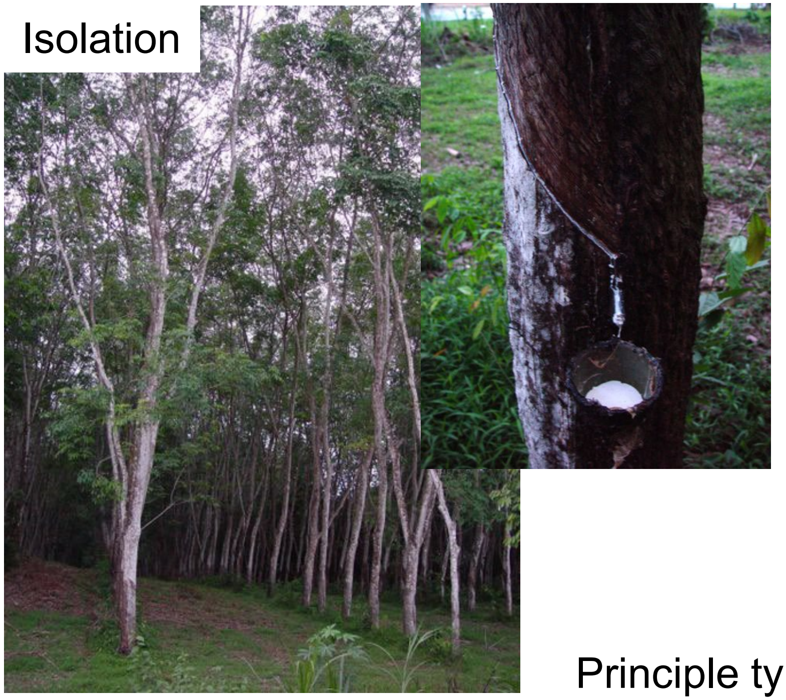
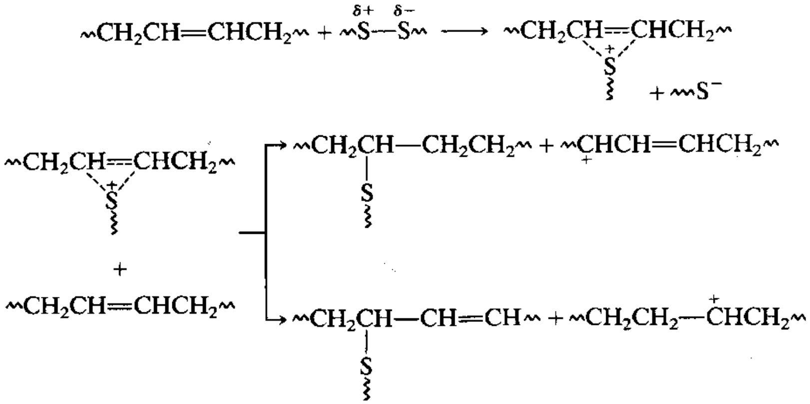
# How to Make Synthetic Rubber ?!

## Natural Rubber:

Isolation

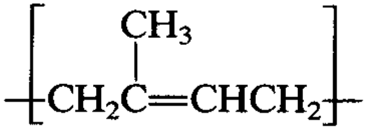


Vulcanization



Principle types of natural rubber

1,4-Polyisoprene

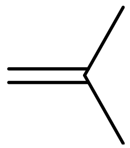


$$-\!\left[ CH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2 \right]\!-$$

| *Name* | *Isoprene Structure* | *Principal Uses* |
|---|---|---|
| Hevea | *cis*-1,4 | Tires, footwear, weather stripping, shock absorbers, sports accessories |
| Guayule | *cis*-1,4 | Latex gloves |
| Gutta percha | *trans*-1,4 | Wire coatings, textile belting, varnishes, orthopedic devices |
| Balata | *trans*-1,4 | Wire coatings, textile belting, varnishes |
| Chicle | *cis*- and *trans*-1,4 | Chewing gum |

# Synthetic Rubber

Isobutylene

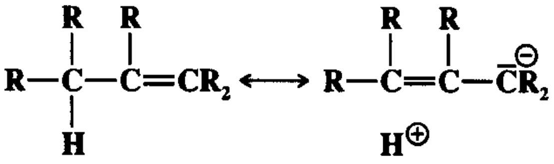


Monomers: Isobutylene + small amounts of isoprene

*How can these be polymerized?*

Radical polymerization of olefins and 1,1-disubstituted alkenes is unfavorable due to:

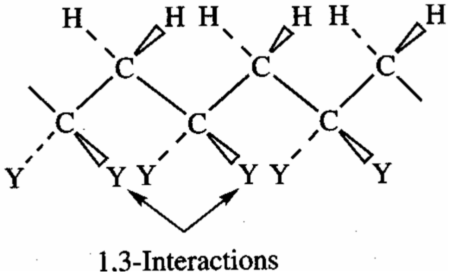
(1) Stabilization of the monomer due to hyperconjugation



$$R-\underset{H}{\overset{R}{C}}-\overset{R}{C}=CR_2 \longleftrightarrow R-\underset{H^{\oplus}}{\overset{R}{C}}=\overset{R}{C}-\overset{\ominus}{\bar{C}}R_2$$

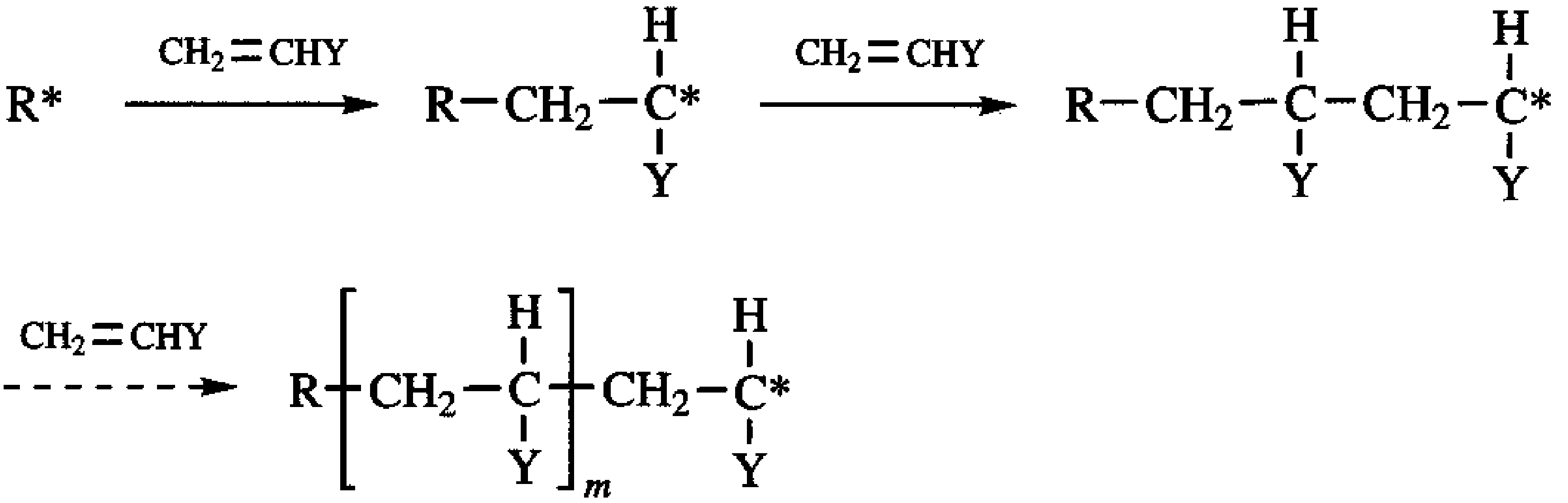
*(can be regarded as overlap of the $\sigma$-orbital of the C-H bond and the $\pi$-orbital of the C-C bond)*

