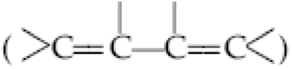
Addition Polymerization or Chain-Growth Polymerization

General Theory of Addition Polymerization

Addition polymerization is a process by which unsaturated monomers are converted to polymers of high molecular weight, exhibiting the characteristics of a typical chain reaction. A large number of different class of unsaturated monomers, such as ethylene ($CH_2 = CH_2$) the simplest olefin, α-olefins ($CH_2 = CHR$, where R is an alkyl group), vinyl compounds ($CH_2 = CHX$, where X = Cl, Br, I, alkoxy, CN, COOH, COOR, C_6H_5, etc., atoms or groups) and conjugated diolefins  $(>C=\overset{|}{C}-\overset{|}{C}=C<)$ readily undergo this type of polymerization, mechanistically characterized as chain-growth polymerization or simply chain polymerization.

Addition or chain-growth polymerization, as all other typical chain reactions, are fast reactions typified by three normally distinguishable steps, viz. (i) triggering off or initiation of the chain process, (ii) propagation of the chain or the chain growth process, and (iii) cessation of the chain growth, i.e. the chain termination process.

Overall Scheme of Radical Chain Polymerization

Addition or chain polymerization is also commonly known as vinyl and related polymerization in view of the fact that most of the monomers involved generally contain the chemical group ($CH_2 = CH—$), commonly identified as the vinyl group. In radical or free radical polymerization, the chain propagating species is a free radical and the process is usually initiated using a free radical generating catalyst or initiator in the monomer or the polymerization medium.

3.2.1. Chain Polymerization using a Free Radical Initiator

The polymerization of a vinyl or related monomer M, induced in presence of a free radical initiator, I may be schematically expressed as follows:

Initiator decomposition:

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

(3.3)

followed by *Chain initiation:*

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{RM}_1^{\bullet}$$

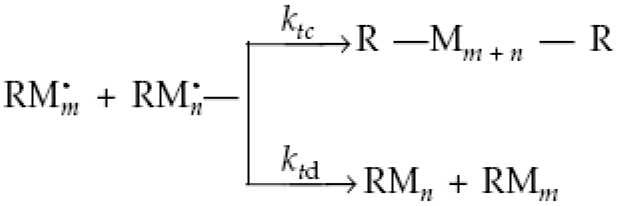
(3.4)

Chain propagation:

$$\left.\begin{array}{r}\mathrm{RM}_1^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}_2^{\bullet} \\ \mathrm{RM}_2^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}_3^{\bullet} \\ \mathrm{RM}_{n-1}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}_n^{\bullet}\end{array}\right\}$$

(3.5)

Chain termination:



$$RM_m^{\bullet} + RM_n^{\bullet} \xrightarrow{k_{tc}} R-M_{m+n}-R$$

$$RM_m^{\bullet} + RM_n^{\bullet} \xrightarrow{k_{td}} RM_n + RM_m$$

(3.6) (3.7)

where $R^{\bullet}$ is a free radical generated from the initiator I and $RM_1^{\bullet}$, $RM_2^{\bullet}$, $RM_3^{\bullet}$, etc. are the growing polymer chains, each bearing a free valency or radical centre at the chain-end and RM_n, RM_m, $R — M_{n+m} — R$, etc., are the (dead) polymer molecules obtained.

It is apparent from the above scheme that the initiator fragments in the form of radical $R^{\bullet}$ are trapped as end groups in the polymer structure, sealing one or both ends of the polymer chains.

Comparison between Chain-growth and Step-growth Polymerization

A comparative account of the differences between chain polymerization or addition polymerization on the one hand and step polymerization or condensation polymerization on the other is given in Table 3.1.

Table 3.1. Comparison of addition polymerization and condensation polymerization

Addition/Chain-growth Polymerizaion	Condensation/Step-growth Polymerization
Proceeds by a chain mechanism characterized by the three distinct steps in the main, viz. chain initiation, chain propagation and chain termination. Under favourable condition, the reaction goes fast almost to completion	Proceeds by an equilibrium step reaction mechanism. The step process is usually much slower than the addition or chain polymerization process
Monomers with carbon–carbon unsaturation undergo addition polymerization	Monomers bearing functional groups of the kind —OH, —COOH, —NH_2, —NCO, etc., undergo condensation polymerization
The growth reaction simply involves addition of monomers with one another in quick succession and the chain carrier is either a free radical, cation (carbonium ion) or an anion (carbanion). No byproduct is eliminated in the process. Growth or propagation involves reaction of only monomer molecules with the active centres	The growth process is characterized by relatively slow intermolecular condensation reaction between related functional groups in successive (distinguishable) steps, normally with the elimination of a small byproduct of condensation such as H_2O, HCl, NH_3, etc., in each step. Any two species of any size, including the monomers may react and contribute to the growth process
Monomer concentration decreases throughout the course of the polymerization process, as the yield of polymer increases. Usually, the conversion of monomer to polymer passes	Monomer disappears much faster in the early stages of the step polymerization

Addition/Chain-growth Polymerizaion	Condensation/Step-growth Polymerization
through a steady rate zone at some early stage of the reaction	
Molecular species in the intermediate stages of growth cannot be isolated. Conversion of monomer to polymer increases with time but the molecular weight of the polymer remains more or less unchanged with progress of reaction	Molecular species in the intermediate stages of growth can be readily isolated. Molecular weight slowly increases throughout the process and it is only at a very high range of conversion that polymer molecules of very high molecular weight are obtained
At any instant of time the reaction mixture consists of full grown polymer molecules, unreacted monomer molecules and a very low concentration (10^{-8}–10^{-3} mol. 1^{-1}), of growing chains or active centres	At any instant of time the reaction mixture consists of molecular species of different sizes in a calculable distribution
Full grown polymers are normally formed at the incidence of the termination reaction, and they are considered as dead polymers, being normally incapable of taking further part in the chain growth process	Molecular species of any size retain the reactive functional groups at their chain ends and hence, they are capable of contributing to further chain growth indefinitely. As such, there can be no termination of the process till it reaches 100% extent of reaction
Usually the backbone of the polymer chains consists of —C—C— linkages and other kinds of atoms such as O, N, S, etc. may appear in the side groups	The condensed interunit links give rise to introduction of hetero atoms such as N, O, S, etc., in the backbone of the polymer chains at regular intervals. A special case of a polymer with alternate C and O atoms in the chain backbone is the polyoxymethylene $—(CH_2—O)_n—$
Addition polymerization is usually done in gas phase, in liquid bulk monomer or under melt condition, or by solution, suspension or emulsion techniques	Condensation polymerization is usually accomplished in bulk under melt condition or in solution and employing the biphasic interfacial polymerization technique
Control of molecular weight is achieved by selecting appropriate initiator and monomer concentrations and temperature of polymerization and for a given set of conditions by using calculated amount of a chain transfer agent	Control of molecular weight is achieved by using a stoichiometric imbalance of the reacting functional groups or a calculated amount of an appropriate monofunctional monomer

3.4. Kinetics of Chain Polymerization Initiated by a Free Radical Initiator

3.4.1. Rate of Initiator Decomposition and Chain Initiation

Equation (3.3) shows a unimolecular decomposition of the initiator I to produce a pair of initiator or primary radicals. In many instances the decomposition of the lone initiator, I involves homolytic cleavage of the weak bond in the molecules such that the chain initiating radicals are generated in pairs. Hence, R_d, the rate of initiator decomposition may be expressed as:

$$R_\mathrm{d} = -\frac{d[\mathrm{I}]}{dt} = k_\mathrm{d}\ [\mathrm{I}]$$

(3.12)

The rate of radical generation $d[\dot{\mathrm{R}}]/dt$ would then be expressed as:

$$\frac{d[\dot{\mathrm{R}}]}{dt} = 2k_\mathrm{d}\ [\mathrm{I}]$$

(3.13)

since, for each incidence of decomposition of an initiator molecule, two initiator radicals ($R^\bullet$) are produced. As the radicals are transient species and they give rise to chain initiation as soon as they are generated in the monomer system, the rate of chain initiation, R_i will be the same as the rate of radical generation in the absence of undesirable wastage of the chain initiating radicals, $R^\bullet$ by side reactions. Hence,

$$\mathrm{R_i} = \left(\frac{d[\mathrm{M}^\bullet]}{dt}\right)_\mathrm{i} = k_\mathrm{i}[\mathrm{R}^\bullet]\,[\mathrm{M}] = 2k_\mathrm{d}\ [\mathrm{I}]$$

(3.14)

Thus, $R_i = 2k_d$ [I] marks the ideal case of hundred per cent efficiency of chain initiation by the primary radicals. For all practical purposes, however, the expression is modified as:

$$R_\mathrm{i} = 2f\,k_\mathrm{d}\ [\mathrm{I}]$$

(3.15)

where, the factor f is the initiator efficiency or the efficiency of initiation, representing the fraction of primary radicals ($R^\bullet$) which actually contributes to chain initiation as given by Eq. (3.4). Realistically, the value of f is less than unity due to side reactions leading to measurable wastage of primary radicals. f will be dependent on monomer concentration [M] if the wastage of $R^\bullet$ is high due to side reactions and in that case R_i should depend on [M]. However, the general independence of f on [M] has in a large measure simplified the kinetic treatment of vinyl and related polymerizations.

