Polymer Chemistry

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Polymer Science and Technology

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5. Addition Polymerization

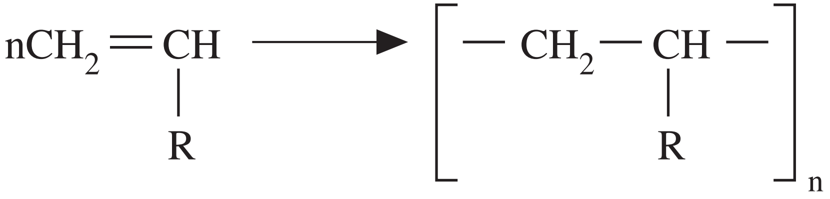
II. CHAIN-REACTION POLYMERIZATION

As an important industrial method of polymer preparation, it involves the addition of unsaturated molecules (e.g. vinyl monomers) to a rapidly growing chain.

The growing polymer in chain-reaction polymerization is an active species (e.g. free radical and ions) and polymerization proceeds via chain mechanism.

Chain-reaction polymerization is induced by the addition of free-radical forming reagents or by ionic initiators.

Like all chain reactions, it involves **three** fundamental **steps**: **initiation**, **propagation**, and **termination**. In addition, a fourth step called **chain transfer** may be involved.



$$nCH_2{=}\underset{\displaystyle R}{\underset{|}{CH}} \longrightarrow \left[-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-\right]_n$$

RADICAL POLYMERIZATION

A. INITIATION

Initiation involves the acquisition of an active site by the monomer. This may occur spontaneously by the absorption of **heat**, **light** (ultraviolet), or **high-energy irradiation**.

Initiation of free-radical polymerization is brought about by the addition of small quantities of compounds called **initiators**.

Typical initiators include peroxides, azo compounds, Lewis acids, and organometallic reagents.

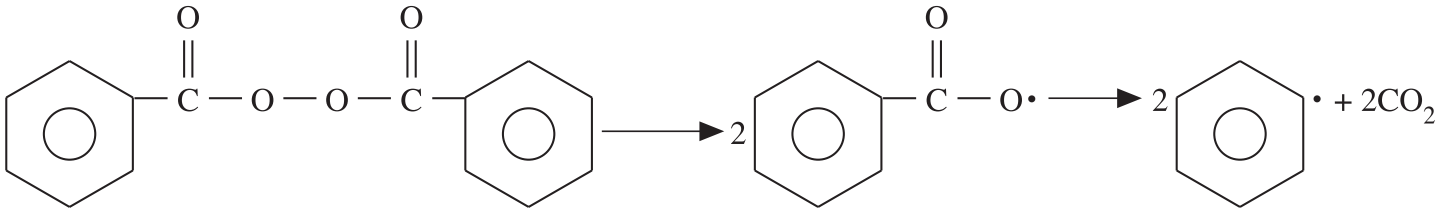
While initiators trigger initiation of the chain and exert an accelerating influence on polymerization rate, they are not exactly catalysts since they are changed chemically in the course of polymerization.

An initiator is usually a weak organic compound that can be decomposed thermally or by irradiation to produce free radicals, which are molecules containing atoms with unpaired electrons.

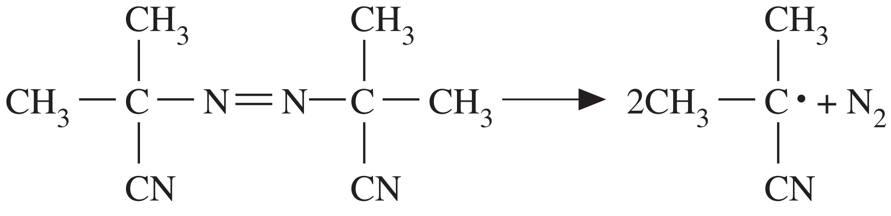
A variety of compounds decompose when heated to form free radicals. Dialkylperoxides (ROOR), diacylperoxides (RCO–O–O–CO–R), hydroperoxides (ROOH), and azo compounds (RN≡NR) that can be decomposed thermally to produce free radicals.

The thermal decomposition of benzoyl peroxide, which takes place between 60-90 °C, involves the homolytic cleavage of the O–O bond to yield benzoyl free radicals that may react to yield phenyl radicals and carbon dioxide.

Photochemically-induced free-radical formation is the decomposition of azo-bisisobutyronitrile by short-wavelength visible light or near-ultraviolet radiation at temperatures as low as 0 °C, where no thermal initiation occurs.

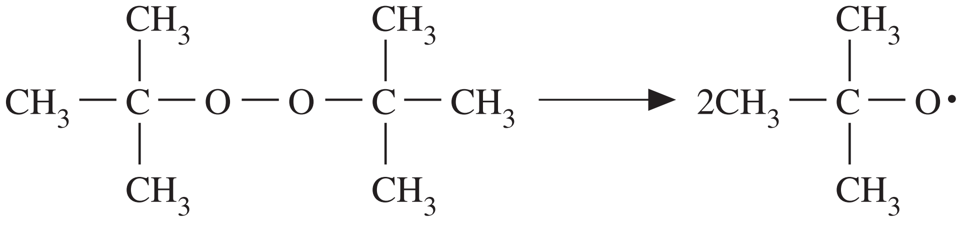


benzoyl peroxide



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow 2CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot + N_2$$

azobisisobutyronitrile (AIBN)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow 2CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\cdot$$

di-*t*-butylperoxide

In free-radical polymerization carried out **in aqueous medium**, the decomposition of peroxide or persulfate is greatly accelerated by the presence of a reducing system. This method of free-radical initiation is referred to as **redox initiation**.

The initiation resulting from the thermal decomposition of organic compounds discussed above is appropriate only for polymerizations carried out at room temperature or higher.

The enhanced rate of free-radical formation in redox reactions permits polymerization at relatively lower temperatures (e.g. for emulsion polymerization):

$$S_2O_8^{2-} + HSO_3^{-} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + HSO_3^{\cdot}$$

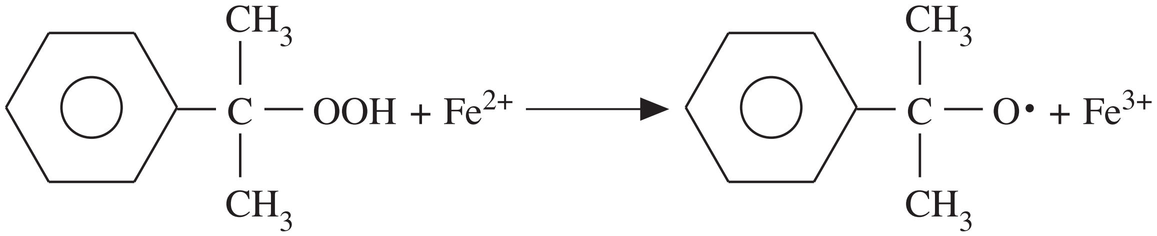
$$S_2O_8^{2-} + S_2O_3^{-} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + S_2O_3^{-\cdot}$$

$$HSO_3^{-} + Fe^{3+} \rightarrow HSO_3^{\cdot} + Fe^{2+}$$

Persulfate ion initiator (e.g., from $K_2S_2O_8$) reacts with a reducing agent such as a bisulfite ion (e.g., from $NaHSO_3$) to produce radicals for redox initiation.

Ferric ion may also be used as a source of radicals.

Redox reactions involve the use of alkyl hydroxides and a reducing agent such as ferrous ion.



Free-radical polymerization of some monomers can be initiated by heating or exposing the monomers to light or high-energy irradiation such as X-rays, γ-rays, and α-rays.

High-energy irradiation of monomers can be carried out either in bulk or in solution. It is certainly not as selective as photolytic initiation.

When choosing an initiator for free-radical polymerization, the important parameters that must be considered are the temperature range to be used for the polymerization and the reactivity of the radicals formed.

The presence of certain promoters and accelerators and the nature of the monomer often affect the rate of decomposition of initiators. For example, the decomposition of benzoyl peroxide may be accelerated at room temperature by employing ternary or quaternary amines.

Free-radical initiation processes do not require stringent exclusion of atmospheric moisture, but can be **inhibited** by substances such as **oxygen**. Free radicals are inactivated by reaction with oxygen to form peroxides or hydroperoxides.

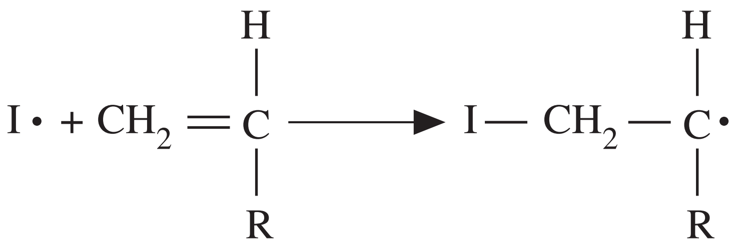
For monomers such as styrene and methylmethacrylate that are susceptible to such inhibition, initiation reactions are carried out in an **oxygen-free** atmosphere such as nitrogen.

It must be emphasized also that organic peroxides, when subjected to shock or high temperature, can detonate. Therefore these compounds must be handled with caution.

The initiation of polymerization occurs in two successive steps. The first step involves the formation of radicals:

$$I\text{-}I \rightarrow 2I\cdot$$

The second step is the addition of the initiator radical to a vinyl monomer molecule:



$$I\bullet + CH_2{=}C(H)(R) \longrightarrow I{-}CH_2{-}C(H)(R)\bullet$$

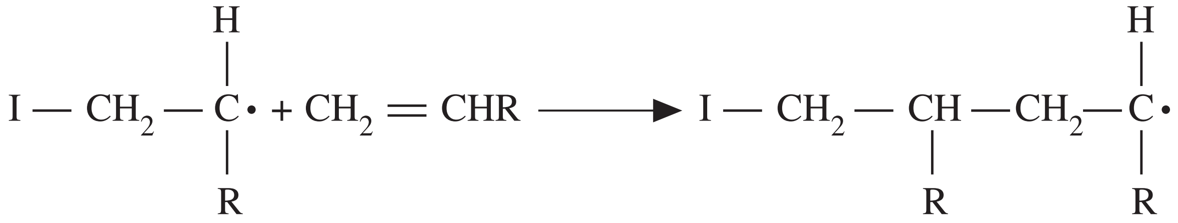
Initiator fragments have been shown by end-group analysis to become part of the growing chain. In commercial practice, 60 to 100% of all the free radicals generated do initiate polymerization.