(2) 1,1-Substitution pattern of the monomer leads to energetically unfavorable 1,3–interactions in the polymer



Cationic polymerization does not overcome problem (2), but the substituents provide stabilization of the propagating species

# Chain Polymerization



R* = radical, cation, anion

# Radical versus Ionic Chain Polymerization

## 1. Selectivity $CH_2=CHY$

Radicals are not selective
Cationic polymerization: electron releasing substituent Y
Anionic polymerization: electron withdrawing substituent Y

## 2. Nature of the propagating species

Radical polymerization: single species

Ionic polymerization: multiple (coexisting) species

| $-BA$ | $-B^+A^-$ | $-B^+\|\|A^-$ | $-B^+ + A^-$ |
|---|---|---|---|
| *Covalent species* | *Tight/contact ion pair (charges not separated by solvent)* | *Solvent separated/ loose ion pair* | *Free ions* |

## 3. Termination

Radical polymerization: predominantly via coupling (bimolecular)

Ionic polymerization: propagating chains react with solvent, counter ion or something else

# Selectivity of Ionic Chain Polymerizations

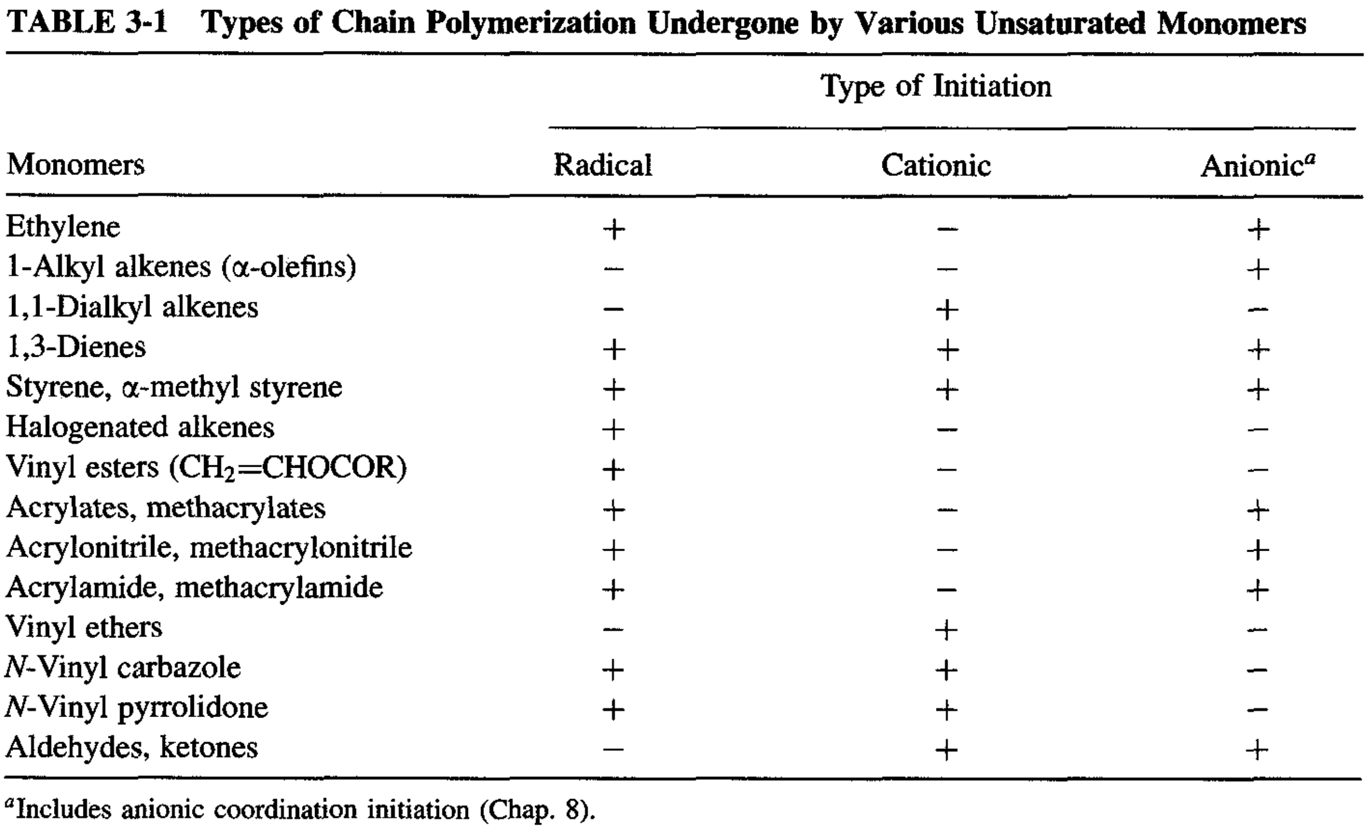


**TABLE 3-1 Types of Chain Polymerization Undergone by Various Unsaturated Monomers**

| | Type of Initiation | | |
|---|---|---|---|
| Monomers | Radical | Cationic | Anionic[a] |
| Ethylene | + | − | + |
| 1-Alkyl alkenes (α-olefins) | − | − | + |
| 1,1-Dialkyl alkenes | − | + | − |
| 1,3-Dienes | + | + | + |
| Styrene, α-methyl styrene | + | + | + |
| Halogenated alkenes | + | − | − |
| Vinyl esters ($CH_2{=}CHOCOR$) | + | − | − |
| Acrylates, methacrylates | + | − | + |
| Acrylonitrile, methacrylonitrile | + | − | + |
| Acrylamide, methacrylamide | + | − | + |
| Vinyl ethers | − | + | − |
| *N*-Vinyl carbazole | + | + | − |
| *N*-Vinyl pyrrolidone | + | + | − |
| Aldehydes, ketones | − | + | + |

[a] Includes anionic coordination initiation (Chap. 8).