3.4.2. Rate of Chain Termination

The rate of overall chain termination (R_t) may be expressed by Eq. (3.16), considering the termination reaction in a simplified and general form as given by the reaction (3.11). Thus,

$$R_\mathrm{t} = -\left(\frac{d[\mathrm{M}^\bullet]}{dt}\right)_\mathrm{t} = 2k_\mathrm{t}\ [\mathrm{M}^\bullet]^2$$

(3.16)

The factor 2 is used for the simple reason that for each incidence of a termination reaction, 2 chain radicals disappear from the scene. It is important to note that as radicals are generated in pairs, they are also destroyed in pairs.

3.4.3. The Overall Rate of Polymerization

a. ***Rate of Propagation*** Considering the chain propagation reaction in the general form given by the reaction (3.8), the rate of propagation or chain growth, R_p may be expressed as:

$$R_p = k_p\,[M^{\bullet}]\,[M]$$

(3.17)

The equation (3.17) is not directly useful for evaluating R_p as it contains the term for the concentration of the transient chain radicals, $[M^{\bullet}]$ and because the radical concentrations are very difficult to measure as they are very low ($\simeq 10^{-8}$ mol 1^{-1}). An expression free from the radical concentration term will be useful in that event.

b. ***Steady-state Assumption*** In order to eliminate the radical concentration term $[M^{\bullet}]$ from Eq. (3.17), it is necessary to find an expression for it in terms of known or measurable parameters. For this, the steady-state assumption is made. According to this assumption, soon after chain initiation, a state is attained when the value of $[M^{\bullet}]$ becomes essentially constant or steady as radicals are formed and destroyed at equal rates, i.e. $R_i = R_t$. On the basis of the steady-state assumption and combining Eqs (3.15) and (3.16), $[M^{\bullet}]$ may be expressed as:

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

(3.18)

combining Eqs (3.17) and (3.18), the expression for rate of propagation, R_p reduces to

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

(3.19)

c. ***Overall Rate of Polymerization*** Examination of the overall scheme of polymerization represented by Eqs (3.3) to (3.7) clearly shows that monomer disappearance takes place at chain initiation and chain propagation steps only. Hence, the overall rate of monomer disappearance ($-d[M]/dt$), which is the same as the overall rate of polymerization, may be equated as:

$$-\left(\frac{d\,[M]}{dt}\right) = R_i + R_p$$

(3.20)

As the number of monomer molecules consumed at the initiation step is far less or insignificant compared to the number consumed in the long sequence of reactions in the propagation step, the overall rate of polymerization is, for all practical purposes, simply equated to the rate of propagation, R_p. Therefore, overall rate of polymerization, $\left(-\dfrac{d\,[M]}{dt}\right) = R_p$

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

(3.21)

Equation (3.19) or (3.21) may also be expressed as:

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

(3.22)

Initiation and Initiator Systems

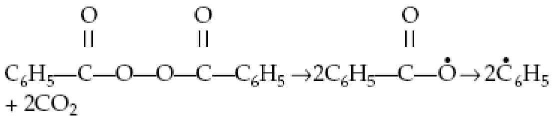
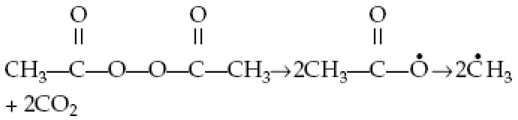
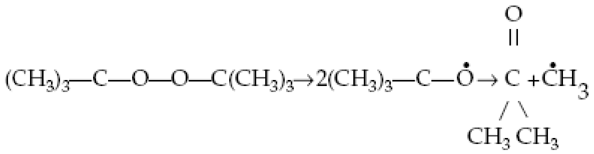
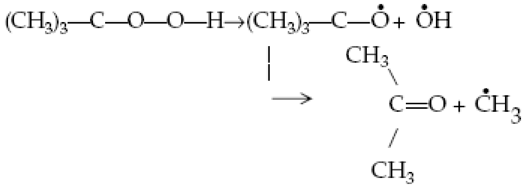
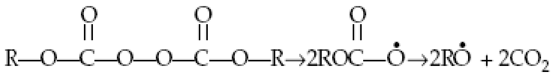
Unimolecular Initiating Systems

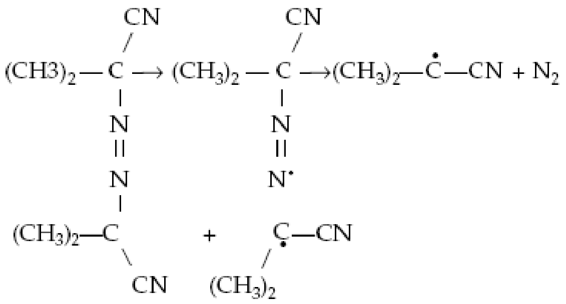
Initiator compounds characterized by unimolecular decomposition through dissociation of a relatively weak bond in them leading to generation of a pair of chain initiating radicals as typified by the general reaction (3.3) are exemplified by such compounds as peroxides, hydroperoxides and azo compounds. Decomposition of some of these classes of compounds and the transient radicals and other products that they generate are listed in Table 3.2. In many instances, such as with benzoyl peroxide (Bz_2O_2), acetyl peroxide (Ac_2O_2) or azobisisobutyronitrile (AIBN), the radicals from the unimolecular decomposition step further undergo decomposition leading to loss of a small molecule. It is necessary to consider[5] a somewhat complex kinetic scheme as detailed in the sequence of reactions (3.23) for even a first approach to a detailed decomposition mechanism.

$$\begin{tikzcd}
I \arrow[r, shift left, "k_d"] & (R^{\bullet} + R^{\bullet})_{cage} \arrow[l, shift left] \arrow[r, "k_D"] \arrow[d, "k_x"'] & 2R^{\bullet} \\
R - R' + X & (R^{\bullet} + R'^{\bullet} + X)_{cage} \arrow[l, "k_c"'] \arrow[r, "k_D"] & R^{\bullet} + R'^{\bullet} + X
\end{tikzcd}$$

(3.23)

Table 3.2. Some initiator systems and radical generation reactions

Initiator System	*General Mechanism*	*Primary Radical Generation Reaction*
Unimolecular or lone initiator system (peroxy/azo compounds)		
(a) Benzoyl peroxide (Bz_2O_2)	Cleavage of peroxy linkage by thermal or photo activation	 $C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \rightarrow 2C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}\dot{O} \rightarrow 2\dot{C}_6H_5 + 2CO_2$
(b) Acetyl peroxide (Ac_2O_2)	″	 $CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \rightarrow 2CH_3{-}\overset{O}{\overset{\|}{C}}{-}\dot{O} \rightarrow 2\dot{C}H_3 + 2CO_2$
(c) Di-*t*-butyl peroxide (DTBP)	″	 $(CH_3)_3{-}C{-}O{-}O{-}C(CH_3)_3 \rightarrow 2(CH_3)_3{-}C{-}\dot{O} \rightarrow \underset{CH_3\ CH_3}{\overset{O}{\overset{\|}{C}}} + \dot{C}H_3$
(d) *t*-Butyl hydroperoxide (TBHP)	″	 $(CH_3)_3{-}C{-}O{-}O{-}H \rightarrow (CH_3)_3{-}C{-}\dot{O} + \dot{O}H \rightarrow \underset{CH_3}{\overset{CH_3}{C}}{=}O + \dot{C}H_3$
(e) Hydrogen peroxide (H_2O_2)	″	$H{-}O{-}O{-}H \rightarrow 2\dot{O}H$
(f) Persulphate ion ($S_2O_8^{=}$)	″	$^{-}O_3S{-}O{-}O{-}SO_3^{-} \rightarrow 2O_3S\dot{O}^{-} (2\,S\bar{O}_4^{\bullet})$
(g) Peroxy dicarbonate	″	 $R{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}R \rightarrow 2RO\overset{O}{\overset{\|}{C}}{-}\dot{O} \rightarrow 2R\dot{O} + 2CO_2$