B. PROPAGATION

During propagation, the initiated monomer adds other monomers in rapid succession.

This involves the addition of a free radical to the double bond of a monomer, with regeneration of another radical.

The active center is thus continuously relocated at the end of the growing polymer chain.



$$I-CH_2-\underset{R}{\overset{H}{C}}\cdot + CH_2=CHR \longrightarrow I-CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{H}{C}}\cdot$$

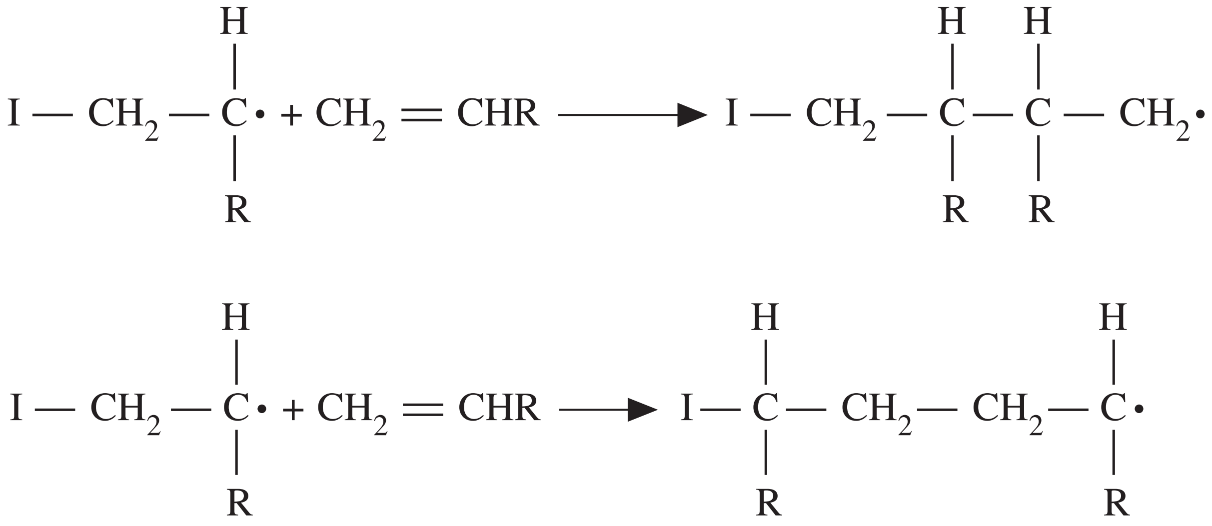
Propagation continues until the growing chain radical is deactivated by chain termination or transfer.

The substituted carbon atom is regarded as the head and the unsubstituted carbon atom the tail of the vinyl monomer.

There are, therefore, three possible ways for the propagation step to occur: head-to-tail, head-to-head, and tail-to-tail.

A random distribution of these species along the molecular chain might be expected.

It is found that head-to-tail linkages in which the substituents occur on alternate carbon atoms predominate; only occasional interruptions of this arrangement by head-to-head and tail-to-tail linkages occur.



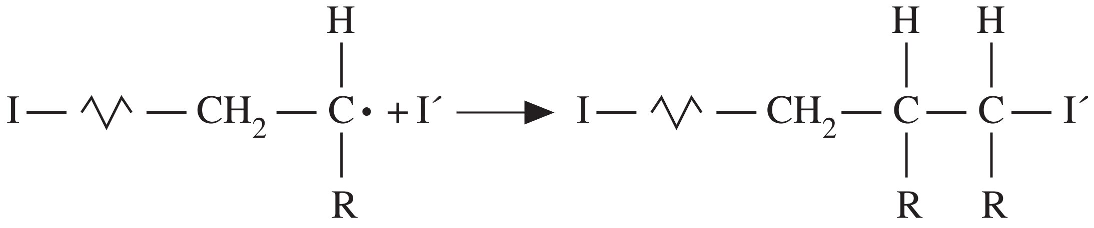
$$\mathrm{I-CH_2-\underset{R}{\overset{H}{C}}\cdot + CH_2=CHR \longrightarrow I-CH_2-\underset{R}{\overset{H}{C}}-\underset{R}{\overset{H}{C}}-CH_2\cdot}$$

$$\mathrm{I-CH_2-\underset{R}{\overset{H}{C}}\cdot + CH_2=CHR \longrightarrow I-\underset{R}{\overset{H}{C}}-CH_2-CH_2-\underset{R}{\overset{H}{C}}\cdot}$$

C. TERMINATION

In termination, the growth activity of a polymer chain radical is destroyed by reaction with another free radical in the system to produce polymer molecule(s).

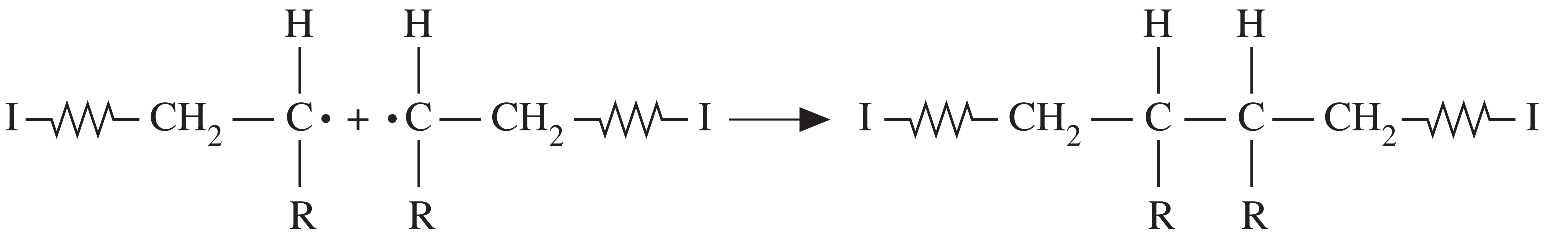
Termination can occur by the reaction of the polymer radical with initiator radicals. This type of termination process is unproductive and can be controlled by maintaining a low rate for initiation.



$$\mathrm{I{-}\!\sim\!{-}CH_2{-}\overset{H}{\underset{R}{C}}\bullet + I' \longrightarrow I{-}\!\sim\!{-}CH_2{-}\overset{H}{\underset{R}{C}}{-}\overset{H}{\underset{R}{C}}{-}I'}$$

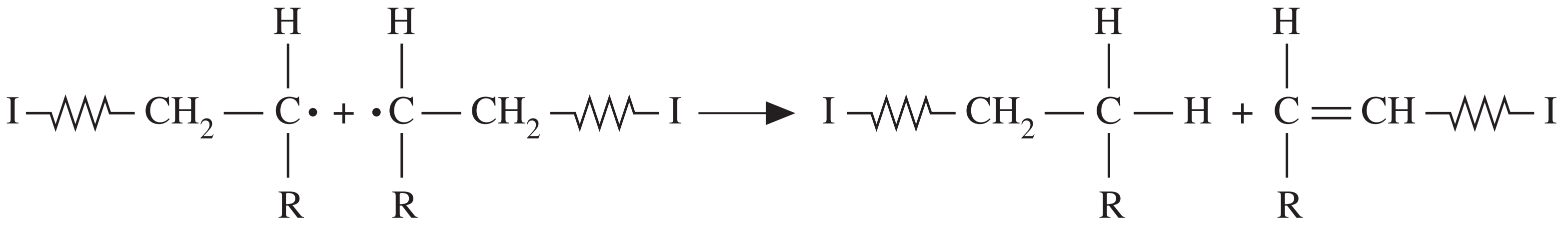
The termination reactions that are more important in polymer production are **combination** (or coupling) and **disproportionation**.

In termination by **combination**, two growing polymer chains react with the mutual destruction of growth activity.



$$\mathrm{I{\sim\!\sim}CH_2{-}\overset{H}{\underset{R}{C}}\bullet + \bullet\overset{H}{\underset{R}{C}}{-}CH_2{\sim\!\sim}I \longrightarrow I{\sim\!\sim}CH_2{-}\overset{H}{\underset{R}{C}}{-}\overset{H}{\underset{R}{C}}{-}CH_2{\sim\!\sim}I}$$

In **disproportionation**, a labile atom (usually hydrogen) is transferred from one polymer radical to another.



$$I\sim\sim CH_2-\overset{H}{\underset{R}{C}}\cdot + \cdot\overset{H}{\underset{R}{C}}-CH_2\sim\sim I \longrightarrow I\sim\sim CH_2-\overset{H}{\underset{R}{C}}-H + \overset{H}{\underset{R}{C}}=CH\sim\sim I$$

Coupling reactions produce a single polymer, while disproportionation results in two polymers from the two reacting polymer chain radicals.

The predominant termination reaction depends on the nature of the reacting monomer and the temperature.

Since **disproportionation** requires energy for breaking of chemical bonds, it should become more pronounced **at high reaction temperatures**; **combination** of growing polymer radicals predominates **at low temperatures**.

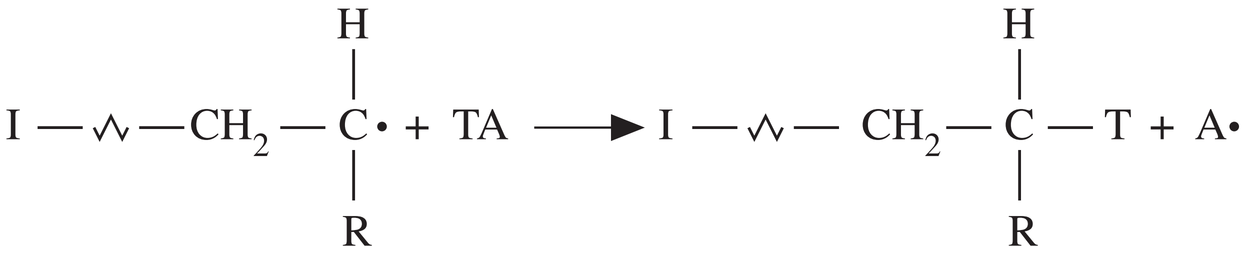
D. CHAIN TRANSFER

In chain-transfer reactions, a growing polymer chain is deactivated or terminated by transferring its growth activity to a previously inactive species.