In contrast to radical chain polymerization, ionic chain polymerizations are very selective:

- Cationic polymerization: C=C monomers with electron releasing substituents
- Anionic polymerization: C=C monomers with electron withdrawing substituents

# Propagating Species in Ionic Chain Polymerization

Nature of the propagating species:

| $\sim BA$ | $\sim B^{+}A^{-}$ | $\sim B^{+} \| A^{-}$ | $\sim B^{+} + A^{-}$ |
|---|---|---|---|
| *Covalent species* | *tight, or contact ion pair (intimate ion pair)* | *Solvent separated or loose ion pair* | *Free ion* |

Most ionic polymerizations involve two types of propagating species, an ion pair and a free ion, coexisting in equilibrium. The nature of the ion pair depends on the reaction conditions, especially the solvent (cf. controlled radial polymerization; dormant and active species). The relative concentrations of free ions and ion pairs determine the overall polymerization rate

Polar solvents are needed to solvate the ions, but polar protic solvents (water, alcohols, ...) cannot be used since they react with and destroy the ionic initiator/ propagating chain end

# Cationic Polymerization of C=C Monomers

1. Initiation
2. Propagation
3. Chain Transfer & Termination
4. Kinetics

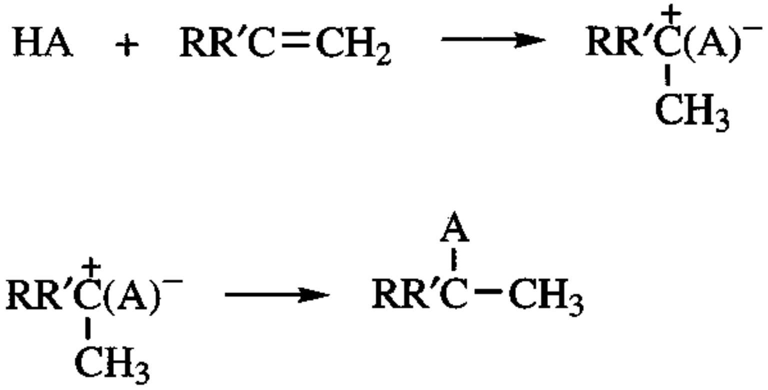
# 1. Initiation

Initiation:

1. Protonic acids
2. Lewis acids
3. Halogen
4. Photoinitiation by onium salts
5. Electroinitiation
6. Ionizing radiation

# 1. Protonic acids/Brønsted acids

- Protonation of the olefin
- Acids are needed that are sufficiently strong to produce a reasonable concentration of the protonated species, but whose anion should not be nucleophilic to avoid termination of the protonated olefin by combination (i.e. by covalent bond formation)



$$HA + RR'C{=}CH_2 \longrightarrow RR'\underset{|\atop CH_3}{\overset{+}{C}}(A)^-$$

$$RR'\underset{|\atop CH_3}{\overset{+}{C}}(A)^- \longrightarrow RR'\overset{A\atop |}{C}-CH_3$$

- Most strong acids (HCl, HBr, ...) are not useful as initiator
- Perchloric, sulfuric, phosphoric, fluoro- and chlorosulfonic, trifluoromethanesulfonic acids do initiate cationic polymerization, but produce only moderately high molar mass polymers

## 2. Lewis Acids

- Most important class of initiators for cationic chain polymerization
- Produce high MW polymers at high yields, generally at low T
  - ⇒ Metal halides: $AlCl_3$, $BF_3$, $SnCl_4$, $SbCl_5$, $ZnCl_2$, $TiCl_4$
  - ⇒ Corresponding organometallic derivatives: $RAlCl_2$, $R_2AlCl$, $R_3Cl$

Initiation by Lewis acids requires/is faciliated by:

(i) a proton donor/protogen, e.g. water, hydrogen halide, alcohol, carboxylic acid, or

(ii) a carbocation donor/cationogen, e.g. alkyl halide, ester, ether, or anhydride

| | |
|---|---|
| Protogen<br>Cationogen | initiator |
| Lewis acid | coinitiator |

Initiator and coinitiator react to form an initiator-coinitiator complex:

$$BF_3 + H_2O \rightleftharpoons BF_3 \cdot OH_2$$

**[often shown as: $H^+(BF_3OH)^-$]**

$$BF_3 \cdot OH_2 + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_3C^+(BF_3OH)^-$$

$$AlCl_3 + (CH_3)_3CCl \rightleftharpoons (CH_3)_3C^+(AlCl_4)^-$$

$$(CH_3)_3C^+(AlCl_4)^- + \phi CH{=}CH_2 \longrightarrow (CH_3)_3CCH_2\overset{+}{C}H\phi(AlCl_4)^-$$

Or, more general:

$$I + ZY \xrightleftharpoons{K} Y^+(IZ)^-$$

$$Y^+(IZ)^- + M \xrightarrow{k_i} YM^+(IZ)^-$$

I = coinitiator
ZY = initiator
M = monomer

Initiation by combination of a Lewis acid and protogen/cationogen has the advantage over initiation by a Brønsted acid that the anion $IZ^-$ is far less nucleophilic than $A^-$, which prolongs the lifetime of the propagating carbocation and allows access to high molecular weight polymer

# 2. Propagation

The initiator ion pair proceeds to propagate by successive additions of monomer molecules. Monomer addition proceeds via insertion of monomer between the carbocation and its negative counterion:

$$H\text{+}CH_2C(CH_3)_2\text{+}_n^{+}(BF_3OH)^- + (CH_3)_2C{=}CH_2 \longrightarrow$$

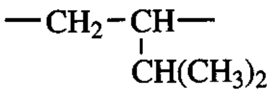
$$H\text{+}CH_2C(CH_3)_2\text{+}_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^-$$

$$HM_n^+(IZ)^- + M \xrightarrow{k_p} HM_nM^+(IZ)^-$$

Propagation can be complicated by the occurence of intramolecular rearrangements due to 1,2-hydride ($H{:}^-$) or 1,2-methide ($CH_3{:}^-$) shifts. Polymerizations proceeding with rearrangement are referred to as isomerization polymerizations. The extent of rearrangement depends on the relative stabilities of the propagating and rearranged carbocations and on the relative rates of propagation and isomerization

