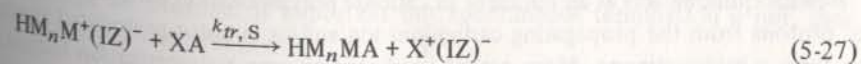
Water, alcohols, acids, anhydrides, and esters have varying chain transfer properties [54]. The presence of any of these transfer agents in sufficient concentrations

results in Reaction 5-27 becoming the dominant mode of termination. Termination by these compounds involves transfer of HO, RO, and RCOO, respectively, to the propagating carbenium ion. Aromatic compounds, ethers, and alkyl halides are relatively weak chain transfer agents. Transfer to aromatics occurs primarily by alkylation of the aromatic ring.

Although a chain transfer agent decreases the degree of polymerization in proportion to its concentration (see Sec. 5-2d-1), it is not expected to affect the polymerization rate since the initiator–coinitiator complex should be regenerated upon transfer (Eq. 5-27). However, one finds that the more active transfer agents such as water do affect the polymerization rate, since they also function as inhibitors. As indicated in Sec. 5-2a-2 the polymerization rate is usually observed to increase with increasing initiator concentration (at constant coinitiator concentration), reach a maximum, and then either decrease or level off.

Chain transfer to polymer has also been noted to occur to some extent. For monomers which are reactive in cationic polymerization, this may lead to small amounts of branching. Transfer to polymer probably accounts for the synthesis of only low molecular weight polymers from α-olefins such as propylene. The propagating carbenium ions are reactive secondary carbenium ions which can [55] abstract tertiary hydrogens from the polymer

$$\text{\sim\sim}CH_2-\overset{+}{\underset{H}{C}}R + \text{\sim\sim}CH_2-\overset{H}{\underset{R}{C}}\text{\sim\sim} \longrightarrow$$

$$\text{\sim\sim}CH_2-\overset{H}{\underset{H}{C}}R + \text{\sim\sim}CH_2-\overset{+}{\underset{R}{C}}\text{\sim\sim} \qquad (5\text{-}28)$$

5-2c-6 Retardation

Certain substances such as amines, triaryl or trialkylphosphines, and thiophene act as inhibitors or retarders of cationic polymerization. Termination by amines involves formation of stable quaternary ions which are unreactive to propagation [56], for example,

$$HM_nM^+(IZ)^- + :NR_3 \longrightarrow HM_n\overset{+}{M}NR_3(IZ)^- \qquad (5\text{-}29)$$
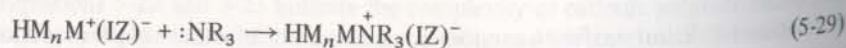
Thiophene and phosphines act similarly. (Phosphines have been advantageously used to convert propagating carbenium ions to highly stable phosphonium ions which can be observed with ^{31}P NMR [57].)

p-Benzoquinone acts as an inhibitor in cationic polymerization because of transfer of protons from the propagating carbenium ion and/or initiator-protonated species to form *p*-hydroquinone. More recent work for styrene polymerization indicates that copolymerization between *p*-benzoquinone and styrene is also important in explaining the inhibiting effect of *p*-benzoquinone [58b].

5-2d Kinetics

5-2d-1 Different Kinetic Situations

The overall kinetics vary considerably depending largely on the mode of termination in a particular system. Consider the case of termination by combination of the propagating ion pair with the counterion (Eq. 5-21). The kinetic scheme of initiation, propagation, and termination consists of Eqs. 5-3, 5-4, 5-17, and 5-21, respectively. The derivation of the rate expression for this polymerization under steady-state conditions ($R_i = R_t$) follows in a manner analogous to that used in radical polymerization (Sec. 3-3b). The rates of initiation, propagation, and termination are given by

$$R_i = Kk_i[I][ZY][M] \qquad (5\text{-}30)$$

$$R_p = k_p[YM^+(IZ)^-][M] \qquad (5\text{-}31)$$

$$R_t = k_t[YM^+(IZ^-)] \qquad (5\text{-}32)$$

where $[YM^+(IZ)^-]$ is the total concentration all sized propagating centers,

$$[YM^+(IZ)^-] = \frac{Kk_i[I][ZY][M]}{k_t} \qquad (5\text{-}33)$$

Combining Eqs. 5-31 and 5-33 yields the rate of polymerization as

$$R_p = \frac{R_i k_p[M]}{k_t} = \frac{Kk_i k_p[I][ZY][M]^2}{k_t} \qquad (5\text{-}34)$$

The number-average degree of polymerization is obtained as the propagation rate divided by the termination rate

$$\overline{X}_n = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} \qquad (5\text{-}35)$$

When chain breaking involves chain transfer to monomer (Eq. 5-19) and/or spontaneous termination (Eq. 5-20) in addition to combination with the gegenion, the concentration of propagating species remains unchanged and the polymerization rate is again given by Eq. 5-34. However, the degree of polymerization is decreased by these other chain-breaking reactions and is given by the polymerization rate divided by the sum of all chain-breaking reactions. For example, when chain transfer to monomer is important but spontaneous termination is not, the degree of polymerization is given by

$$\overline{X}_n = \frac{R_p}{R_t + R_{tr,M}} \qquad (5\text{-}36)$$