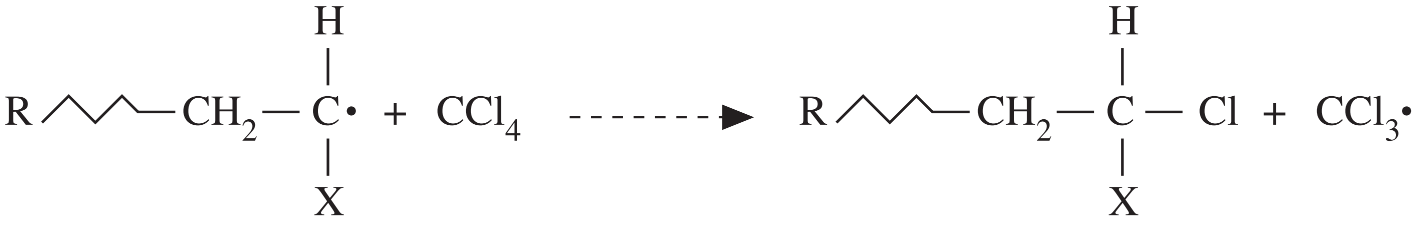
The species, **TA**, could be a monomer, polymer, solvent molecule, or other molecules deliberately or inadvertently introduced into the reaction mixture. Depending on its reactivity, the new radical, A·, may or may not initiate the growth of another polymer chain.

If the reactivity of A· is comparable to that of the propagating chain radical, then a new chain may be initiated. If its reactivity toward a monomer is less than that of the propagating radical, then the overall reaction rate is **retarded**. If A· is unreactive toward the monomer, the entire reaction could be **inhibited**. Transfer reactions do not result in the creation or destruction of radicals; the overall number of growing radicals remains unchanged.

The occurrence of transfer reactions results in the **reduction** of the average polymer **chain length**, and in the case of transfer to a polymer it may result in **branching**.

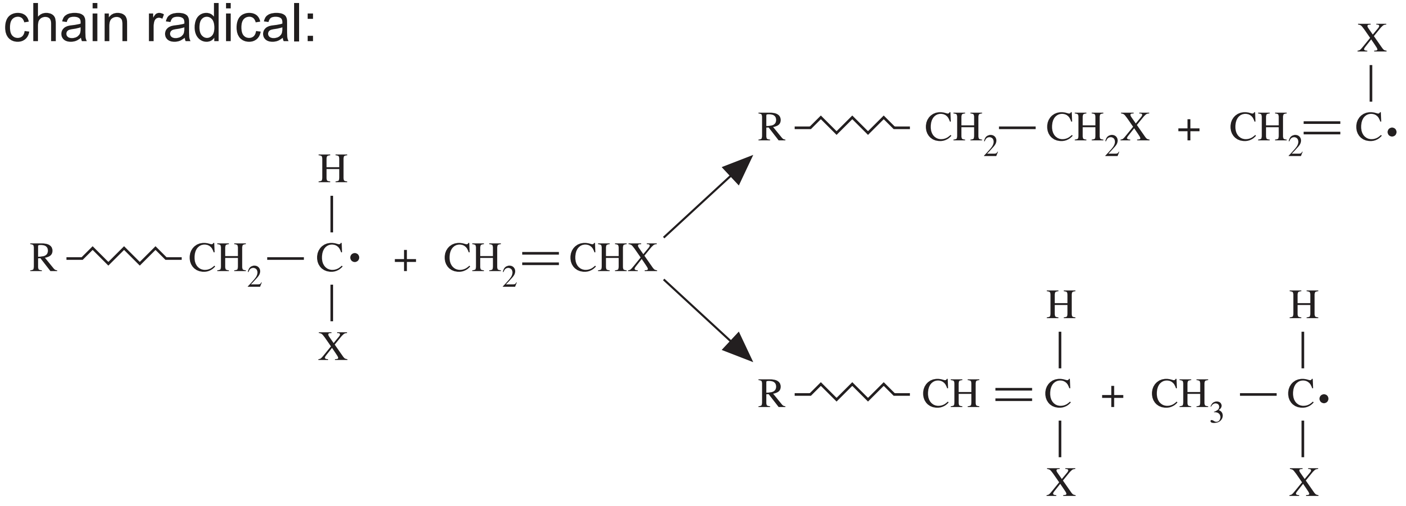


$$\mathrm{I} - \sim - \mathrm{CH_2} - \underset{\displaystyle \mathrm{R}}{\overset{\displaystyle \mathrm{H}}{\mathrm{C}}}\bullet + \mathrm{TA} \longrightarrow \mathrm{I} - \sim - \mathrm{CH_2} - \underset{\displaystyle \mathrm{R}}{\overset{\displaystyle \mathrm{H}}{\mathrm{C}}} - \mathrm{T} + \mathrm{A}\bullet$$



$$\mathrm{R}\sim\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot + \mathrm{CCl_4} \dashrightarrow \mathrm{R}\sim\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}-\mathrm{Cl} + \mathrm{CCl_3}\cdot$$

if the molecule is unsaturated, like a monomer, the atom can be transferred to either the monomer or the chain radical:



$$\mathrm{R}\sim\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot + \mathrm{CH_2{=}CHX} \rightarrow \mathrm{R}\sim\mathrm{CH_2}-\mathrm{CH_2X} + \mathrm{CH_2}{=}\overset{\mathrm{X}}{\mathrm{C}}\cdot$$

$$\mathrm{R}\sim\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot + \mathrm{CH_2{=}CHX} \rightarrow \mathrm{R}\sim\mathrm{CH}{=}\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}} + \mathrm{CH_3}-\overset{\mathrm{H}}{\underset{\mathrm{X}}{\mathrm{C}}}\cdot$$

Retarders and inhibitors generally operate by chain-transfer mechanism. These substances may be impurities in the system or are formed by side reactions during polymerization.

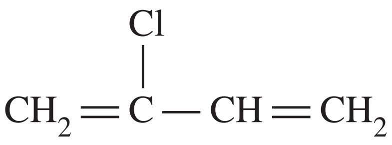
In some cases, they are added **deliberately** to the system to prevent inadvertent polymerization during transportation or storage. A typical example is hydroquinone, normally added to styrene must be subsequently stripped of the **inhibitor** before polymerization.

E. DIENE POLYMERIZATION

Conjugated dienes such as butadiene (1), chloroprene (2), and isoprene (3) constitute a second group of unsaturated compounds that can undergo polymerization through their double bonds.

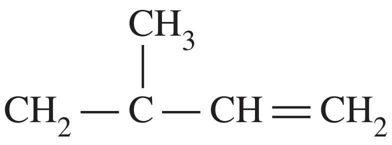
$CH_2{=}CH-CH{=}CH_2$

(1)



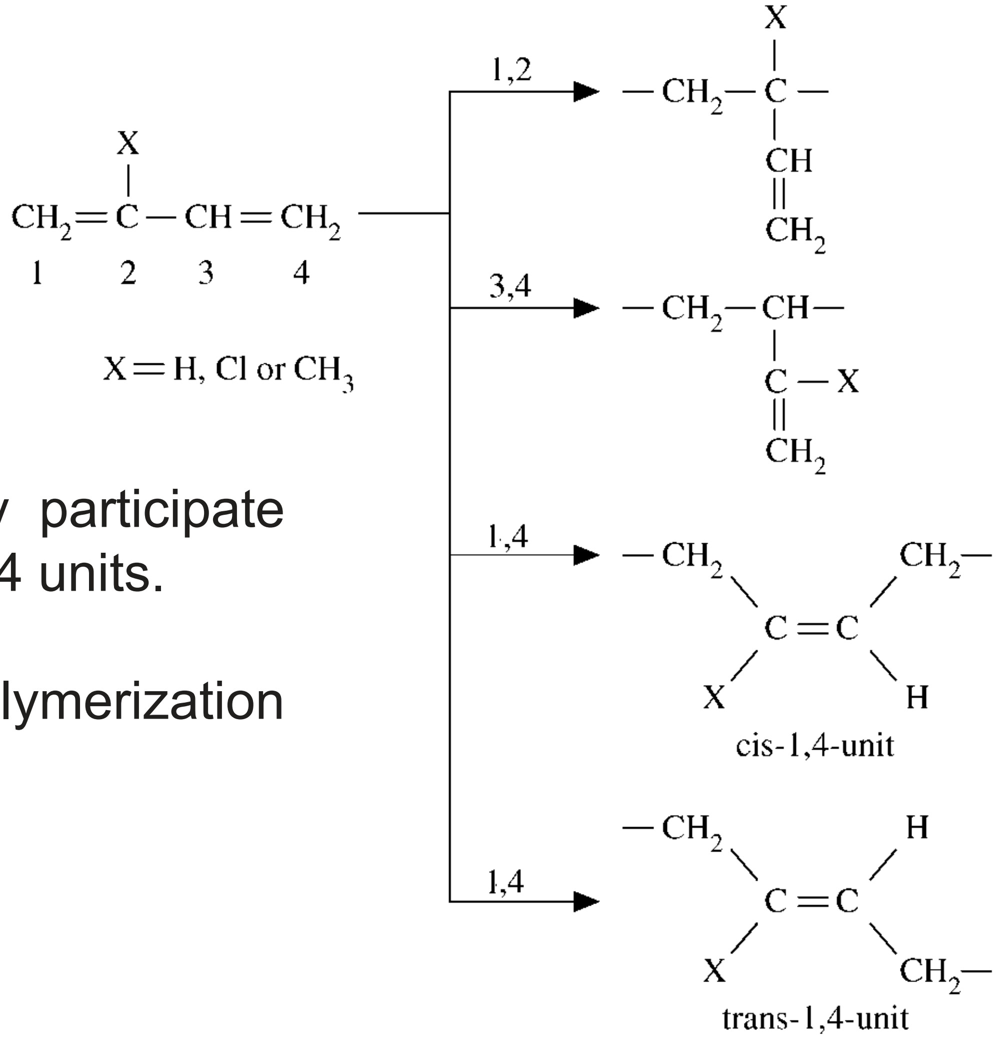
$CH_2{=}\overset{Cl}{\overset{|}{C}}-CH{=}CH_2$

(2)



$CH_2-\overset{CH_3}{\overset{|}{C}}-CH{=}CH_2$

(3)



The double bonds in the 1,2 and 3,4 positions may participate independently in polymerization giving rise to 1,2 and 3,4 units.