$\Rightarrow$ 1-olefins: propene, butene and higher 1-alkenes

# Polymerization of 3-methyl-1-butene

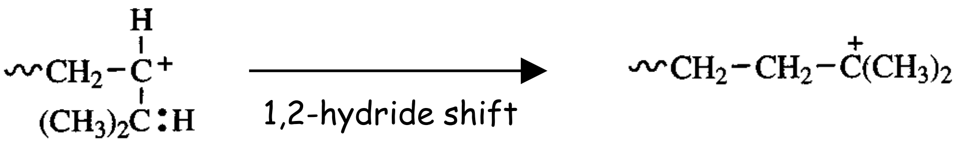


$-CH_2-\underset{CH(CH_3)_2}{CH}-$

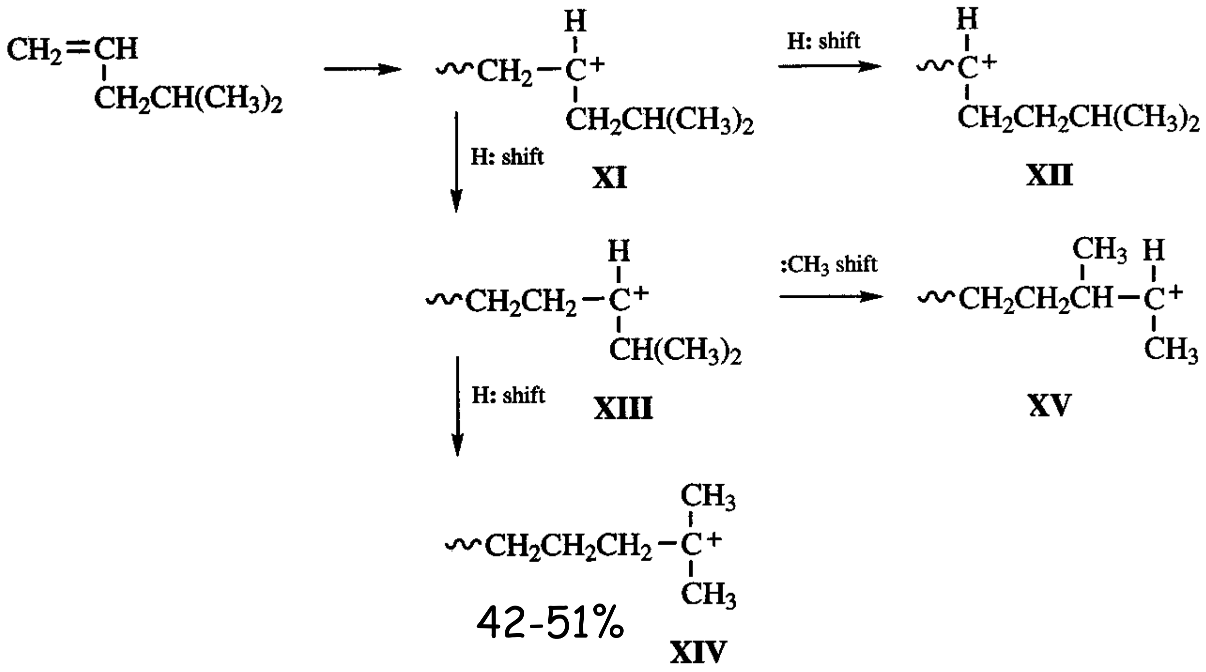
*First formed repeating unit*

$-CH_2-CH_2-C(CH_3)_2-$

*Rearranged repeating unit*

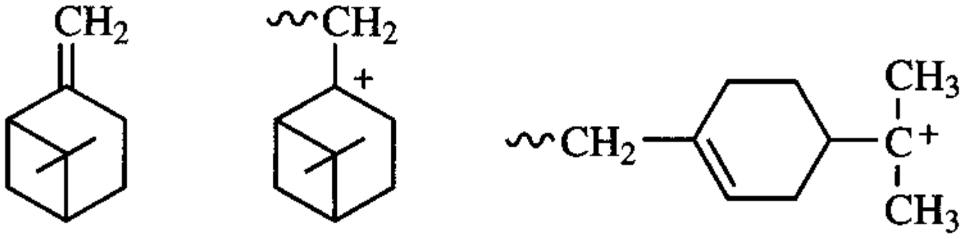


# Polymerization of 4-methyl-1-pentene



# The driving force in some isomerization polymerizations is relief of steric strain:

e.g. cationic polymerization of β-pinene; rearrangement involves cleavage of the strained four-membered ring and migration of the resulting *gem*-dimethyl carbocation center



# 3. Chain Transfer & Termination

## 1. Proton transfer (= most important)

a. Proton transfer to monomer (= predominant)
b. Hydride ion transfer from monomer to polymer (reverse of a.)
c. Chain transfer to counter ion/spontaneous termination

- a. and b. are kinetically indistinguishable, but a. gives polymers with unsaturated endgroups and b. in polymers with saturated endgroups.
- a., b. and c. limit polymer molecular weight, but **DO NOT** terminate the kinetic chain

## 2. Combination with counterion

Terminates the kinetic chain

## 3. Chain transfer to polymer

- Electrophilic aromatic substitution -> backbiting or branching
- Intermolecular hydride transfer -> branching

## 4. Other chain transfer and termination reactions

# Chain Transfer & Termination

## β-Proton transfer

(i) Chain transfer to monomer = transfer of a β-proton to monomer

$$\mathrm{H\!\left[CH_2C(CH_3)_2\right]_{\mathit{n}}CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- + CH_2{=}C(CH_3)_2 \longrightarrow}$$

$$\mathrm{(CH_3)_3C^+(BF_3OH)^- + H\!\left[CH_2C(CH_3)_2\right]_{\mathit{n}}CH_2C(CH_3){=}CH_2}$$

$$\mathrm{+\ H\!\left[CH_2C(CH_3)_2\right]_{\mathit{n}}CH{=}C(CH_3)_2}$$

$$\mathrm{HM_{\mathit{n}}M^+(IZ)^- + M \xrightarrow{\mathit{k}_{\mathit{tr},\,M}} M_{\mathit{n}+1} + HM^+(IZ)^-}$$

For isobutylene and some other monomers different unsaturated endgroups can be formed, the relative amounts depending on the counterion, identity of the propagating center and other reaction conditions

(ii) Hydride ion transfer from monomer to the propagating center

$$\mathrm{H\!\left[CH_2C(CH_3)_2\right]_{\mathit{n}}CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- + CH_2{=}C(CH_3)_2 \longrightarrow}$$

$$\mathrm{CH_2{=}C(CH_3){-}\overset{+}{C}H_2(BF_3OH)^- + H\!\left[CH_2C(CH_3)_2\right]_{\mathit{n}}CH_2CH(CH_3)_2}$$

Especially in case of unreactive monomers such as 1- and 2-alkenes. Hydride transfer by monomer is less likely a mode of termination for more reactive monomers such as isobutylene since the tertiary carbocation formed by proton transfer is more stable than the allyl carbocation formed by hydride transfer

# (iii) Chain transfer to counterion / spontaneous termination

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

$$BF_3\cdot OH_2 \;+\; H\!\left[CH_2C(CH_3)_2\right]_n CH_2C(CH_3){=}CH_2$$

$$HM_nM^+(IZ)^- \xrightarrow{k_{ts}} M_{n+1} + H^+(IZ)^-$$

- Transfer of a β-proton to the counterion
- The initiator-coinitiator is regenerated by its expulsion from the propagating species
- Chain transfer to counterion is zero-order in monomer; chain transfer to monomer first order

The various β-proton transfer reactions limit polymer molecular weight, but do not terminate the kinetic chain

# Combination with counterion

$$\mathrm{HM}_n\mathrm{M}^+(\mathrm{IZ})^- \xrightarrow{k_t} \mathrm{HM}_n\mathrm{MIZ}$$