(h) Azobisisobutyronitrile (AIBN)	Cleavage of C—N bond by thermal/photo activation	 $(CH3)_2\overset{CN}{C}—N{=}N—\overset{CN}{C}(CH_3)_2 \longrightarrow (CH_3)_2\overset{CN}{C}—N{=}N^{\bullet} + \dot{C}(CN)(CH_3)_2 \longrightarrow (CH_3)_2—\dot{C}—CN + N_2$
Bimolecular initiator system (redox initiator)	Reduction activation (thermal/photochemical)	
(a) Reducing metal ion and peroxide or hydroperoxide	Electron transfer	$M^{(n-1)+} + R—O—O—R \rightarrow M^{n+} + \dot{O}R + \bar{O}R$ (R = H atom, alkyl/aryl group or ^-O_3S—group, etc.)
(b) Oxidizing metal ion and reducing (Sulphoxy) compounds ($SO_3^=$, $S_2O_3^=$, $S_2O_4^=$, etc.)	" "	$S_xO_y^{n-} + M^{m+} \longrightarrow \dot{S}_xO_y^{(n-1)-} + M^{(m-1)+}$
(c) Amines and peroxides	Complexation followed by proton transfer	$R_2NH + R'—O—O—R' \rightleftharpoons [R_2NH(OR')]^+ (OR')^- \rightarrow R_2\dot{N} + \dot{O}R' + R'OH$
Metal, metal salts, complexes or chelates, etc.		
(a) Ion-pair complex of Fe^{3+} ion	Electron transfer	$(Fe^{3+} X^-) \rightarrow Fe^{2+} + \dot{X}$ ($\dot{X}$ = Cl, Br, OH, etc.)
(b) Some metal ions in higher oxidation states (Mn^{4+}, Ce^{4+} Co^{3+}, Ag^{3+}, etc.) as salts or complexes, in aqueous medium	"	$M^{(n+1)+} + H_2O \rightarrow M^{n+} + H^+ + \dot{O}H$

The initiator molecule's net rate of decomposition, characterized by the rate constant k_d produces a pair of free radicals ($R^\bullet$) which are entrapped in a cage whose walls are the solvent molecules that surround the original initiator molecule. Each of the radicals may undergo a net translational diffusion out of the cage (characterized by the rate constant k_D), or a small molecule such as N_2 or CO_2 may be released within the cage through further decomposition of one or both the radicals present (characterized by the rate constant k_x) before they diffuse out of the solvent cage. Should the release of a small molecule occur as described, combination of the resultant radical $R'^\bullet$ with $R^\bullet$ might produce a totally inactive or stable species for radical initiation. This is one of the major causes of initiator efficiency and at the same time a source of additional information giving the details of the initiation process.

Bimolecular Initiating Systems

A good many number of free radical polymerizations, particularly those accomplished at low temperatures are induced by two-component initiator systems. They can be activated both thermally and photochemically. Many of such bimolecular initiator systems generate radicals by redox or electron transfer reaction mechanism involving the two initiator components or via formation of intermolecular complexes of different degrees of heat or light stability, often through donor-acceptor or charge transfer mechanism. Examples of such different types of initiator systems and the respective radical generation reactions are listed in Table 3.2. In aqueous media, initiation of polymerization by $\dot{O}H$ radicals, at least in part, is a good possibility, since ions and radicals in the system have ample chance to react with H_2O molecules to produce $\dot{O}H$ radicals which may then survive long in water by a regenerative transfer mechanism.

For a bimolecular initiator system, such as the common redox initiator systems, aqueous or non-aqueous, ordinary second order kinetics are generally obeyed if monomer concentration is high[19] and in such a case, R_p may be expressed as in Eq. (3.27), analogous to Eq. (3.21), showing the initiator concentration [I] substituted by the product of the reducing agent concentration, a, and the oxidizing agent concentration, b:

$$R_p = \frac{k_p}{k_t^{1/2}} (fk_d)^{1/2} \, (a \cdot b)^{1/2} \, [M]$$

(3.27)

Autoacceleration or Gel Effect in Radical Polymerization

Considering normal behaviour for the first order transformation of monomer to polymer including general independence of initiator efficiency, f on monomer concentration and gradual depletion of initiator during polymerization, one would normally expect the reaction rate, R_p to fall with time, particularly after an initial short steady zone or period. But in many instances, just the opposite pattern of behaviour is observed, i.e. R_p follows an increasing trend, often very sharp, with increasing conversion or time of polymerization either from the very onset of polymerization or from an intermediate stage of conversion depending on the nature of the monomer–polymer system. The reaction medium transforms fast into a highly viscous mass not only as a consequence of increase in reaction rate but also due to sharp rise in molecular weight of the product polymer accompanying this phenomenon, commonly termed as the autoacceleration effect or gel effect,[20, 21] which is also referred to as Trommsdorff effect or Norrish–Smith effect.

The gel effect is more effectively manifested in undiluted monomers than in diluted systems where the non-ideal or unusual effect may be minimized or even eliminated. In some monomer systems the autoacceleration effect may be so high as to be accompanied with large rise in temperature[22] and using undiluted methyl acrylate, acrylic acid and acrylonitrile, the autoacceleration effect associated with the polymerization process may even lead to explosion. The deviation from normal kinetics would not be eliminated even if isothermal conditions are maintained; the effect of autoacceleration and its lowering or elimination with progressive dilution with benzene as the solvent for polymerization of methyl methacrylate, shown in Fig. 3.3, is a typical example.[4]

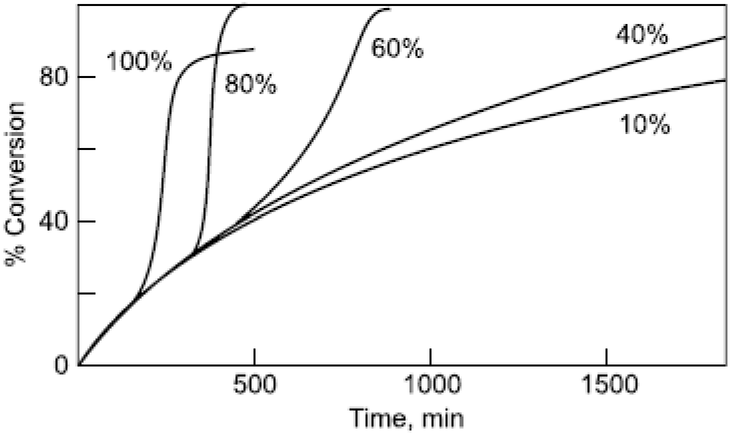


Figure 3.3. Influence of dilution in controlling auto-acceleration: per cent conversion vs time plots for benzoyl peroxide-initiated polymerization of methyl methacrylate[4] at 50°C (monomer concentration shown along each curve was varied using benzene as the solvent) (Schulz, 1947; ***Courtesy****, Huthig & Wepf Verlag, Basel)*

In explaining the autoacceleration effect, keeping the rate Eq. (3.21) in view, alternative causes may be examined. The effect being independent of initiator, an increase in the value of $(f \cdot k_d)$ to explain the effect seems untenable. The other idea that appears more reasonable and acceptable is a sharp increase in the value of the kinetic parameter ($k_p/k_t^{1/2}$), which may arise as a consequence of increase in k_p or a decrease in k_t or both. However, a decrease in the termination rate constant with increase in conversion appears to be the most convincing reason. The decreasing trend in the k_t value with conversion, usually beyond a critical conversion range is believed to be due to progressive increase in viscosity of the monomer–polymer mixture. It is known that the k_t values are higher than k_p values by a factor of 10^7 –10^5; so perturbation of the kinetics from what is expected from Eq. (3.21) due to enhanced propagation would be of much lesser significance, if it occurs at all, than that due to hindered termination, the result being a significant gain in ($k_p/k_t^{1/2}$) value. Termination, considered to be bimolecular in nature, involves reaction between two very big chain radicals and the propagation reaction involves the reaction between a macroradial and a small monomer molecule. Naturally, the higher medium viscosity at higher conversion would hinder the termination reaction much more than affecting the propagation reaction. It is likely that the intrinsic reactivity of the chain radicals practically remains unchanged, but with the increasing medium viscosity acting as a much greater physical barrier for the diffusion of macroradicals than for the diffusion of small monomer molecules, there is sharp reduction in the likelihood of reaction between two macro (chain) radicals, the net result being a reduction in the value of k_t and a rise in the concentration of chain radicals as a consequence. R_p, therefore, sharply rises and an increase in the degree of polymerization with conversion follows. All these factors combine into an autoacceleration effect.[23–26]

Ionic Polymerization

Ionic Polymerization: Introduction

Different features of ionic polymerization will be taken up for discussion and analysis in this chapter. Unlike free radical polymerization, ionic polymerization is associated with what may be termed as monomer selectivity. Generally, monomers with electron-releasing substituents such as alkoxy, 1,1 dialkyl or aryl-alkyl, phenyl and vinyl groups exemplified by isobutyl vinyl ether, isobutylene or *α*-methyl styrene, styrene and butadiene are readily susceptible to cationic polymerization and not really or not as readily to anionic polymerization. The comparatively basic character of their double bonded carbon atoms induces them to share a pair of electrons with an electrophilic reagent, and the propagation takes place by a carbocationic or carbonium ion mechanism. Monomers with electron-withdrawing substituents, such as nitrile, carboxyl, ester groups, etc. (exemplified by acrylonitrile, acrylic acid, methyl acrylate, etc.), are readily susceptible to anionic polymerization. Phenyl and vinyl substituents also make the monomer (styrene, butadiene, etc.) capable of polymerizing anionically. Mayo and Walling[1] gave the following order of reactivity: Vinyl ethers > isobutylene > *α*-methyl styrene > isoprene > styrene > butadiene for cationic polymerization, and acrylonitrile > methacrylonitrile > methyl methacrylate > styrene > butadiene for anionic polymerization. Interestingly, styrene and the dienes, capable of polymerizing by radical means are also polymerized by both cationic and anionic routes.[1] However, they are placed low in each series in the order of reactivity.