A further possibility is that both bonds are involved in polymerization through conjugate reactions, resulting in 1,4 units.

Diene polymerization thus gives rise to polymers that contain various isomeric units. With symmetrical dienes such as butadiene, the 1,2 and 3,4 units are identical.

The 1,4 unit may occur in the ***cis*** or ***trans*** configuration.

The relative abundance of each unit in the polymer molecule depends on the **nature of the initiator**, **experimental conditions**, and **the structure of the diene**.

The proportion of each type of structure incorporated into the polymer chain influences both **thermal** and **physical** properties.

For example, butadiene can be polymerized by free-radical addition at **low temperature** to produce a polymer that consists almost entirely of ***trans*-1,4 units** and only about 20% 1,2 units.

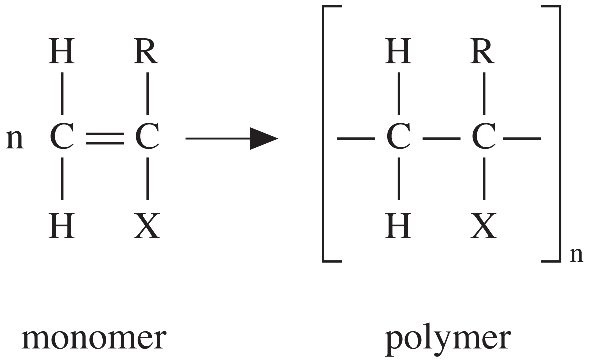
As the **temperature is increased**, the relative proportion of ***cis*-1,4 units** increases, while the proportion of 1,2 structure remains fairly constant.

Anionic diene polymerization with lithium or organolithium initiators like *n*-butyllithium in nonpolar solvents such as pentane or hexane yields polymers with high *cis*-1,4 content.

When higher alkali metal initiators or more polar solvents are used, the relative amount of *cis*-1,4 units decreases.

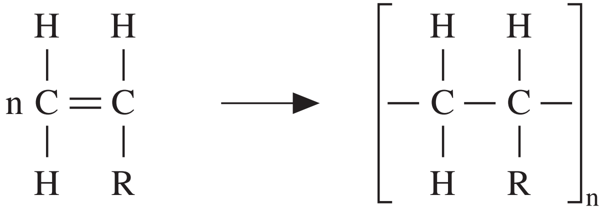
Stereoregularity can also be controlled by the use of coordination catalysts like Ziegler–Natta catalysts. Heterogeneous **Alfin catalysts** (combinations of alkenyl sodium compounds, alkali metal halides, and an alkoxide) give high molecular-weight polymers with high content of *trans*-1,4 units.

The **structural unit** in addition polymers is **chemically identical** to the monomer employed in the polymerization reaction:



$$n\ \mathrm{HHC{=}CRX} \longrightarrow \left[\,\begin{matrix} & \mathrm{H} & & \mathrm{R} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & - \\ & | & & | & \\ & \mathrm{H} & & \mathrm{X} & \end{matrix}\,\right]_n$$

Table 2.1 *Some Representation Addition Polymers*



$$n\,\mathrm{CH_2{=}CHR} \longrightarrow \left[-\mathrm{CH_2}-\mathrm{CHR}-\right]_n$$

monomer polymer

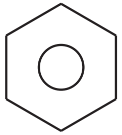
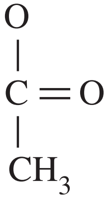
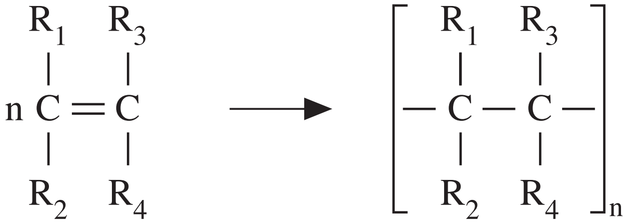
R	Monomer	Polymer
H	Ethylene	Polyethylene
CH_3	Propylene	Polypropylene
Cl	Vinyl chloride	Poly(vinyl chloride)
CN	Acrylonitrile	Polyacrylonitrile
	Styrene	Polystyrene
 $-O-C(=O)-CH_3$	Vinyl acetate	Poly(vinyl acetate)
 $-C(=O)-O-CH_3$	Methyl acrylate	Poly(methyl acrylate)

Table 2.1 (continued) *Some Representation Addition Polymers*



$$n\,\mathrm{C(R_1)(R_2){=}C(R_3)(R_4)} \longrightarrow \left[-\mathrm{C(R_1)(R_2)}-\mathrm{C(R_3)(R_4)}-\right]_n$$

R_1	R_2	R_3	R_4	Monomer	Polymer
H	H	CH_3	 $-C(=O)-O-CH_3$	Methyl methacrylate	Poly(methyl methacrylate)
H	H	Cl	Cl	Vinylidene chloride	Poly(vinylidene chloride)
H	H	F	F	Vinylidene fluoride	Poly(vinylidene fluoride)
F	F	F	F	Tetrafluoro-ethylene	Polytetrafluoroethylene

STEADY-STATE KINETICS OF FREE-RADICAL POLYMERIZATION

The overall mechanism for the conversion of a monomer to a polymer via free-radical initiation may be described by rate equations according to the following scheme.

A. INITIATION

A two-step process involving:

1. The decomposition of the initiator into primary radicals

$$I \xrightarrow{k_d} 2R\bullet$$

2. The addition of a monomer to the primary free radical

$$R\bullet + M \xrightarrow{k_a} RM_i\bullet$$

The constants k_d and k_a are the rate constants for **initiator dissociation** and **monomer addition**, respectively.

Since **initiator dissociation** is much slower than monomer addition, the first step of the initiation step (initiator dissociation) is the **rate-limiting step**.

Some of the initiator radicals may undergo side (secondary) reactions, such as combination with another radical, that preclude monomer addition. Therefore only a fraction, **f** (an **efficiency factor**), of the initial initiator concentration is effective in the polymerization process.

Decomposition of each initiator molecule produces a **pair of free radicals**, either or both of which can initiate polymerization.

Based on these observations, the rate expression for initiation may be written as:

$$R_i = \frac{d[M.]}{dt} = 2\ fk_d[I]$$

where [I] represents the initiator concentration.

B. PROPAGATION

The successive addition of monomers during propagation may be represented as follows:

$$RM_1\cdot + M \xrightarrow{k_p} RM_2\cdot$$

$$RM_2\cdot + M \xrightarrow{k_p} RM_3\cdot$$

In general,

$$RM_x\cdot + M \xrightarrow{k_p} RM_{x+1}^{\Sigma}$$

On the assumption, radical **reactivity** is **independent** of chain **length**, therefore the propagation steps have the same rate constants k_p.

Propagation is a fast process. For example, under typical reaction conditions, a polymer of molecular weight of about 10^7 may be produced in 0.1 s.

The rate of polymerization equals essentially the rate of consumption of monomers in the propagation step.

The rate expression for polymerization rate can be written:

$$R_p = -\frac{d[M]}{dt} = k_p[M*][M]$$

where $[M^*] = \sum RM_x\bullet$, the sum of the concentrations of all chain radicals of type RM_x.

C. TERMINATION

Chain growth may be terminated at any point during polymerization by either or both of two mechanisms:

- Combination (coupling) $$M_x\cdot + M_y\cdot \xrightarrow{k_{tc}} M_{x+y}$$
- Disproportionation $$M_x\cdot + M_y\cdot \xrightarrow{k_{td}} M_x + M_y$$

If there is no need to distinguish between the two types of termination, which in any case are kinetically equivalent, then termination may be represented as:

$$M_x\cdot + M_y\cdot \xrightarrow{k_t} P$$

where $k_t(k_{tc} + k_{td})$, k_{tc}, and k_{td} are the rate constants for overall termination process: termination by coupling and termination by disproportionation, respectively.

The termination rate is given by: $$R_t = \frac{-d[M\cdot]}{dt} = 2k_t[M\cdot]^2$$

The factor of 2 arises from the fact that at each incidence of termination reaction, two radicals disappear.

Over the course of polymerization (at **steady state**), the total radical **concentration remains constant;** the radicals are being produced and destroyed at equal rates (i.e., $R_i = R_t$):

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

Since the overall polymerization rate is essentially the rate of monomer consumption during propagation:

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

According to the above equation, rate of polymer formation in free-radical polymerization is **first order in monomer concentration** and **half order in initiator concentration**.

This assumes that the initiator efficiency is **independent** of monomer concentration.

AUTOACCELERATION (TROMMSDORFF EFFECT)

Since the initiator concentration remains fairly unchanged in the course of vinyl polymerization, first-order kinetics with respect to the monomer is expected (if the initiator efficiency is independent of monomer concentration).

The polymerization of certain monomers shows a marked deviation from such first-order kinetics. At a certain stage in the polymerization process, a considerable increase in both the reaction rate and the molecular weight is observed. This observation is referred to as ***autoacceleration*** or ***gel effect***.

It occurs **independent** of an initiator and is observed even under isothermal conditions. As there is no effective dissipation of heat, autoacceleration results in a large increase in temperature.

To understand the physical phenomena during autoacceleration, the following rate equation is considered:

$$R_p \propto k_p \left(\frac{fk_d}{k_t}\right)^{1/2}$$

Since autoacceleration is not a function of the initiator, an increase in the factor fk_d does not provide an explanation for the observation. Consequently, the autoacceleration could be due to an **increase** in the propagation rate constant $\mathbf{k_p}$ and/or a **decrease** in the termination rate constant $\mathbf{k_t}$.

Trommsdorff attributed autoacceleration to a decrease in the termination rate. As the concentration of polymer molecules generated builds up, the viscosity of the medium increases. This **reduces** the overall **diffusion rate** of growing radical-bearing polymer molecules even though the intrinsic **reactivity** of the radical remains **unaffected**.

As a result, the bimolecular annihilation of **radical reactivity** becomes **diffusion-controlled**.

This reduction in termination rate, in turn, increases the concentration of active radicals, and the rate of local consumption of monomers increases proportionately.