- Trifluoroacetic acid initiated polymerization of styrene:

$$\mathrm{H}\left(\mathrm{CH_2CH}\phi\right)_n\mathrm{CH_2}\overset{+}{\mathrm{C}}\mathrm{H}\phi(\mathrm{OCOCF_3})^- \longrightarrow \mathrm{H}\left(\mathrm{CH_2CH}\phi\right)_n\mathrm{CH_2CH}\phi-\mathrm{OCOCF_3}$$

- Combination of the propagating ion with an anionic fragment from the counterion

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

$$\mathrm{H}\left[\mathrm{CH_2C(CH_3)_2}\right]_n\mathrm{CH_2C(CH_3)_2OH} + \mathrm{BF_3}$$

$$\mathrm{H}\left[\mathrm{CH_2C(CH_3)_2}\right]_n\mathrm{CH_2}\overset{+}{\mathrm{C}}\mathrm{(CH_3)_2(BCl_3OH)}^- \longrightarrow$$

$$\mathrm{H}\left[\mathrm{CH_2C(CH_3)_2}\right]_n\mathrm{CH_2C(CH_3)_2Cl} + \mathrm{BCl_2OH}$$

- Cationic polymerization with aluminium alkyl-alkyl halide initiating systems

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

Alkylation: transfer of an alkyl group to the propagating center

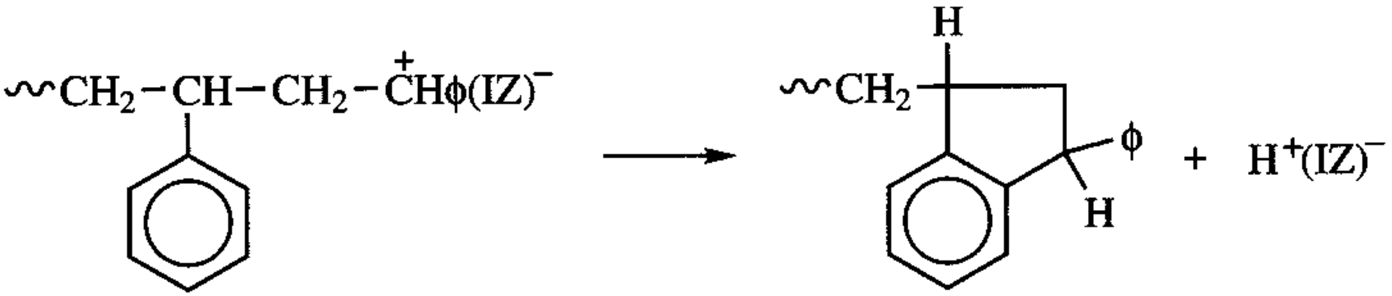
$$\sim CH_2-\overset{+}{C}(CH_3)_2([CH_3CH_2]_3AlCl)^- \longrightarrow$$
$$\sim CH_2CH(CH_3)_2 + CH_2{=}CH_2 + (CH_3CH_2)_2AlCl$$

Hydridation: transfer of a hydride ion from the alkyl anion to the propagating center (preferred when the trialkyl aluminium contains $\beta$-hydrogens)

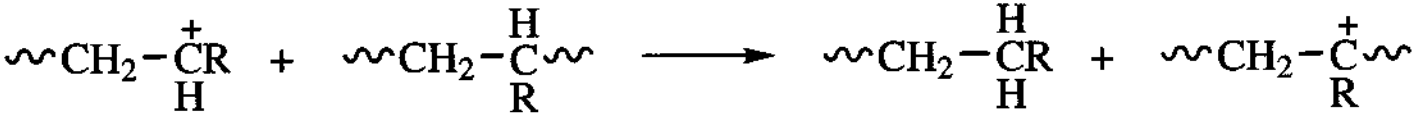
# Chain transfer to polymer

- Electrophilic aromatic substitution
- Hydride transfer

*Intramolecular electrophilic aromatic substitution (backbiting); polymerization of styrene:*



*Intermolecular hydride transfer to polymer in the polymerization of 1-alkenes leads to short chain branching:*



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

# Other chain transfer and termination reactions

Various transfer agents present as solvent, impurity or deliberately added can terminate the growing polymer chain by transfer of a negative fragment $A^-$:

$$HM_nM^+(IZ)^- + XA \xrightarrow{k_{tr,S}} HM_mMA + X^+(IZ)^-$$

XA includes e.g.: water, alcohols, acids, anhydrides and esters, which transfer HO, RO or RCOO to the propagating species

# 4. Kinetics

## Kinetic scheme:

$$\mathrm{I} + \mathrm{ZY} \overset{K}{\rightleftharpoons} \mathrm{Y^+(IZ)^-}$$

$$\mathrm{Y^+(IZ)^-} + \mathrm{M} \xrightarrow{k_i} \mathrm{YM^+(IZ)^-}$$

$$\mathrm{HM}_n^+\mathrm{(IZ)^-} + \mathrm{M} \xrightarrow{k_p} \mathrm{HM}_n\mathrm{M^+(IZ)^-}$$

$$\mathrm{HM}_n\mathrm{M^+(IZ)^-} \xrightarrow{k_t} \mathrm{HM}_n\mathrm{MIZ}$$

- Termination exclusively by combination of the propagating center with the counterion
- Steady-state conditions (i.e. $R_i = R_t$)

$$R_i = Kk_i[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]$$

$$R_p = k_p[\mathrm{YM^+(IZ)^-}][\mathrm{M}]$$

$$R_t = k_t[\mathrm{YM^+(IZ^-)}]$$

$R_i = R_t$

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

$$R_p = \frac{R_i k_p[\mathrm{M}]}{k_t} = \frac{Kk_i k_p[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]^2}{k_t}$$

If transfer to S leads to termination of the kinetic chain, this becomes:

$$R_p = \frac{Kk_i k_p[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]^2}{k_t + k_{tr,\mathrm{S}}[\mathrm{S}]}$$

NB. 1.: The assumption of a steady state for $[\mathrm{YM^+(IZ)^-}]$ is not valid in many, if not most, cationic polymerizations, which proceed so fast that steady state is not achieved

NB. 2.: Contrary to $R_p$, the derivations for $X_n$ do not assume steady state conditions

# Comparison: Radical and Cationic Polymerization

## Radical

$$R_p = k_p[\mathrm{M}]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

$$R_p = k_p[\mathrm{M}]\left(\frac{fk_d[\mathrm{I}]}{k_t}\right)^{1/2}$$

$$R_p \sim R_i^{1/2}$$

## Cationic

$$R_p = \frac{R_i k_p[\mathrm{M}]}{k_t} = \frac{K k_i k_p[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]^2}{k_t}$$

$$R_p \sim R_i$$

Difference due to different modes of termination: termination is second-order in the propagating species in radical polymerization, but first-order in cationic polymerization

## Number-average degree of polymerization:

$$\overline{X}_n = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}]}{k_t}$$

Polydispersity index (PDI) = $X_w/X_n$ = 2

(as was derived for free radical polymerizations terminated by disproportionation)