Polarity differences of monomers play more significant roles in their reaction with an ionic chain-propagating centre than with a free radical centre. The relative reactivities for different monomers are nearly independent of terminal unit carrying the charge, as the charge on the propagating centre is much the same for different terminal units.

Thus, monomer reactivities can be understood without reference to the specific unit bearing the carbonium ion or carbanion and ideal copolymerization is approached more closely by the ionic propagation than by free radical propagation. Bimolecular termination as prevalent in the free radical polymerization is totally prohibitive in the ionic polymerization, as like charges repel each other and cannot come close enough for mutual interaction and annihilation. Unimolecular termination or termination due to transfer to monomer or solvent are the consequential mechanisms of termination of ionic polymerization. Ionic polymerizations are generally not favoured or rather inhibited or strongly retarded in aqueous medium, although traces of moisture have sometimes been reported to produce significant cocatalytic effects in some cationic polymerization. Basic solvents or additives prevent or inhibit the cationic propagation while acidic solvents or additives inhibit anionic growth. Solvents of such polarity as to favour formation of ion-pairs and as not to permit large scale ion dissociation offer different degrees of stability and reactivity for the propagating ion centres; often very low temperatures, usually in the range of –40 to –100°C, are needed for ionic polymerization at desirable or optimum rates and to obtain optimum or high degrees of polymerization. Methyl chloride, ethylene dichloride, pentane, hexane, nitrobenzene offer good media for ionic polymerization. Usually, a counter ion stays close to the propagating ion throughout its lifetime. Initially, limited separation between the two ions of the ion pair helped by increased polarity or solvating power of the medium becomes more favourable for ionic polymerization, but a highly polar medium or additive such as water, alcohol, etc., reacts with and destroys most ionic catalysts or reduces their catalytic activity to insignificance.

Cationic Polymerization

Protonic acids such as H_2SO_4 and $HClO_4$ or Lewis acids such as BF_3, $SnCl_4$, $AlCl_3$, $AlBr_3$, $TiCl_4$, etc., which are strong electron acceptors, readily induce polymerization of monomers having electron releasing substituents by cationic (carbonium ion) mechanism. Almost all Lewis acids or Friedel-Crafts catalysts become effective in presence of a cocatalyst which complexes with the catalyst and acts as a proton donor. The cocatalyst may be water, alcohol, organic acid, alkyl halide or even a hydrocarbon. Early studies on cationic polymerization were done using boron trifluoride, BF_3 as the catalyst for the polymerization of isobutylene $CH_2 = C(CH_3)_2$. Polymerization occurs almost instantaneously at –100°C to give polymers of high degrees of polymerization (~10^5). Cationic polymerizations of this kind are characterized by a low or negative temperature coefficient—both rate and degree of polymerization dropping down sharply with rise in temperature in some cases.[2]

BF_3 was found to be ineffective to induce polymerization of isobutylene when the reactants were taken in a high degree of purity and free from moisture. The catalyst is however very effective in the presence of traces of moisture or similar polar additives as a cocatalyst.[3,4]

Traces of moisture (H_2O) react with BF_3 to form the catalyst-cocatalyst complex, i.e., boron trifluoride monohydrate, $BF_3 \cdot H_2O$. The mechanism of polymerization of isobutylene in the presence of $BF_3 \cdot H_2O$ is as follows:[5,6]

$$\underset{\text{(ion pair formation)}}{BF_3 \cdot H_2O \rightleftharpoons H^+(BF_3 \cdot OH)^-}$$

Kinetics of Cationic Polymerization

Cationic initiator systems (catalyst–cocatalyst complex C) may be either soluble or insoluble in the monomer–solvent media used. The kinetics of polymerization is better studied and understood using soluble catalyst complexes and homogeneous systems. A generalized overall reaction scheme may be written as:

Chain Initiation:

$$A + SH \overset{K}{\rightleftharpoons} A \cdot SH \xrightarrow{k_i} H^+AS^- \qquad \text{(a)}$$

$$(H^+\ AS^-)\ A \cdot SH + M \xrightarrow{k_i} HM^+ + AS^- \qquad \text{(b)}$$

Chain Propagation:

$$M_n^+ + AS^- + M \xrightarrow{k_p} M_{n+1}^+ + AS^- \qquad \text{(c)}$$

Chain Termination:

$$M_n^+ + AS^- \xrightarrow{k_t} P_n + A \cdot SH \qquad \text{(d)}$$

$$M_n^+ + AS^- + M \xrightarrow{k_{tr}} P_n + HM^+ + AS^- \qquad \text{(e)}$$

Here, A represents the catalyst, SH the cocatalyst and P_n, the polymer molecule of degree of polymerization *n*, and all other terms have their usual significances. Initiation of polymerization involves a proton transfer from the complex $A \cdot SH$ (or H^+AS^-) to the monomer M. Termination of a growing chain may take place by abstraction of a proton from the terminal unit by the counter ion AS^- or by monomer transfer. The exact nature and concentration of the complex are often uncertain, and for kinetic purposes, the concentration of the catalyst component or the cocatalyst whichever is present in stoichiometric deficiency is taken to represent the concentration of the complex formed. The rates of initiation, propagation and termination are given by

$$R_i = \frac{d[M^+]}{dt} = k_i[C][M]$$
(5.7)

$$R_p = -\frac{d[M]}{dt} = k_p[M^+][M]$$
(5.8)

$$R_t = -\frac{d[M^+]}{dt} = k_t[M^+]$$
(5.9)

In view of the presence of the counter ion AS^- in the vicinity of the cationic centre throughout its growth and at the point of termination as conceived in the reaction scheme (5.6), the concentration of AS^- is not considered in the expressions for R_p and R_t, and [C] in Eq. (5.7) would be given by $[C] = K[A] \cdot [SH]$. In case the initiating complex $A \cdot SH$ is largely split into ions as in Eq. (5.6)(a), R_i would be independent of [M] and the overall kinetics should be modified accordingly.

Steady State Assumption:

Despite some uncertainty about attainment of steady state, one may find a simple and workable expression for R_p assuming a **steady state concentration [$R_i = R_t$]** of M^+ such that

$$[M^+] = \frac{k_i}{k_t} \cdot [C][M]$$
(5.10)

and hence,

$$R_p = \frac{k_i k_p}{k_t} \cdot [C][M]^2$$
(5.11)

The average degree of polymerization $\overline{X}_n$, assuming little chain transfer, may be expressed as

$$\overline{X}_n = \frac{R_p}{R_t} = \frac{k_p[M^+][M]}{k_t[M^+]} = \frac{k_p}{k_t} \cdot [M]$$
(5.12)

On the other hand, for termination exclusively by monomer transfer [Eq. (5.6)(e)], one may write:

$$\overline{X}_n = \frac{k_p[M^+][M]}{k_{tr}[M^+][M]} = \frac{k_p}{k_{tr}}$$
(5.13)

Differences between Cationic and Addition Polymerization

Therefore, for cationic polymerization, the overall rate of polymerization is proportional to the first power of catalyst concentration and to the square of monomer concentration. Thus, in respect of rate-dependence on catalyst or initiator concentration, cationic polymerization differs from the free radical polymerization for which R_p normally follows a square root dependence. The difference arises as a consequence of the difference in their termination mechanism which is second order in the growing species in free radical polymerization and first order in ionic polymerization.

The degree of polymerization in cationic polymerization is independent of the catalyst concentration and for true termination, $\overline{X}_n$ is directly proportional to [M], while for termination exclusively by monomer transfer, $\overline{X}_n$ is a constant given by the ratio of propagation rate constant and the rate constant for the transfer reaction.

The rate of cationic polymerization is determined by the ratio k_p/k_t (or k_p/k_{tr}, as the case may be), while that of radical polymerization is determined by the parameter $k_p/k_t^{1/2}$. The k_p and k_t values in cationic polymerization of a monomer are far less than those in free radical polymerization.