The overall rate of propagation remains relatively unaffected since the diffusion of monomers is hardly affected by the **high** medium **viscosity**. This **reduction in termination** rate leads to a **rapid rise** in the **molecular weight**.

Propagation becomes monomer **diffusion-controlled**.

III. IONIC POLYMERIZATIONS

Ionic polymerizations involve chain carriers or reactive centers that are organic ions or charged organic groups.

In **anionic** polymerization, the growing chain end carries a negative charge or **carbanions**, while **cationic** polymerization involves a growing chain end with a positive charge or **carbonium** ion.

The mechanisms of ionic polymerizations are more complex and are not as clearly understood as those of free radical polymerization.

Initiation of ionic polymerization usually involves the transfer of an ion or an electron to or from the monomer.

Many monomers can polymerize by more than one mechanism, but the most appropriate polymerization mechanism for each monomer is **related** to the **polarity of the monomers** and the **Lewis acid–base strength of the ion** formed.

A. CATIONIC POLYMERIZATION

Monomers with **electron-donating groups** like isobutylene form stable positive charges and are readily converted to polymers by cationic catalysts.

Typical catalysts that are effective for cationic polymerization include $AlCl_3$, $AlBr_3$, BF3, $TiCl_4$, $SnCl_4$, and sometimes H_2SO_4. With the exception of H_2SO_4, these compounds are all Lewis acids with strong electron-acceptor capability. To **be effective**, these catalysts require the presence of a **Lewis** base such as water, alcohol, or acetic acid as a **cocatalyst**.

Cationic polymerizations proceed at **high rates** in **solutions** and frequently at **temperatures** as **low** as –80 to –100 °C at **low temperatures**. For example, the polymerization at –100 °C of isobutylene with BF_3 or $AlCl_3$ as catalysts yields, within a few seconds, a polymer with **molecular weight** as high as **10^6**.

Both the **rate of polymerization** and the **molecular weight** of the polymer **decrease** with **increasing temperature**. The molecular weights of polyisobutylene obtained at room temperature and above are lower than those obtained through radical polymerization.

Mechanism

The mechanism for cationic polymerization involves carbonium ion chain carrier.

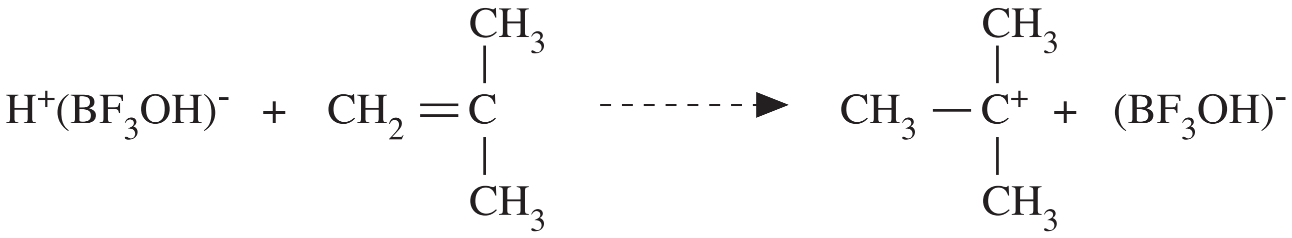
1. During **initiation**, a proton adds to the monomer to form a carbonium ion, which forms an association with the counterion.

The polymerization of isobutylene with BF_3 as the catalyst can be represented thus:

First, the catalyst and cocatalyst (e.g., water) form a complex:

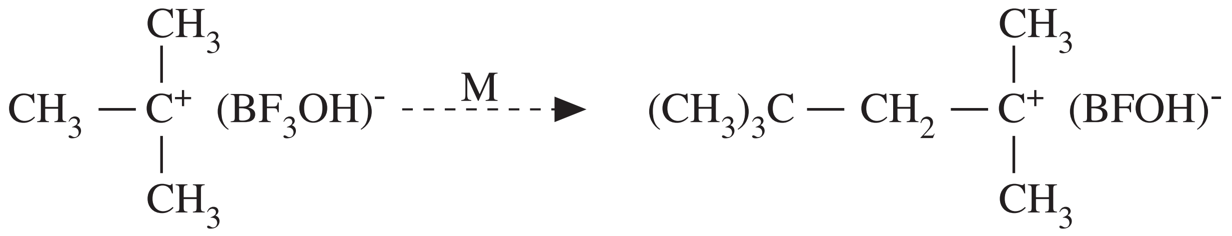
$$BF_3 + H_2O \longrightarrow H^+(BF_3OH)^-$$

The complex then donates a proton to an isobutylene molecule to form a carbonium ion:



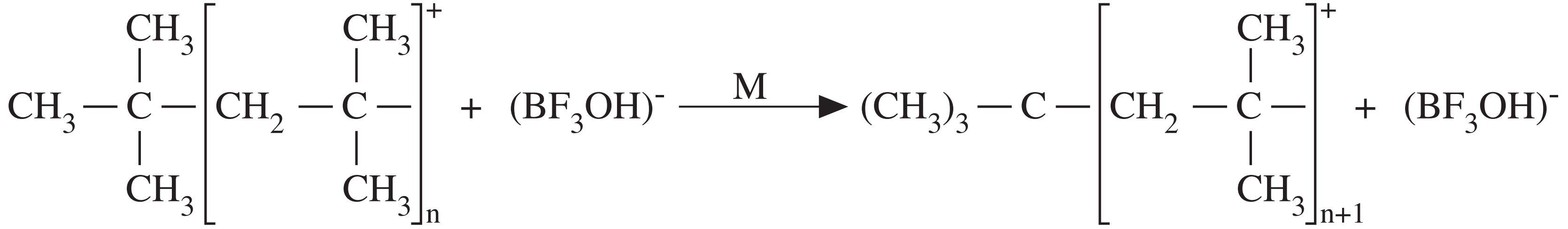
$$H^+(BF_3OH)^- + CH_2{=}C(CH_3)_2 \dashrightarrow CH_3{-}C^+(CH_3)_2 + (BF_3OH)^-$$

2. Propagation involves the consecutive additions of monomer molecules to the carbonium ion at the growing chain end.



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C^+}}\ (BF_3OH)^- \xrightarrow{M} (CH_3)_3C-CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C^+}}\ (BFOH)^-$$

In general, the propagation reaction can be written as:



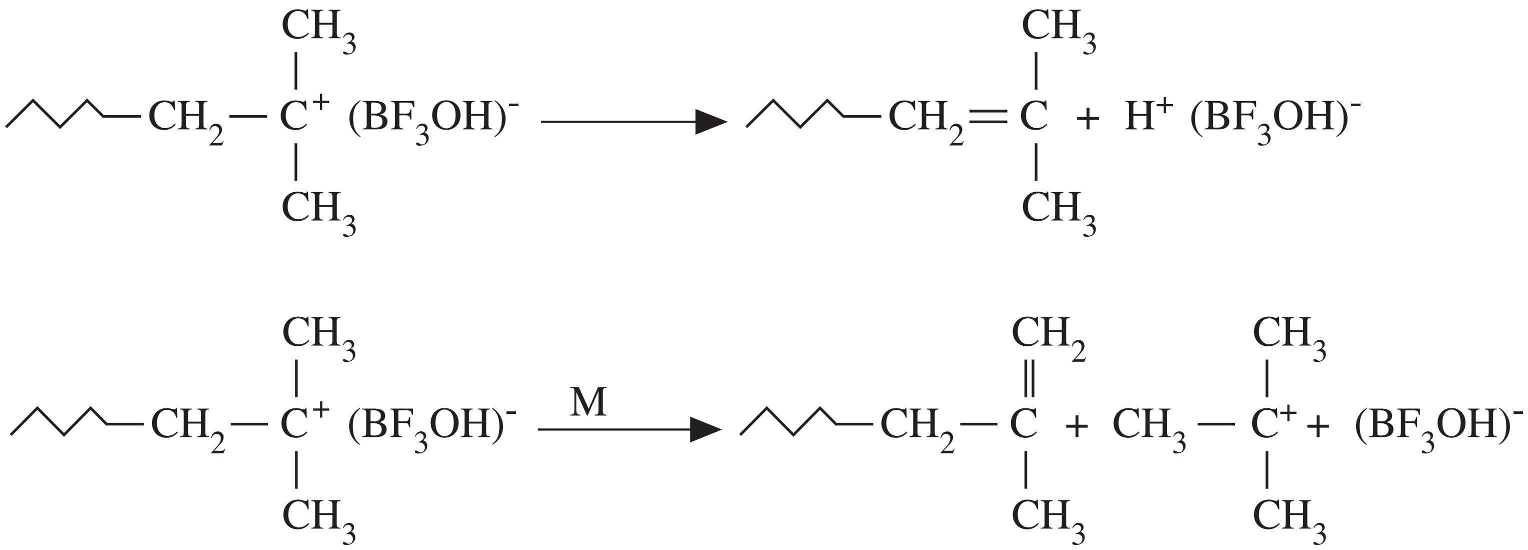
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\left[CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\right]_n^+ + (BF_3OH)^- \xrightarrow{M} (CH_3)_3-C-\left[CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\right]_{n+1}^+ + (BF_3OH)^-$$

Since cationic polymerization is generally carried out in hydrocarbon **solvents** that have **low dielectric constants**, separation of the ions would require a large amount of energy.

The cation and the counterion in cationic polymerization remain in close proximity. If the association between the **ion pair is too strong**, monomer insertion during **propagation will be prevented**. The **choice of solvent** in cationic polymerization has to be made carefully.

A linear **increase in polymer chain length** and an exponential **increase in the reaction rate** usually occur as the **dielectric strength** of the solvent **increases**.

3. Termination in cationic polymerization usually involves rearrangement to produce a polymer with an unsaturated terminal unit and the original complex or chain transfer to a monomer and possibly to the polymer or solvent molecule.



$$\sim\!\sim\!-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}}\ (BF_3OH)^- \longrightarrow \sim\!\sim\!-CH_2=\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\ +\ H^+\ (BF_3OH)^-$$

$$\sim\!\sim\!-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}}\ (BF_3OH)^- \xrightarrow{M} \sim\!\sim\!-CH_2-\overset{\displaystyle CH_2}{\overset{\|}{\underset{\displaystyle CH_3}{C}}}\ +\ CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^+}}+\ (BF_3OH)^-$$

Unlike free-radical polymerization, termination by **combination** of two cationic polymer growing chains does **not occur**.