In case chain breaking also involves chain transfer to monomer, spontaneous termination and chain transfer to transfer agent $R_p$ is unaffected, but

$$\overline{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,\mathrm{M}} + R_{tr,\mathrm{S}}}$$

with:

$$R_{ts} = k_{ts}[\mathrm{YM}^+(\mathrm{IZ})^-]$$

$$R_{tr,\mathrm{M}} = k_{tr,\mathrm{M}}[\mathrm{YM}^+(\mathrm{IZ})^-][\mathrm{M}]$$

$$R_{tr,\mathrm{S}} = k_{tr,\mathrm{S}}[\mathrm{YM}^+(\mathrm{IZ})^-][\mathrm{S}]$$

$$\overline{X}_n = \frac{k_p[\mathrm{M}]}{k_t + k_{ts} + k_{tr,\mathrm{M}}[\mathrm{M}] + k_{tr,\mathrm{S}}[\mathrm{S}]}$$

$$\frac{1}{\overline{X}_n} = \frac{k_t}{k_p[\mathrm{M}]} + \frac{k_{ts}}{k_p[\mathrm{M}]} + C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]}$$

- Mayo equation for cationic polymerization
- $C_M = k_{tr,M}/k_p$ and $C_S = k_{tr,S}/k_p$

# Some Words of Caution

The determination of the various rate constants ($k_i$, $k_p$, $k_t$, $k_{ts}$, $k_{tr}$) for cationic chain polymerization is much more difficult than in radical polymerization

*Problems with interpreting rate constants:*

The previous equations were all written in terms of one type of propagating species, usually the ion pair, which is incorrect. Both ion pairs and free ions are simultaneously present (in equilibrium) and both contribute to propagation

The correct expression for $R_p$:

$$R_p = \underbrace{k_p^+ [\mathrm{YM}^+][\mathrm{M}]}_{\textit{Free ions}} + \underbrace{k_p^{\pm} [\mathrm{YM}^+(\mathrm{IZ})^-][\mathrm{M}]}_{\textit{Ion pairs}}$$

Most reported $k_p$ values are only apparent/pseudo or global rate constants, $k_p^{app}$ obtained from the polymerization rate using the expression:

$$R_p = k_p^{\mathrm{app}} [\mathrm{M}^*][\mathrm{M}]$$

# Comparison of Rate Constants

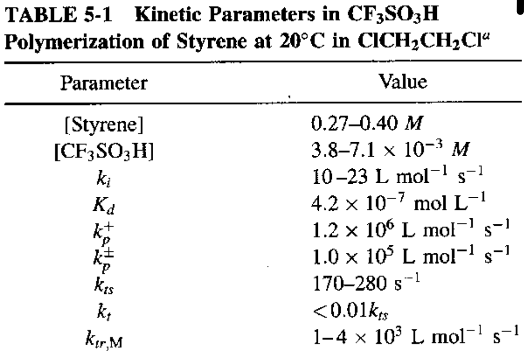


**TABLE 5-1 Kinetic Parameters in $CF_3SO_3H$ Polymerization of Styrene at 20°C in $ClCH_2CH_2Cl$**[a]

| Parameter | Value |
|---|---|
| [Styrene] | 0.27–0.40 *M* |
| $[CF_3SO_3H]$ | $3.8–7.1 \times 10^{-3}$ *M* |
| $k_i$ | 10–23 $L\ mol^{-1}\ s^{-1}$ |
| $K_d$ | $4.2 \times 10^{-7}$ $mol\ L^{-1}$ |
| $k_p^+$ | $1.2 \times 10^6$ $L\ mol^{-1}\ s^{-1}$ |
| $k_p^\pm$ | $1.0 \times 10^5$ $L\ mol^{-1}\ s^{-1}$ |
| $k_{ts}$ | 170–280 $s^{-1}$ |
| $k_t$ | $<0.01 k_{ts}$ |
| $k_{tr,M}$ | $1–4 \times 10^3$ $L\ mol^{-1}\ s^{-1}$ |

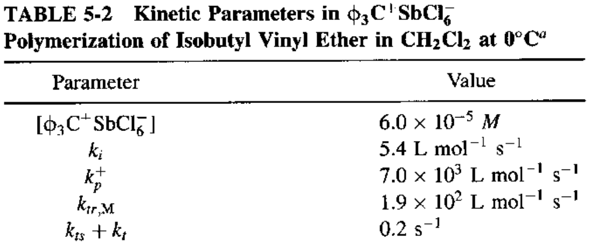
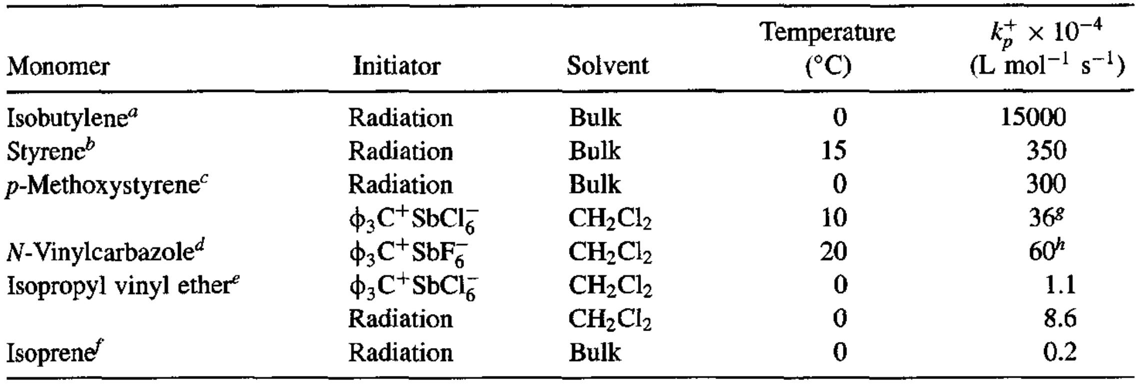


**TABLE 5-2 Kinetic Parameters in $\phi_3C^+SbCl_6^-$ Polymerization of Isobutyl Vinyl Ether in $CH_2Cl_2$ at 0°C**[a]

| Parameter | Value |
|---|---|
| $[\phi_3C^+SbCl_6^-]$ | $6.0 \times 10^{-5}$ *M* |
| $k_i$ | 5.4 $L\ mol^{-1}\ s^{-1}$ |
| $k_p^+$ | $7.0 \times 10^3$ $L\ mol^{-1}\ s^{-1}$ |
| $k_{tr,M}$ | $1.9 \times 10^2$ $L\ mol^{-1}\ s^{-1}$ |
| $k_{ts} + k_t$ | 0.2 $s^{-1}$ |



| Monomer | Initiator | Solvent | Temperature (°C) | $k_p^+ \times 10^{-4}$ ($L\ mol^{-1}\ s^{-1}$) |
|---|---|---|---|---|
| Isobutylene[a] | Radiation | Bulk | 0 | 15000 |
| Styrene[b] | Radiation | Bulk | 15 | 350 |
| *p*-Methoxystyrene[c] | Radiation | Bulk | 0 | 300 |
| | $\phi_3C^+SbCl_6^-$ | $CH_2Cl_2$ | 10 | 36[g] |
| *N*-Vinylcarbazole[d] | $\phi_3C^+SbF_6^-$ | $CH_2Cl_2$ | 20 | 60[h] |
| Isopropyl vinyl ether[e] | $\phi_3C^+SbCl_6^-$ | $CH_2Cl_2$ | 0 | 1.1 |
| | Radiation | $CH_2Cl_2$ | 0 | 8.6 |
| Isoprene[f] | Radiation | Bulk | 0 | 0.2 |