However, the rates of polymerization in cationic systems, are usually much faster than those in radical polymerization. The former represents a case favouring polymerization at a high rate and the concentration of the propagating species (carbonium ions) in cationic polymerization (10^{-3} molar) is generally much higher than the same (concentration of radicals) in the case of a radical polymerization (10^{-8} molar). In ionic polymerization, large increases in the rate and degree of polymerization are usually effected through increases in the solvating power of the polymerization medium.

Anionic Polymerization

Basic compounds such as amides, alkoxides, alkyls and aryls of alkali metals and different Grignard reagents have been used as catalysts for anionic polymerization of monomers having electron-withdrawing substituents. The catalysts (BA) break up into cations (B^+) and anions (A^-) under the reaction conditions. In anionic polymerization, the anion adds to the double bond of the monomer to generate a carbanion as the active centre for chain-growth.

$$CH_2 = CHX + BA \rightarrow A{-}CH_2{-}\overset{(-)}{C}HX + B^{(+)}$$
(5.14)

Different catalysts exhibit different reactivities depending on their basicities producing different rates of chain initiation in the presence of an appropriate monomer. The ease of polymerization is dependent not only on the catalyst system used for a given monomer, but also on the structure of the monomer for a given catalyst.

The propagation occurs by addition of monomer molecules, M, to the carbanion by the entry of successive monomers between the ions of the active species:

$$A{-}CH_2{-}\overset{(-)}{C}HX + B^{(+)} + (n-1)M \rightarrow A{-}(CH_2{-}CHX)_{n-1}{-}CH_2{-}\overset{(-)}{C}HX + B^{(+)}$$
(5.15)

The nature of the medium is highly influential at this stage as it determines the distance of separation between the ions at the active site. Termination often takes place by chain transfer involving solvent or some other additive (SH) used such as water, alcohol, etc.

$$A \sim CH_2{-}\overset{(-)}{C}HX + B^{(+)} + SH \rightarrow A \sim CH_2{-}CH_2X + BS$$
(5.16)

The kinetics of anionic polymerization may be considered and appropriate expressions for rate and degree of polymerization may be deduced using the following scheme of polymerization for an appropriate monomer, say styrene, using potassium amide catalyst in liquid ammonia.[10]

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

$$\mathrm{NH_2^-} + \mathrm{M} \xrightarrow{k_i} \mathrm{H_2N{-}M^-}$$

$$\mathrm{H_2N{-}M^-} + (n-1)\mathrm{M} \xrightarrow{k_p} \mathrm{H_2N{-}(M)_{\mathit{n}-1}{-}M^-}$$

$$\mathrm{H_2N{-}M_{\mathit{n}}^-} + \mathrm{NH_3} \xrightarrow{k_{tr}} \mathrm{H_2N{-}M_{\mathit{n}}{-}H} + \mathrm{NH_2^-}$$

(5.17)

The rates of initiation (R_i), propagation (R_p) and termination by solvent transfer (R_{tr}) may then be expressed as

$$R_i = k_i[\mathrm{NH_2^-}][\mathrm{M}] = \frac{k_i K[\mathrm{M}][\mathrm{KNH_2}]}{[\mathrm{K^+}]}$$

(5.18)

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

(5.19)

$$R_{tr} = k_{tr}[\mathrm{M^-}][\mathrm{NH_3}]$$

(5.20)

Using the steady state assumption for the active chain ends ($\mathrm{M^-}$), and combining the Eqs (5.18–20):

$$R_p = \frac{K k_i k_p [\mathrm{M}]^2 [\mathrm{KNH_2}]}{k_{tr}[\mathrm{K^+}][\mathrm{NH_3}]} = \frac{k_i k_p [\mathrm{M}]^2 [\mathrm{NH_2^-}]}{k_{tr}[\mathrm{NH_3}]}$$

(5.21)

The number average degree of polymerization $\overline{X}_n$ is given by (R_p/R_{tr}), i.e.,

$$\overline{X}_n = \frac{k_p[\mathrm{M^-}][\mathrm{M}]}{k_{tr}[\mathrm{M^-}][\mathrm{NH_3}]} = \frac{k_p}{k_{tr}} \cdot \frac{[\mathrm{M}]}{[\mathrm{NH_3}]}$$

(5.22)

The gegen ion, $\mathrm{K^+}$, has not been included in the reaction scheme (5.17) in view of high dielectric constant of the liquid ammonia medium. Termination of a given chain essentially involves chain transfer with solvents, thereby releasing a new anionic centre at the incidence of termination of each growing chain.

Living Polymers

There are many cases of anionic polymerization which are not associated with termination reaction and for which propagation continues till complete consumption of the monomers. The carbanions would remain active without termination in such solvents as tetrahydrofuran and dioxane, because of non-occurrence of termination due to proton transfer from the solvent. The polymers thus obtained are termed as 'living polymers'. The propagating carbanions are sometimes coloured and the colour and its intensity remain undiminished throughout polymerization and even beyond complete conversion. Addition of more monomer to the living polymer system leads to its polymerization also quantitatively causing further increase in degree of polymerization, the number of growing species remaining unchanged. Polymerization of methyl methacrylate with metal alkyls produces such enhancement of molecular weight with conversion through the second stage polymerization on fresh monomer addition after complete conversion in the first stage.

Stereo-Regular Polymerization

Stereo-regularity in olefin or vinyl polymerization that proceeds anionically is largely dependent on the physical conditions of the reaction and the chemical environment including the solvent and the positive counterion.

The statistical nature of polymers and the polymerization reaction is important in relation to stereo-regularity, and for quantitative purposes it is required to describe a polymer in terms of relative orders or percentages of isotactic, syndiotactic and atactic sequences.

Stereo-regular polymerization is mostly characterized by (a) anionic propagation, (b) hair-like growth, and (c) exclusive head-to-tail arrangement of repeating monomer units. The features have been widely studied and better understood using the so-called Ziegler catalysts or Ziegler–Natta catalysts. Such catalysts are prepared by interaction between an aluminium alkyl, such as aluminium triethyl, $Al(C_2H_5)_3$ and a transition metal halide, such as titanium tetrachloride, $TiCl_4$. The exact nature of the catalyst activity is contingent upon the tendency of the transition metal and aluminium to operate with coordination valencies. Usually, the Ziegler–Natta catalysts are of high activity allowing low temperature initiation and imparting stability to the growing chain end. This is a prerequisite for the production of polymers of very high molecular weight.

In polymerization with Ziegler-Natta catalysts, a radical mechanism is not tenable as it cannot explain the stereo–regularity and formation of isotactic polymers. An ionic mechanism is, of necessity, widely favoured and accepted.

In a truly anionic initiation, the anion from the initiator system would have to add an additional electron to the already existing π electron pair of an olefin, say ethylene, to generate a carbanion that may lead to chain propagation. In a system of poor resonance, such as with ethylene, this is energetically unfavourable under normal or moderate conditions. Thus, metal alkyl catalysts do not favourably initiate polymerization of ethylene and related monomers by their carbanions but do so by their metal cations.

In presence of a cation centre as the initiator, there would be attractions between the cation centres and the π electrons of the olefinic monomers and under a favourable situation an anchorage of the monomer on the cation would create a carbonium ion at the remote end of the monomer segment due to acceptance of a π electron by the cation.

The catalyst combination forms ionic complexes that precipitate out when the two components are mixed together in a hydrocarbon solvent. The initial complex formation using aluminium triethyl ($AlEt_3$) and titanium tetrachloride ($TiCl_4$) or the trichloride ($TiCl_3$) may be written as:

$$TiCl_4 + AlEt_3 \rightarrow (TiCl_3)^+(AlEt_3Cl)^-$$

$$TiCl_3 + AlEt_3 \rightarrow (TiCl_2)^+(AlEt_3Cl)^-$$

(5.34)

When a non-polar monomer such as an α-olefin is used, initiation of polymerization is performed by the transition metal cation; propagation then follows in the negative complex ion of aluminium and only heterogeneous Ziegler–Natta catalysts yield isotactic polymers. Titanium based complexes are the most common of the heterogeneous catalysts. Among the other transition metal, vanadium has been more widely used, and vanadium-based systems commonly provide homogeneous catalysts.

For stereo-regular polymerization, the catalysts must not only initiate polymerization, but they must also effectively regulate: (a) the entry and orientation of the successive monomer units during initiation (anchorage) on the cation site and (b) the migration and propagation of the successive incoming monomer units on the anionic site. The prerequisite for a constant specific orientation of the monomer is a fixed location of both cation and anion; if either is soluble or dispersible, poor steric regularity, or atactic poly (α-olefin) structures would result. Syndiotacticity is obtained in a few instances also by soluble catalysts. The chain propagation via the anionic coordination mechanism involves insertion of an oriented monomer molecule at a carbanion centre permitting head-to-tail addition and hair-like growth on the anionic site, the rate determining step being the electrophilic attack by the catalyst fragment.