Also, unlike in free-radical polymerization, the **catalyst is not attached to the resulting polymer** molecule, and in principle many polymer molecules can be produced by each catalyst molecule.

Kinetics

For cationic polymerization, the individual reaction steps can be represented as follows:

$$A + RH \overset{K}{\rightleftharpoons} H^{+}\ AR^{-}$$

$$H^{+}\ AR^{-} + M \xrightarrow{k_i} HM^{+}\ AR^{-}$$

$$HM_n^{+}\ AR^{-} + M \xrightarrow{k_p} HM_{n+1}^{+}\ AR^{-}$$

$$HM_n^{+}\ AR^{-} \xrightarrow{k_t} M_n + H^{+}\ AR^{-}$$

$$HM_n^{+}\ AR^{-} + M \xrightarrow{k_{tr}} M_n + HM^{+}\ AR^{-}$$

A represents the catalyst and **RH** the cocatalyst, **M** the monomer, and the catalyst–cocatalyst complex $H^{+}AR^{-}$.

The rate of initiation R_i is given by $R_i = k_i\left[H^{+}\ AR^{-}\right]\left[M\right] = k_i K\left[A\right]\left[RH\right]\left[M\right]$

If the complex H^+AR^- is the rate-limiting step, then the rate of initiation is independent of the monomer concentration. Since AR^- remains in the close vicinity of the growing center, the termination step is first order:

$$R_t = K_t \left[M^+\right]$$

where $[M^+]$ is the concentration of all the chain carriers $[HM_n^+AR^-]$.

Assuming that **steady state** holds, then $R_i = R_t$ and

$$\left[M^+\right] = \frac{K\,k_i}{k_t}[A][RH][M]$$

The overall rate of polymerization, R_p is given by

$$R_p = k_p\left[M^+\right][M] = K\,\frac{k_i\,k_p}{k_t}[A][RH][M]^2$$

The number-average degree of polymerization, assuming predominance of termination over chain transfer, is

$$\overline{X}_n = \frac{R_p}{R_i} = \frac{k_p}{k_t}\frac{\left[M^+\right]\left[M\right]}{\left[M^+\right]} = \frac{k_p}{k_t}\left[M\right]$$

If chain transfer dominates, then

$$\overline{X}_n = \frac{R_p}{R_{tr}} = \frac{k_p\left[M^+\right]\left[M\right]}{k_t\left[M^+\right]\left[M\right]} = \frac{k_p}{k_{tr}}$$

In this case, the average degree of polymerization is **independent** of both the concentration of the monomer and the concentration of the catalyst.

B. ANIONIC POLYMERIZATION

Monomers that are suitable for anionic polymerization generally contain **electron-withdrawing** substituent groups. They polymerize readily in the presence of active centers bearing whole or partial negative charges.

Typical electron-withdrawing substituents that permit the anionic polymerization of a monomer include –CN, –COOR, $–C_6H_5$, and $–CH=CH_2$. The electronegative group pulls electrons from the double bond and consequently renders the monomer susceptible to attack by an electron donor.

For example, a high-molecular-weight polymer is formed when methacrylonitrile is added to a solution of sodium in liquid ammonia at –75 °C.

The **initiator** in anionic polymerization may be any compound providing a strong nucleophile, including **Grignard reagents, organometallic** compounds (e.g. organosodium compounds), alkali metal amides, alkoxide, and hydroxides.

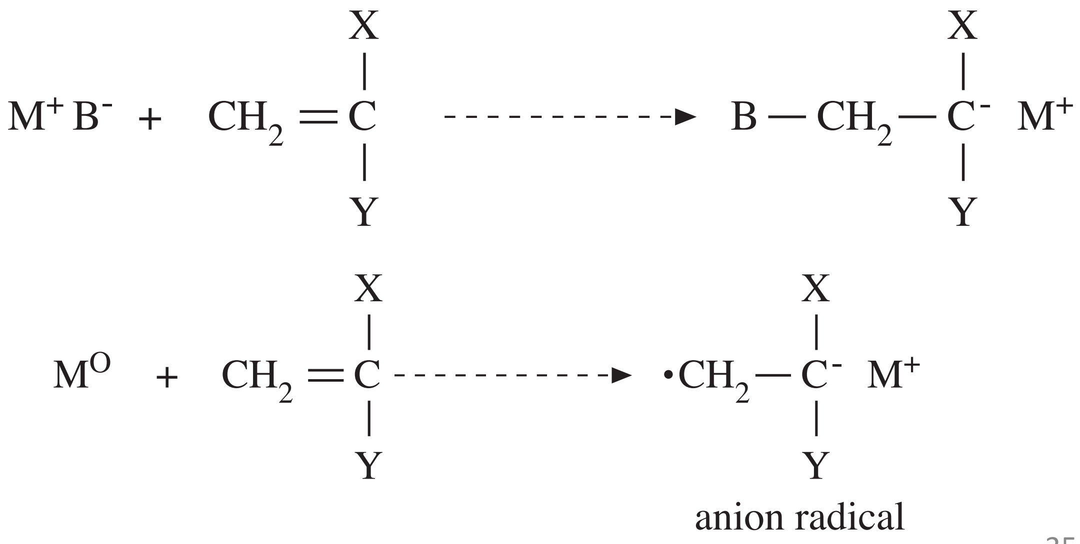
Mechanism

1. Initiation involves the addition of the initiator to the double bond of the monomer:

$$n - C_4H_9^- \; Li^+ + CH_2 = CH_2 \longrightarrow n - C_4H_9 - CH_2 - CH^- \, Li^+$$

The reaction produces a carbanion at the head end to which is associated the positively charged lithium counterion.

Initiation may occur in two ways: a direct attack of a base on the monomer to form a carbanion or by transfer of an electron from a donor molecule to the monomer to form an anion radical:



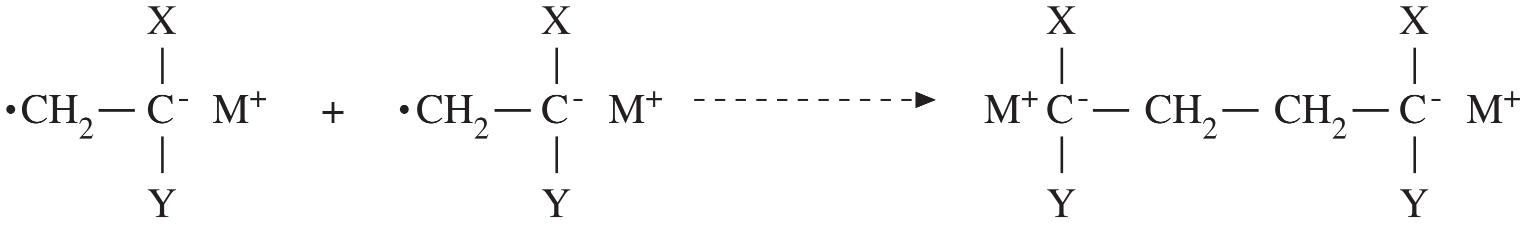
$$M^+B^- + CH_2 = \underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C}} \dashrightarrow B - CH_2 - \underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C^-}} \; M^+$$

$$M^O + CH_2 = \underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C}} \dashrightarrow \bullet CH_2 - \underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C^-}} \; M^+$$

$M^+B^–$ may be a metal amide, alkoxide, alkyl, aryl, and hydroxide depending on the nature of the monomer.

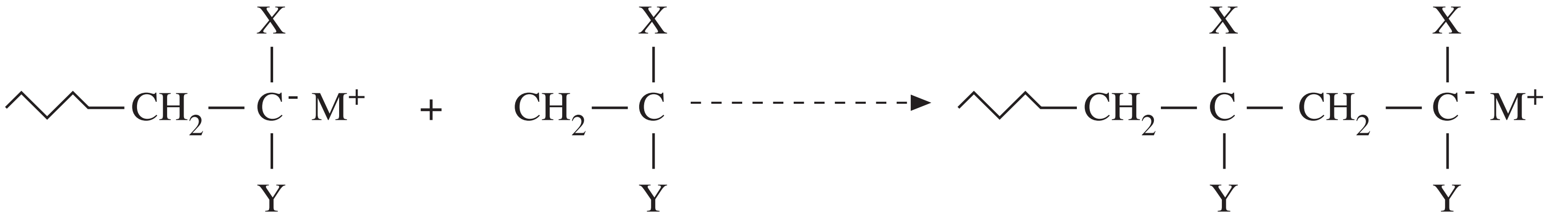
The effectiveness of the catalyst in the initiation process depends on its basicity and the acidity of the monomer.

If the donor molecular is an alkali metal, the electron transfer results in the formation of a positively charged alkali metal counterion and an anion radical. Pairs of anion radicals combine to form a dianion



$$\cdot CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+ \quad + \quad \cdot CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+ \dashrightarrow M^+\,\overset{X}{\underset{Y}{C^-}}-CH_2-CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+$$