The reactivity of free ions is generally no more than a factor of 5-20 greater than the reactivity of ion pairs in cationic polymerization. The counterion is typically quite large for cationic polymerization ($SbCl_6^-$, $CF_3SO_3^-$) and as a result the ion pair is a very loose ion pair with little difference in availability of the positively charge center for reaction compared to the free ion

Cationic polymerization is faster than radical polymerization:
Cationic polymerization: $R_p \sim k_p/k_t$
Radical polymerization: $R_p \sim k_p/k_t^{1/2}$

$k_p$ for cationic polymerization is similar to or even greater than for radical polymerization. $k_t$, however, for cationic polymerization is considerably smaller. Also the concentration of propagating species in cationic polymerization is much higher

# Solvent Effects

Solvent polarity affects $R_p$ (and MW) through:

(i) Altering the concentration of propagating centers (i.e. affecting the equilibrium between free ions and ion pairs)

(ii) Changing propagation rate constants (e.g. $k_p^+$ generally decreases with increasing solvent polarity)

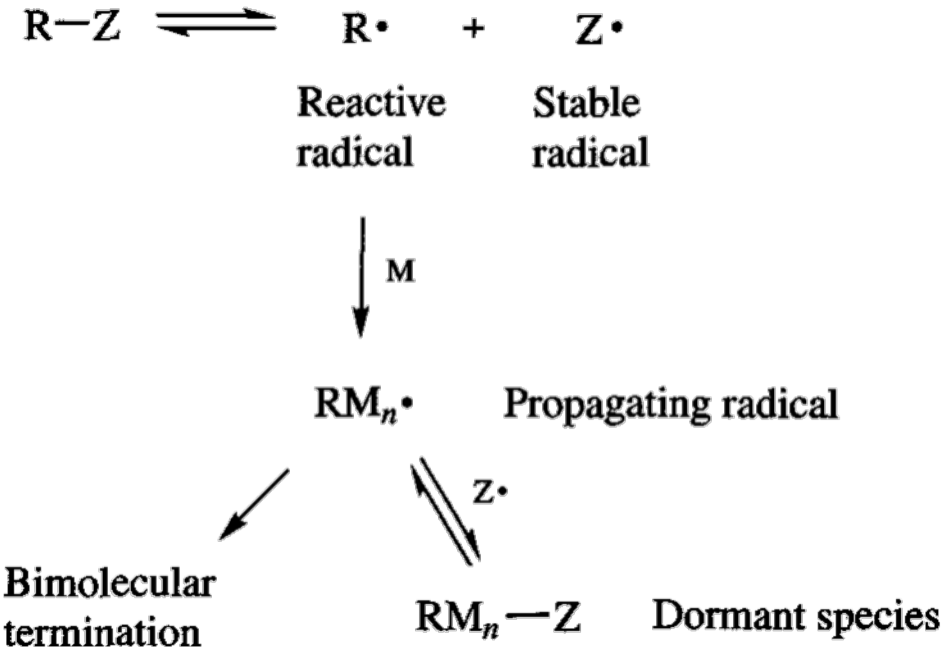
# Living Cationic Polymerization (LCP)

- Living anionic polymerization is relatively easy to achieve with a well-purified reaction system without water or other agents that terminate anionic propagating centers by proton transfer.
- Living cationic polymerization is more difficult to achieve since cationic propagating centers have a „built-in“ termination reaction; transfer of $\beta$-protons to monomer, counterion or some other basic species present

- The major approach to extending the lifetime of the propagating species in cationic polymerization involves reversible conversion of the active centers to dormant species such as covalent esters or halides by using initiating systems with Lewis acids that supply an appropriate nucleophilic counterion.
- The equilibrium is further driven towards the dormant species by adding a salt that supplies the same counterion as supplied by the Lewis acid („*common ion effect*“)
- The components of the reactions are choosen so as to provide a fast equilibrium between active and dormant species

Slower, but more controlled polymerization
with all features of a „living polymerization“

# For Comparison: Living Radical Polymerization



LRP: Buildup in the concentration of the stable radicals during polymerization

Propagating radical concentration:
$10^{-7}$ – $10^{-8}$ M
Concentration of dormant species:
$10^{-1}$ – $10^{-3}$ M

- Suppression of bimolecular termination
- Average lifetime of polymers increase by at least 4 orders of magnitude

- The stable radical is often called the persistent radical
- The resulting suppression of bimolecular termination is referred to as the persistent radical effect

# Living Cationic Polymerization: $R_p$ and $X_n$

Assumptions:

1. Free ions are absent and propagation proceeds through ion pairs
2. Initiation is very fast (i.e. the concentration of propagating ion pairs equals the concentration of ion pairs derived from initiator and coinitiator)

$$R_p = k_p^{\pm}[\mathrm{Y^+(IZ^-)}][\mathrm{M}]$$

$$\mathrm{I} + \mathrm{ZY} \overset{K_1}{\rightleftharpoons} \mathrm{IZY} \overset{K_2}{\rightleftharpoons} \mathrm{Y^+(IZ^-)}$$

$$[\mathrm{Y^+(IZ^-)}] = K_1K_2[\mathrm{I}][\mathrm{ZY}]$$

$$\Downarrow$$

$$R_p = k_p^{\pm}K_1K_2[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]$$

$X_n$ = [concentration of monomer consumed] / [total concentration of all propagating chains (dormant and active)]

$$\overline{X}_n = \frac{p[\mathrm{M}]_0}{[\mathrm{ZY}]_0}$$

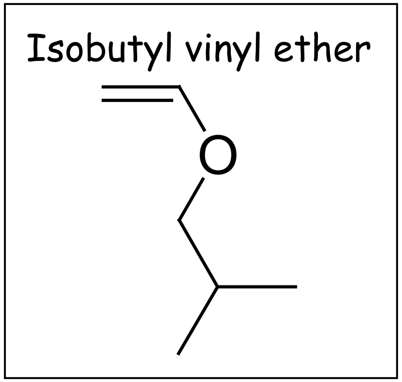
$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + \frac{1}{\overline{X}_n}$$

$[\mathrm{M}]_0$ = initial concentration of monomer
$[\mathrm{ZY}]_0$ = initial concentration of initiator
p = fractional conversion of monomer at any time in the reaction