Mechanisms proposed for different systems are based on the overall principle detailed above but often they are so specific in detail that they can seldom be generalized beyond the systems for which they are suggested. The course of isotactic placement of successive monomer units during polymerization of propylene using a bimetallic catalyst complex may be depicted in a simplified manner by reaction steps in Fig. 5.2, highlighting bimetallic mechanism.

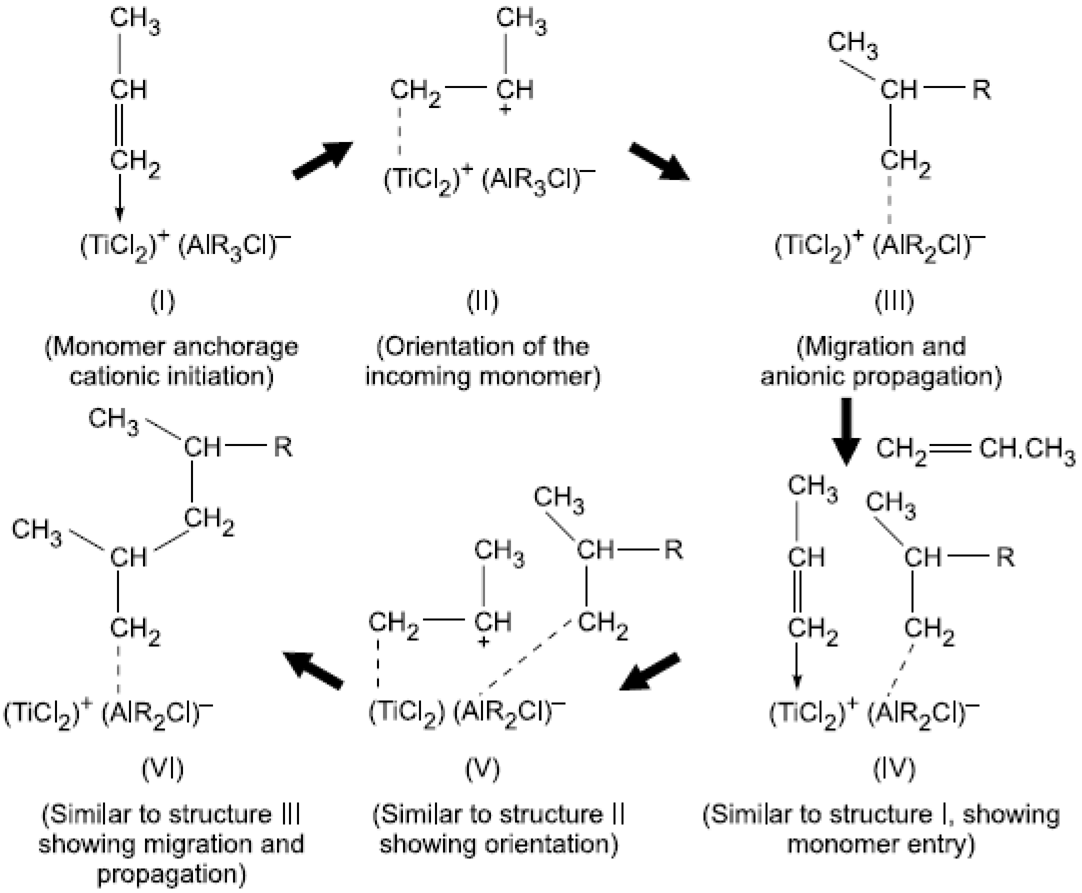


Figure 5.2. Formation of isotactic polypropylene using the catalyst system $AlEt_3$– α –$TiCl_3$(bimetallic mechanism)

The catalyst complex of $TiCl_3$ and $AlEt_3$ essentially acts as a template for the successive orientation and isotactic placements of the incoming monomer units. The crystal structure of the catalyst surface and the chemical structure of the catalyst complex determine the orientation(s) permitted to a given monomer as it adds to a propagating chain. One concept ascribes isotactic placement of monomers during chain propagation to steric and electrostatic interactions between the substituent of the incoming monomer and the ligands of the transition metal at the reactive site of the crystal surface, while another concept attributes the isotactic placement to the interactions between the incoming monomer and the Group I-III metallic part of the bimetallic catalyst. There can be little reservation about either concept if both bimetallic and monometallic mechanisms are involved in the Ziegler–Natta polymerization. The monometallic mechanism describes the transition metal (in the present case, titanium) part of the catalyst complex as the only active site for overall polymerization. The monomer is coordinated to the vacant orbital of the transition metal complex and then inserted into the polymer chain at the transition metal—carbon bond giving rise to regeneration of the vacant orbital with a different orientation. Propagation with the species would result in a syndiotactic sequence. Isotactic polymerization is allowed by migration of the polymer chain to its original location causing regeneration of the original vacant orbital, as shown in reaction scheme in Fig. 5.3, using $TiCl_4$ complex for the polymerization of propylene, where the (vacant) square indicates a vacant orbital of the transition metal.

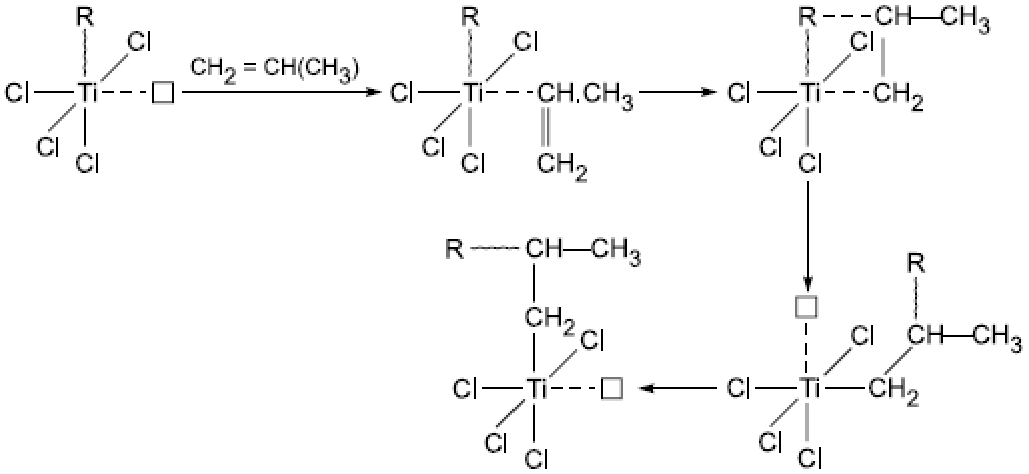


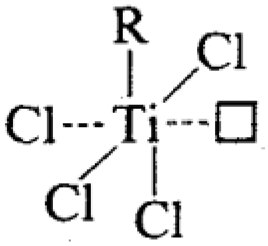
Figure 5.3. Monometallic mechanism for stereo regular (isotactic) polymerization of propylene (□ indicates vacant orbital)

Non-polar monomers, such as the *α*-olefins, having poor coordinating powers with the catalyst, require such catalysts as would specifically hold them in place with strong stereo-regulating influence to give isotactic sequences for the polymer, thus necessitating the use of heterogeneous catalysts. For polar monomers (acrylates, methacrylates, vinyl ethers, etc.) with strong coordinating powers with the catalyst, heterogeneity of the catalyst is not a prerequisite for isotacticity. When non-polar solvents are employed, the polymerization for polar monomers proceeds by anionic coordination mechanism, the gegen ion directing the orientation of each approaching monomer unit into the polymer chain and the ability of the gegen ion to coordinate determining the steric regularity. In polar solvents, the gegen ion is removed from the vicinity of the propagating centre and so the stereochemical influence on the approaching monomer unit is lost resulting in random structures. For such systems, rise of temperature favours atacticity, while lower temperature favours syndiotacticity.[23,24]

Ziegler-Natta Catalysts

The Ziegler-Natta or, often, Ziegler catalysts have the remarkable property of' polymerizing a wide variety of monomers to linear and stereoregular polymers. Ethylene is polymerized to a highly linex chain, in contrast to the products of' radical polymerization (Chapter 13). Polypropylene may be made in either the isotactic or syndiotactic form, but higher or-olefins yield only isotactic polymers Dienes such as butadiene and isoprene may be polymerized to products that are almost exclusively cis-1,4, trans-1,4, isotactic-1,2, 01. syndiotactic-1,2, depending on choice of catalyst and conditions. Many other examples exist.

Ziegler catalysts are complexes formed by the interaction of alkyls of' metals of groups I-III in the periodic table with halides and other derivatives of transition metals of groups IV-VIII. Some typical compositions are listed in Table 4-2. There are literally hundreds of' combinations that are active in polymerization. Current thinking is that the transition metal, with its d orbitals available for both a and n bonding, is the catalyst center (Cossee 1964). A coordination complex is formed with the organometallic part of the system supplying some of' the ligands. At least one empty coordination site accommodates the growing polymer chain; this is indicated here by the square box:



Here a monometallic catalyst is shown; where an organometallic compound plays a role, the metal atoms may be bonded by chlorine or alkyl bridges (Fig. 4-1) The titanium has been reduced fiom Ti(IV) to Ti(III) and the chlorine bridge is a so-called three-center bond.