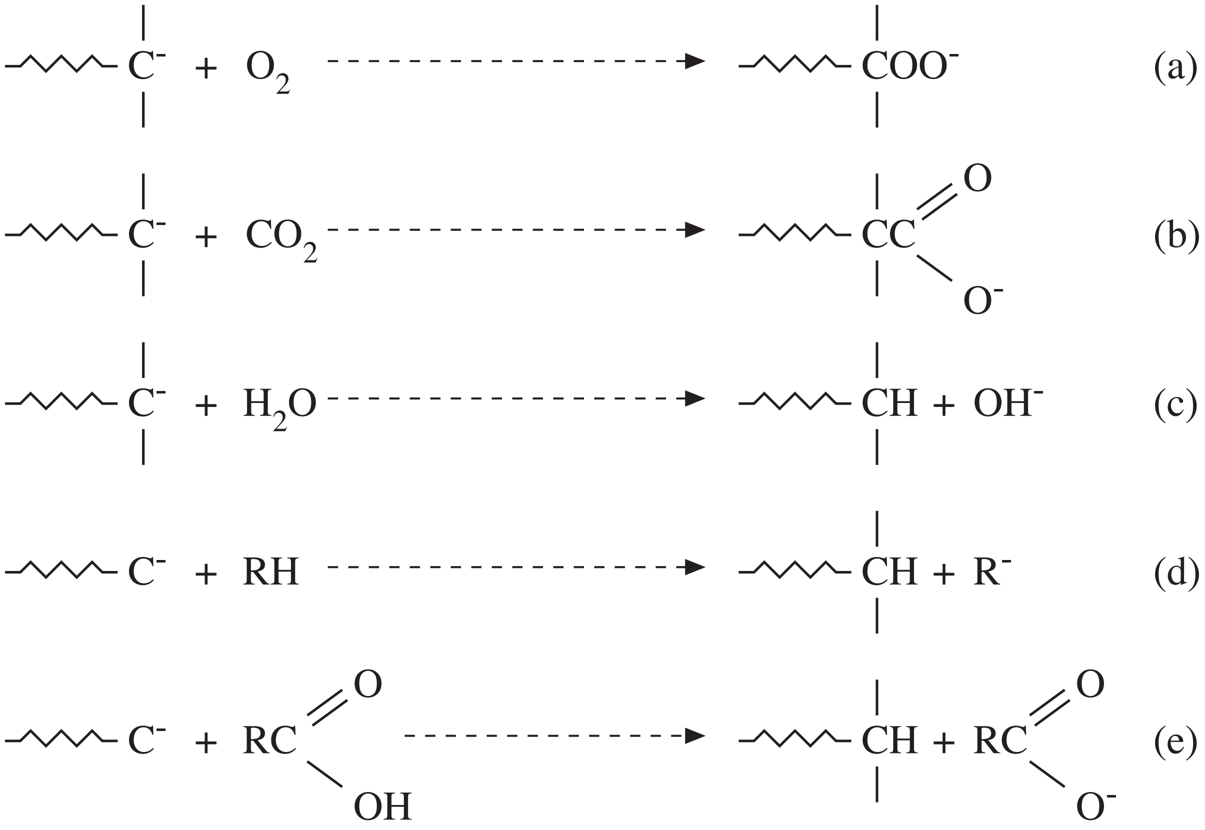
2. Propagation occurs by the successive insertion of monomer molecules by anionic attack of the carbanion.



$$\sim\!\sim CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+ \quad + \quad CH_2-\overset{X}{\underset{Y}{C}} \dashrightarrow \sim\!\sim CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C^-}}\ M^+$$

M^+ represents a counterion that accompanies the growing chain. X and Y are either electron-withdrawing groups or unsaturated groups capable of resonance stabilization of the negative charge.

3. Termination of the growth activity of the polymer chain takes place either **(a)** by the deliberate or accidental introduction into the system of oxygen, carbon dioxide, methanol, water, or **(b)** other molecules that are capable of reacting with the active chain ends.



The terminal groups in Equations a and b cannot propagate, and can effectively terminate polymer growth.

Equations c–e involve proton transfer from the solvent to the growing chain resulting in a **dead polymer**.

Other possible termination reactions include:

1. the transfer of a hydride ion leaving a residual terminal unsaturation (a high-energy process and therefore unlikely);
2. isomerization of the carbanion to give an inactive anion;
3. irreversible reaction of the carbanion with the solvent or monomer.

In general, termination by transfer to the solvent predominates in anionic polymerization.

No chain transfer or branching occurs in **anionic** polymerization, particularly if reactions are carried out at low temperatures.

In **anionic** and free-radical polymerizations, the **initiator or part of it becomes part of the resulting polymer molecule**, attached to the nongrowing chain end. This **contrasts** with **cationic** polymerization where the catalyst is necessary for initiation and propagation, but it is regenerated at the termination step.

In carefully **controlled systems** (pure reactants and inert solvents), anionic polymerizations do **not** exhibit **termination** reactions. Such systems are referred to as “**living polymers”** because of the absence of termination.

This polymer molecules can **remain active** even after all the monomer molecules are consumed. When fresh monomer is added, polymerization **resumes**.

Since the chain ends grow at the same rate, the molecular weight of living polymers is determined simply by the ratio of monomer concentration to that of the initiator.

$$\text{Degree of Polymerization}\left(\text{DP}\right)=\frac{\left[\text{monomer}\right]}{\left[\text{initiator}\right]}$$

Polymers produced by living polymerization are characterized by **very narrow** molecular weight distribution (**Poisson distribution**), where D, M_w, and M_n are the polydispersity, weight-average molecular weight, and number-average molecular weight, respectively:

$$\mathrm{D}=\overline{\mathrm{M}}_{\mathrm{w}}\Big/\overline{\mathrm{M}}_{\mathrm{n}}=1+1/\mathrm{DP}$$

The absence of termination in living polymerization permits the synthesis of **unusual** and unique **block polymers** — star- and comb-shaped polymers.

For example, if a living polymer with one active end from monomer A can initiate the polymerization of monomer B, then an A–AB–B type copolymer can be obtained (e.g., styrene–isoprene copolymer).

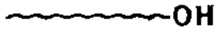
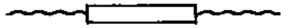
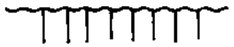
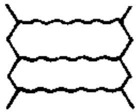
The potential versatility of living polymers is demonstrated by the possibility of formation of polymers with **complex shapes** by employing polyfunctional initiators or terminating monodisperse living polymers with polyfunctional linking agents.

For example, **star-shaped** poly(ethylene oxide) can be prepared with the trifunctional initiator trisodium salt of triethanolamine, $N(CH_2CH_2O^- Na^+)_3$.

Another possible area of utilizing living polymers is in the **introduction of specific end groups** by terminating the living polymer with an appropriate agent.

For example, termination of living polystyrene with CO_2 introduces terminal carboxylic groups, while reaction with ethylene oxide introduces hydroxy end groups.

Table 7.4. Architectural forms of polymers available by living polymerization techniques .(6)

	Polymer	Application
1	 *Functional ended*	Dispersing agents Synthesis of macromonomers
2	 *α,ω difunctional*	Elastomer synthesis Chain extension Cross-linking agents
3	 *AB Block*	Dispersing agents Compatibilizers for polymer blending
4	 *ABA Block*	Thermoplastic elastomers
5	 *Graft*	Elastomers Adhesives
6	 *Comb*	Elastomers Adhesives
7	 *Star*	Rheology control Strengthening agents
8	 *Ladder*	High-temperature plastics Membranes Elastomers
9	 *Cyclic*	Rheology control
10	 *Amphiphilic network*	Biocompatible polymers

Kinetics

Polymerization of styrene by potassium amide in liquid ammonia:

$$\mathrm{KNH_2} \overset{K}{\rightleftharpoons} \mathrm{K^+ + NH_2^-}$$

$$\mathrm{NH_2^- + M \xrightarrow{k_i} NH_2M^-}$$

$$\mathrm{NH_2M_n^- + M \xrightarrow{k_p} NH_2M_{n+1}^-}$$

$$\mathrm{NH_2M_n^- + NH_3 \xrightarrow{k_{tr}} NH_2M_nH + NH_2^-}$$

Considering the relatively high dielectric constant of the liquid ammonia medium, the counterion K⁺ can be neglected.

Assuming **steady-state** kinetics:

$$\mathrm{R_i = k_i\left[NH_2^-\right]\left[M\right]}$$

$$\mathrm{R_t = k_{tr}\left[NH_2 - M_n^-\right]\left[NH_3\right]}$$

Then

$$\left[NH_2-M_n^-\right]=\frac{k_i}{k_{tr}}\frac{\left[NH_2^-\right]\left[M\right]^2}{\left[NH_3\right]}$$

The rate of polymerization becomes

$$R_p=k_p\left[NH_2-M_n^-\right]\left[M\right]$$

$$=k_p\frac{k_i}{k_{tr}}\frac{\left[NH_2^-\right]\left[M\right]^2}{\left[NH_3\right]}$$

Given the predominance of transfer reactions, the degree of polymerization X_n is given by

$$\overline{X}_n=\frac{R_p}{R_t}=\frac{k_p}{k_{tr}}\frac{\left[M\right]}{\left[NH_3\right]}$$

C. COORDINATION POLYMERIZATION

Unbranched and **stereospecific** polymers are also produced by the use of **Ziegler–Natta** catalysts.

Since polymerization processes utilizing these catalysts result in stereoregular structures, they are sometimes called **stereospecific** or **stereoregular polymerization**.

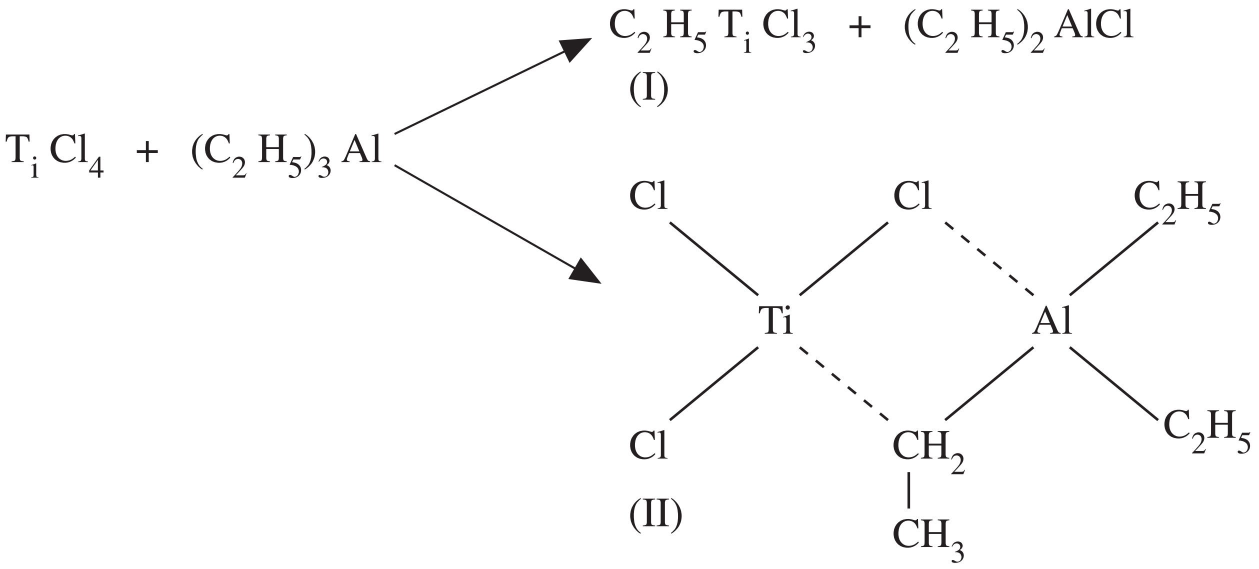
However, the term *coordination polymerization* is used to reflect the mechanism, which is believed to govern the reaction involving these catalysts.