# Examples

- Isobutyl vinyl ether

  - Vinyl ethers form more stable carbocations than most other monomers because the ether group is effective at resonance stabilization of positive charge. This means that the equilibrium between dormant and active species can be achieved using relatively weak initiators



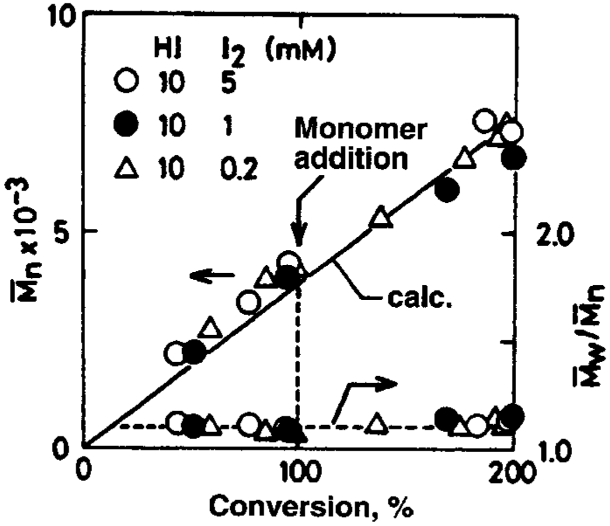
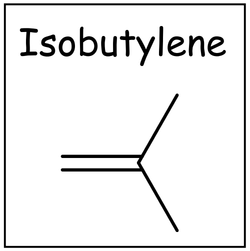


**Fig. 5-2** Dependence of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ on conversion for the polymerization of isobutyl vinyl ether by $HI/I_2$ in $CH_2Cl_2$ at $-15°C$. $[M] = 0.38\ M$ at beginning of each batch; $[HI] = 0.01\ M$; $[I_2] = 0.02\ M$ (△), $0.001\ M$ (●), $0.005\ M$ (○). After Sawamoto and Higashimura [1986] (by permission of Huthig and Wepf Verlag, Basel and Wiley-VCH, Weinheim).

  - The fact that the $M_n$ values for all batches fall on the same line indicates that polymerization proceeds with a constant concentration of propagating species and with negligible termination and transfer

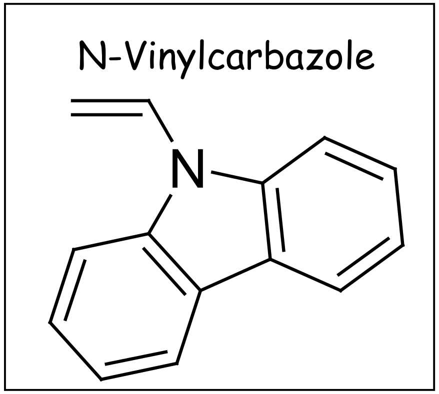
- Isobutylene

  - Isobutylene forms a less stable carbocation than a vinyl ether and requires stronger Lewis acids ($BF_3$, $SnCl_4$, $TiCl_4$) for living cationic polymerization



- N-Vinylcarbazole

  - N-Vinylcarbazole forms a more stable carbocation than does a vinyl ether because of the electron releasing nitrogen and conjugation of the positive charge with the π-electrons of the ring
  - Living cationic polymerization using HI in the absence of a Lewis acid in toluene at 40°C



Note: None of the living cationic polymerizations are as long-lived as the anionic systems that will be discussed later on!!

# Commercial Applications of Cationic Polymerization

## Copolymerization of isobutylene:

- Polyisobutylene (M > $10^5$; rubbery solids: impact modifiers)
- Polybutene: copolymers of isobutylene with 1-alkenes: low molar mass adhesives, lubricants, plasticizers, ....
- Butyl rubber: obtained via copolymerization of isobutylene with isoprene (0.5 – 2.5%). The isoprene introduces double bonds which makes subsequent crosslinking possible

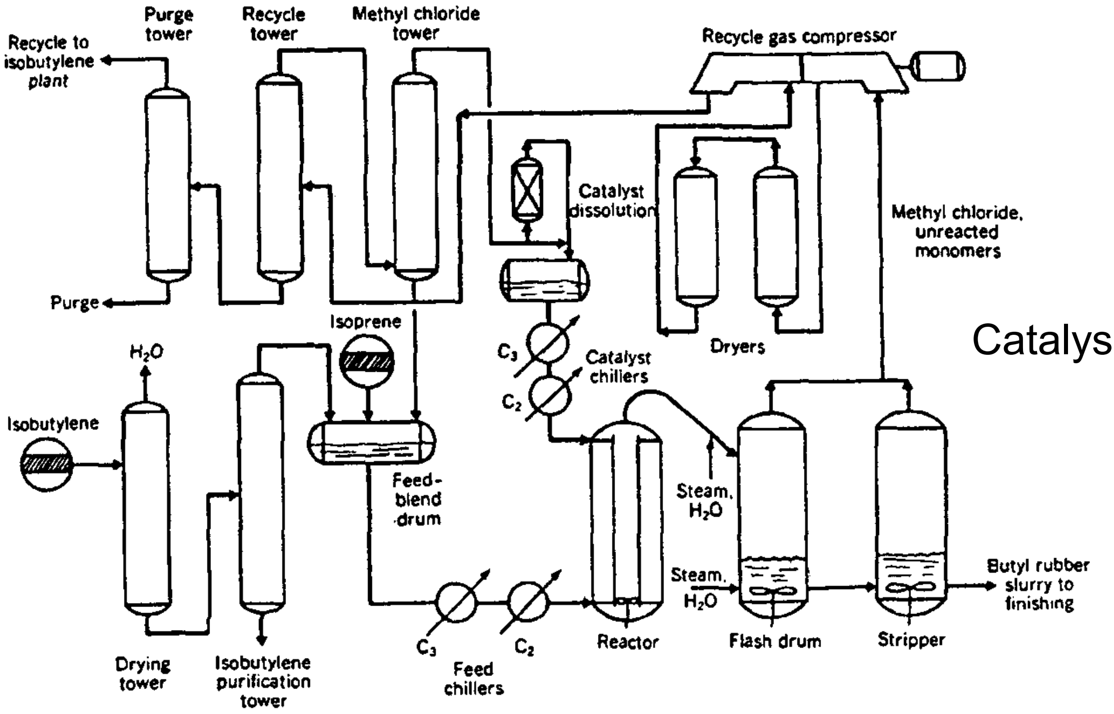


**Fig. 5-4** Slurry process for production of butyl rubber. After Kresge et al. [1987] (by permission of Wiley-Interscience, New York).

Catalyst: $AlCl_3$

# Butyl Rubber vs. Natural Rubber

Amount of isoprene is 0.5 – 2.5 %, depending on the desired degree of crosslinking

Does not crystallize on cooling and remains flexible down to – 50°C

Low degree of unsaturation imparts good resistance to aging, moisture, chemicals and ozone