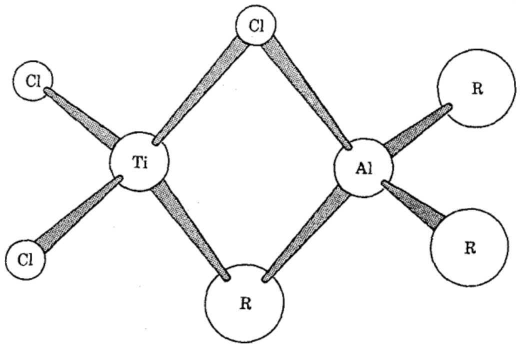
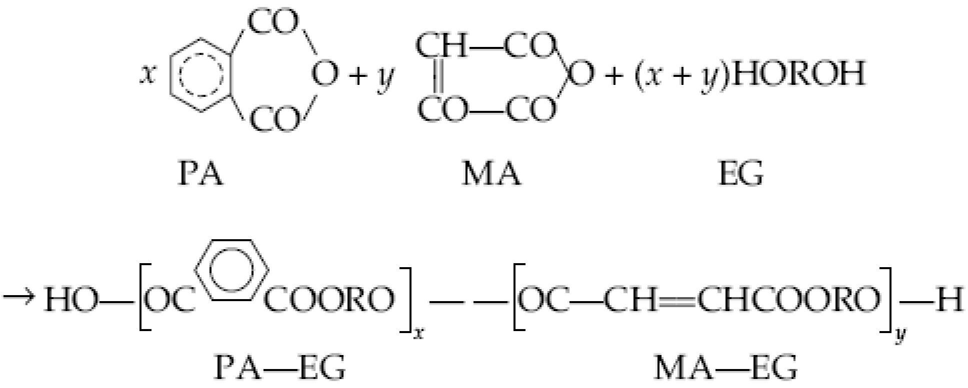


FIG. 4-1. Structure postulated for the metal halide-metal alkyl complex of a typical coordination catalyst

Copolymerization and Techniques of Polymerization

Concept of Copolymerization

A polymer whose chain molecules are composed of more than one kind of repeating chemical units is commonly called a copolymer. A simple case of a step-growth copolymer is the linear unsaturated polyester formed by intermolecular condensation of a mixture of phthalic acid (anhydride) (PA) and maleic acid (anhydride) (MA) with a given diol, say ethylene glycol (EG) resulting in what may be termed as a copolyester with at least two types of distinctly identifiable repeating units in the chain molecules:



(4.1)

Equation (4.1), showing formation of a copolyester by a polycondensation process clearly identifies two types of repeating chemical units, (PA–EG) and (MA–EG), though in a very oversimplified manner. In the actual copolymer the two types of distinguishable chemical units would normally appear at random along the chain, and the overall composition would depend on the relative values of *x* and *y*. Similarly, one can prepare step-growth copolymers with different interunit chemical linkages by proper selection of combinations of different bifunctional monomeric species bearing, —OH, —COOH, —NH_2, —NCO or other functional groups, and using two, three or all the functional species simultaneously or in a phased manner in the presence or absence of a related polyfunctional and monofunctional species during the synthesis. However, polycondensation leading to formation of copolymers from this kind of complicated mixtures of monomeric species is of little or rare practical importance or relevance. More relevant step-growth copolymerization systems involve formation of copolymer structures with a specific interunit linkage such as amide (—CONH—), ester (—COO—), urethane (—NHCOO—), etc., following the approach as in Eq. (4.1). It may also involve chain extension and/or cross-linking reaction introducing similar or different kinds of interunit linkages, using low molecular weight linear or branched polymers and selected bifunctional monomeric species. Examples of this kind of step-growth copolymers are found in the making of polyester urethanes or polyether urethanes, using low molecular weight preformed linear polyesters or polyethers with hydroxyl end groups and allowing them to further react with each other through diisocyanates leading to chain extension and producing useful elastomeric products commonly known as

$$
\begin{aligned}
&n\ \text{HO-polyester—OH} + n\ \text{OCNRNCO} \\
&\qquad \rightarrow \sim\sim [\text{polyester—OOCNHRNHCOO}]_n \sim\sim \\
&\qquad\qquad \text{(polyesterurethane)} \\
&n\ \text{HO-polyether—OH} + n\ \text{OCNRNCO} \\
&\qquad \rightarrow \sim\sim [\text{polyether—OOCNHRNHCOO}]_n \sim\sim \\
&\qquad\qquad \text{(polyetherurethane)}
\end{aligned}
$$

(4.2)

The number of reactions to be necessarily considered to describe the copolymerization of more than one monomer increases geometrically with increase in the number of participating monomers, giving increasingly varied and complicated structures of the copolymer molecules at the same time. A case of a binary copolymerization involving the two monomers M_1 and M_2 may be simply represented as:

$$\underset{\text{monomer mixture}}{n\mathrm{M}_1 + m\mathrm{M}_2} \rightarrow \underset{\text{copolymer}}{\sim\sim(\mathrm{M}_1)_n—(\mathrm{M}_2)_m\sim\sim}$$
(4.4)

The structure of the vinyl copolymer shown in Eq. (4.4) is far too simplified, however; the two monomer units appear in the copolymer structure in a random sequence in general.

Kinetics of Chain Propagation in Binary Copolymerization and Copolymer Composition

The four chain-propagation reactions in a binary copolymerization may be described by the reaction scheme (4.5) shown below:

$$\mathrm{M}_1^{\bullet} + \mathrm{M}_1 \xrightarrow{k_{1,1}} \mathrm{M}_1^{\bullet} \qquad \text{(i)}$$

$$\mathrm{M}_1^{\bullet} + \mathrm{M}_2 \xrightarrow{k_{1,2}} \mathrm{M}_2^{\bullet} \qquad \text{(ii)}$$

$$\mathrm{M}_2^{\bullet} + \mathrm{M}_2 \xrightarrow{k_{2,2}} \mathrm{M}_2^{\bullet} \qquad \text{(iii)}$$

$$\mathrm{M}_2^{\bullet} + \mathrm{M}_1 \xrightarrow{k_{2,1}} \mathrm{M}_1^{\bullet} \qquad \text{(iv)}$$
(4.5)

Here, M_1 and M_2 are the two monomers, and $\mathrm{M}_1^{\bullet}$ and $\mathrm{M}_2^{\bullet}$ represent the chain radicals of all sizes with free radical bearing terminal units M_1 and M_2, respectively. $k_{1,1}$ and $k_{1,2}$ are rate constants for homopropagation and cross-propagation reactions respectively involving $\mathrm{M}_1^{\bullet}$; likewise, $k_{2,2}$ and $k_{2,1}$ refer to the homopropagation and cross-propagation rate constants respectively involving $\mathrm{M}_2^{\bullet}$. For a given rate constant, the first numeral is indicative of the reacting chain radical and the second numeral indicates the reacting monomer. Homopropagation relates to reaction between like radical and monomer and cross propagation relates to reaction between unlike radical and monomer.

Neglecting monomer consumption in the initiation step, the rates of consumption of the two monomers are written as

$$-(d[\mathrm{M}_1]/dt) = k_{1,1}[\mathrm{M}_1^{\bullet}][\mathrm{M}_1] + k_{2,1}[\mathrm{M}_2^{\bullet}][\mathrm{M}_1]$$
(4.6)

$$-(d[\mathrm{M}_2]/dt) = k_{1,2}[\mathrm{M}_1^{\bullet}][\mathrm{M}_2] + k_{2,2}[\mathrm{M}_2^{\bullet}][\mathrm{M}_2]$$
(4.7)

An expression describing relative incorporation of the two monomeric units in the copolymer may be conveniently obtained by elimination of the radical concentration terms using the steady-state concept for each chain radical and then combining Eqs (4.6) and (4.7). Under steady state, the concentration of $\mathrm{M}_1^{\bullet}$ and $\mathrm{M}_2^{\bullet}$ remaining constant, the rates of interconversion of chain radicals must be equal, which prescribes that rates of reactions (ii) and (iv) of scheme (4.5) are equal, i.e.

$$k_{1,2}[M_1^\bullet][M_2] = k_{2,1}[M_2^\bullet][M_1]$$
(4.8)