Monoolefins such as propylene and dienes such as butadiene and isoprene can be polymerized using Ziegler–Natta coordination catalysts.

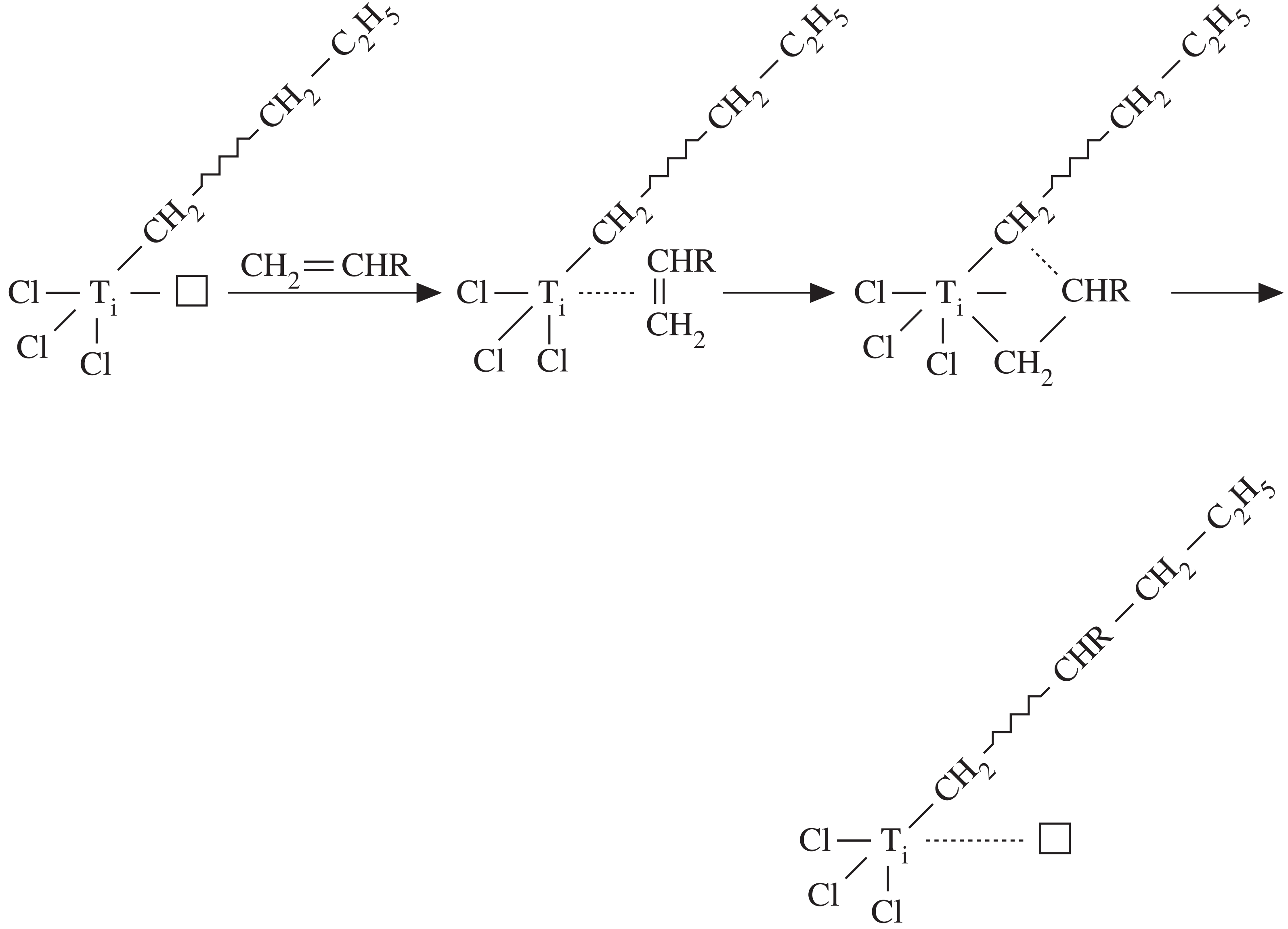
Mechanisms

Ziegler–Natta catalysts are complex catalyst systems derived from a light element of groups IA–IIIA of the periodic table (e.g., Li, Be, Mg, Al) as **organometallic** compounds, and halides derivatives of **transition metals** of groups IVB–VIIIB (e.g., Ti, V, Cr, Mo, Rh, Rn, Co, and Ni).

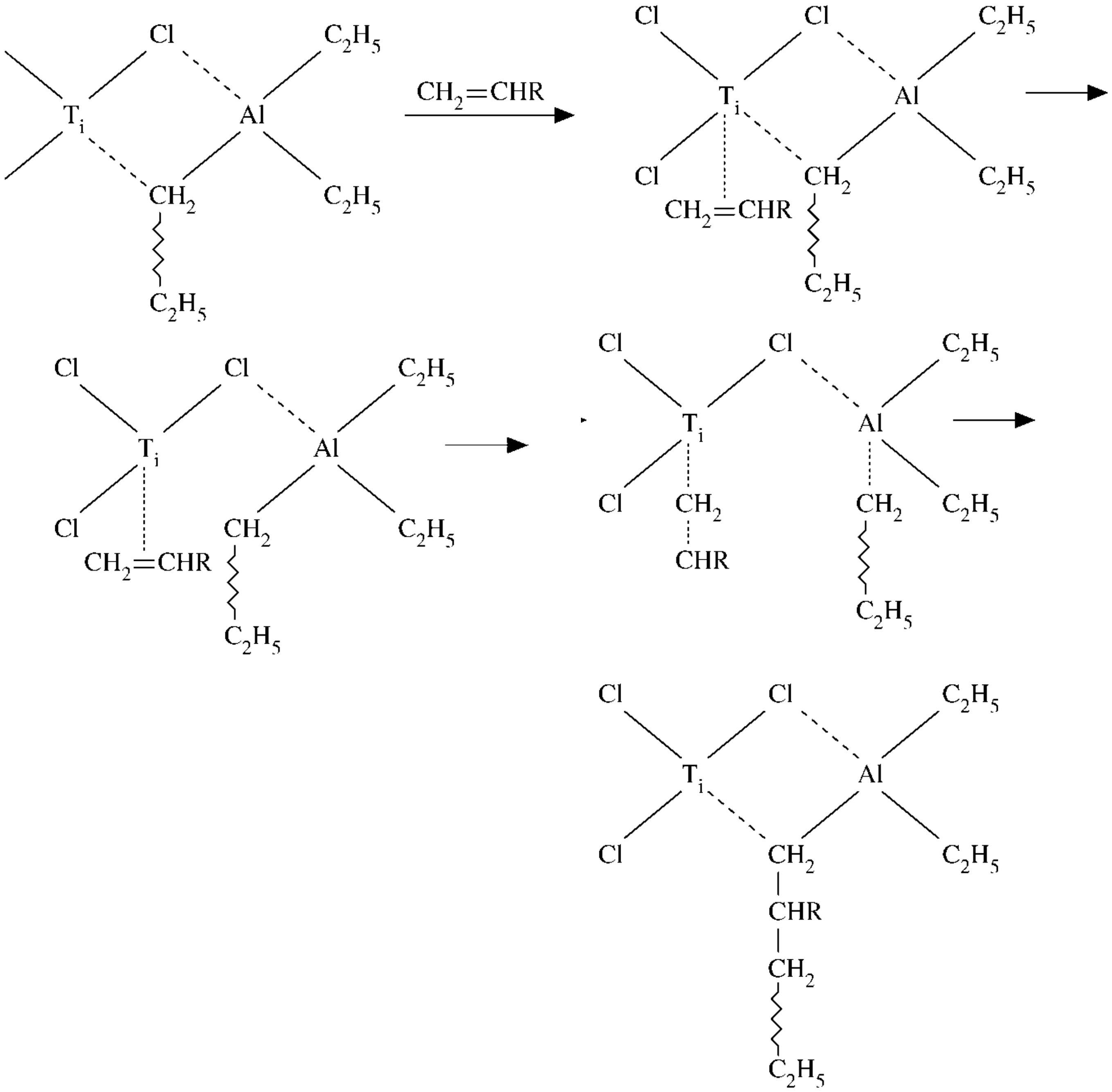
A typical example is the product(s) of the reaction between triethylaluminum and titanium tetrachloride. The composition of the product is not well defined but is believed to be either an alkylated metal halide (**monometallic** I) or a **bimetallic** complex involving a bridge between the two metals (II).



Monomettalic catalyst



Bimetallic catalyst



The **catalysts** function by forming transient **π-complexes** between the monomers and the transition metal species.

It can be involved the overlap of the electrons of the monomer with a vacant sp orbital in the case of groups I–III metals or a vacant d orbital in the case of transition metals.

The **initiating species** is a **metal–alkyl complex** and propagation involves the consecutive insertion of monomer molecules into a **polarized titanium–carbon bond**.

Coordination polymerizations may be **terminated** by introducing **poisons** such as water, hydrogen, aromatic alcohols, or metals like zinc into the reacting system.

The **dominant feature** of the coordination polymerization mechanism is the presence of forces that **orient** and **insert** each incoming monomer into the growing polymer chain according to a particular **steric configuration**.

The **surface** of the crystalline salts of the **transition metals** that constitute part of the catalyst system is thought to play a vital role in this function.

With Ziegler–Natta catalysts, ethylene is polymerized to a **highly linear chain** compared with the branched products from the high-pressure process (radical polymerization).

By a convenient **choice of catalyst** system, isotactic and syndiotactic polypropylene can be obtained. Higher α-olefins yield isotactic polymers with heterogeneous catalyst systems.

The versatility and selectivity of Ziegler–Natta catalysts are demonstrated even more sharply in the polymerization of **conjugated dienes**.

By a suitable choice of catalyst system and reaction conditions, conjugated dienes like butadiene and isoprene can be made to polymerize into any of their isomers almost exclusively: *trans*-1,4; *cis*-1,4; or isotactic or syndiotactic 1,2.