Now, combining Eqs (4.6) and (4.7) and expressing [$M_1^\bullet$] in terms of [$M_2^\bullet$] (or vice versa) with the help of Eq. (4.8), one obtains:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{1,1}[M_1^\bullet][M_1] + k_{2,1}[M_2^\bullet][M_1]}{k_{2,2}[M_2^\bullet][M_2] + k_{1,2}[M_1^\bullet][M_2]}$$
(4.9)

or,

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{1,1}\cdot k_{2,1}[M_2^\bullet][M_1]^2}{k_{1,2}[M_2]} + k_{2,1}[M_2^\bullet][M_1]}{k_{2,2}[M_2^\bullet][M_2] + \dfrac{k_{1,2}\cdot k_{2,1}[M_2^\bullet][M_1][M_2]}{k_{1,2}[M_2]}}$$

or,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{k_{2,1}\dfrac{k_{1,1}}{k_{1,2}}\cdot\dfrac{[M_1]}{[M_2]} + k_{2,1}}{k_{2,2} + k_{2,1}\dfrac{[M_1]}{[M_2]}}$$
(4.10)

Dividing the numerator and the denominator of the right hand side of Eq. (4.10) by $k_{2,1}$, one obtains

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{\dfrac{k_{1,1}}{k_{1,2}}\cdot\dfrac{[M_1]}{[M_2]} + 1}{\dfrac{k_{2,2}}{k_{2,1}} + \dfrac{[M_1]}{[M_2]}}$$
(4.11)

In Eq. (4.11), the left hand side represents relative molar increment of the two monomers in the copolymer. For copolymerization to low conversions, this may be taken as the molar ratio of the two monomer units incorporated in the copolymer, i.e., $([M_1]/[M_2])_{\text{copolymer}}$, while the ratio $[M_1]/[M_2]$ on the right hand side of the equation relates to the feed monomer ratio, i.e. molar ratio of the two monomers in the feed monomer mixture, $([M_1]/[M_2])_{\text{feed}}$. Expressing the ratio of the rate constants by the parameters r_1 and r_2 as shown below:

$$\frac{k_{1,1}}{k_{1,2}} = r_1, \qquad \text{and} \qquad \frac{k_{2,2}}{k_{2,1}} = r_2$$
(4.12)

one may readily express Eq. (4.11) as

$$\left(\frac{[M_1]}{[M_2]}\right)_{\text{copolymer}} = \left(\frac{[M_1]}{[M_2]}\right)_{\text{feed}} \cdot \frac{r_1\left(\frac{[M_1]}{[M_2]}\right)_{\text{feed}} + 1}{r_2 + \left(\frac{[M_1]}{[M_2]}\right)_{\text{feed}}}$$

(4.13)

Equation (4.13) is known as the copolymer composition equation or simply the copolymer equation relating the copolymer composition and feed monomer composition with the help of the kinetic parameters r_1 and r_2, commonly called the monomer reactivity ratios. Equation (4.13) clearly expresses that the copolymer composition is dependent on the molar ratio of the two monomers in the feed (but not actually on the absolute concentrations of the two monomers) and on the kinetic parameters r_1 and r_2, i.e. the monomer reactivity ratios. The copolymer equation may also be expressed as:

$$\left(\frac{[M_1]}{[M_2]}\right)_{\text{copolymer}} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]}$$

(4.14)

where $[M_1]$ and $[M_2]$ on the right hand side stand for molar concentrations of monomer M_1 and M_2 in the reactant or feed monomer mixture.

Significance of Monomer Reactivity Ratios

Examination of one or the other forms of copolymer equation clearly shows that with a knowledge of the feed monomer composition, the copolymer composition may be easily calculated if the monomer reactivity ratios r_1 and r_2 are known. The value of $r_1 > 1$ means that the chain radical $M_1^{\bullet}$ has a preference to add the like monomer, i.e. M_1 over the unlike monomer, M_2, and r_1 value < 1 means just the opposite. The same concept applies to r_2, which gives relative preference of chain radical $M_2^{\bullet}$ to add the like monomer (M_2) over the unlike monomer (M_1).

The absence of the initiation and termination rate constants in the copolymer composition equation, makes it readily apparent that the (instantaneous) copolymer composition is independent of rate of initiation and hence of the overall rate of polymerization and of initiator concentration. The composition is also not measurably affected in most cases due to the presence of solvents or other additives, indicating that the kinetic factors controlling the copolymer composition, i.e. the monomer reactivity ratios r_1 and r_2, remain unaffected by variations in initiator concentration, the overall rate of reaction and by the presence of various additives and solvents. They also usually remain unaffected even in heterogeneous systems as long as the reacting monomers are evenly distributed between the phases. However, the composition of copolymer would vary for differential distribution of monomers between phases.[1,2] The values of r_1 and $r_2$also change significantly for a drastic change in the mechanism of chain propagation from free radical to ionic, and even for ionic mechanism, from cationic to anionic mode of chain propagation.[3] The copolymer equation has been found applicable to almost all comonomer combinations and equally applicable and relevant to radical, cationic and anionic systems, despite wide variations in r_1 and r_2 values depending on the mode of chain propagation. In radical copolymerization, the effect of temperature on monomer reactivity ratios is small or marginal in view of relatively low activation energies of radical propagation reactions and small differences in activation energies of different propagation reactions.

4.3. Types of Copolymerization

1. Ideal Copolymerization [$r_1r_2=1$]

It is the widespread observation and experience that the mole fraction F_1 is seldom equal to f_1 and as a consequence of this feature, both f_1 and F_1 keep on changing with progress of copolymerization. The copolymer produced over a specified time period or range of conversion will consist of a mixture of copolymer molecules differing progressively in their compositions (F_1).

A copolymerization is said to be ideal when each of the two radicals exhibits the same preference to add one of the monomers over the other, i.e.

$$k_{1,1}/k_{1,2} = k_{2,1}/k_{2,2}$$

or

$$r_1 r_2 = 1$$

(4.16)

Equation (4.14) then reduces to:

$$\left(\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\right)_{\text{copolymer}} = r_1\left(\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\right)_{\text{feed}}$$

(4.17)

2. Alternating Copolymerization [$r_1 \sim 0$, $r_2 \sim 0$]

The other typical case of copolymerization of widespread practical relevance is given by $r_1r_2 < 1$. In radical copolymerization, one would seldom experience an instance for which $r_1r_2 > 1$. Although, one finds limited instances of copolymerization approaching ideal behaviour ($r_1r_2 = 1$), the product of the reactivity ratios, i.e. r_1r_2 is less than unity in most cases.

At one extreme, a real case of radical copolymerization may be such as to give very small or even negligible values for r_1 and r_2, which, in other words, means that the system is characterized by very low or negligible values of $k_{1,1}$ and $k_{2,2}$. The shift in the value of the r_1r_2 product from unity to very close to zero leads to higher trends toward alternation, i.e. alternate sequence of the two monomer units in the copolymer structure. The alternation is perfect for both r_1 and r_2 being equal to zero, where homopropagation is strictly prohibited and chain growth takes place only by cross propagation. In this limiting case, the copolymerization equation reduces to:

$$\left(\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\right)_{\text{copolymer}} = 1; \quad \text{or} \quad F_1 = 0.5$$

(4.19)

The copolymer then assumes a 1 : 1 alternating structure as

$$\text{—M}_1\text{—M}_2\text{—M}_1\text{—M}_2\text{—M}_1\text{—M}_2\text{—M}_1\text{—M}_2\text{—}$$

(4.20)

shown in chain sequence (4.20) irrespective of the feed monomer composition. Copolymerization of stilbene (C_6H_5—CH = CH—C_6H_5) or of allyl acetate with maleic anhydride may be cited as examples closely resembling the case of alternation in copolymerization.[4,5] Almost a perfect brand of alternation is shown by copolymers of sulphur dioxide and certain olefins, cycloolefins or vinyl compounds; they are commonly known as polysulphones and are obtained by radical polymerization of the respective monomer in liquid sulphur dioxide.[6-8] The alternation is thought to arise as a consequence of self-polymerization of the 1 : 1 complex formed *in situ* between the olefin or related monomer (donor) and sulphur dioxide (acceptor), (*See* also Eq. (4.31) in Sec. 4.7.4).

3. Azeotropic Copolymerization

$$\left(\frac{[M_1]}{[M_2]}\right)_{\text{copolymer}} = \left(\frac{[M_1]}{[M_2]}\right)_{\text{feed}}$$

Some theoretical curves showing copolymer compositions (F_1) for various feed monomer compositions (f_1) corresponding to different r_1 and r_2 values, where $r_1 r_2 < 1$ (and also for some hypothetical cases given by $r_1 r_2 > 1$), are shown in Fig. 4.2. It may be seen that for both r_1 and $r_2 < 1$ (or > 1), the curves intersect the diagonal, i.e. the line representing $F_1 = f_1$. The point of intersection for a given system corresponds to a condition in which polymerization proceeds without change in composition and the composition of the polymer being formed is just the same as that of the monomer mixture at that point. Copolymerization of these critical mixtures of monomers is commonly known as azeotropic copolymerization. The critical monomer composition is then given by:

$$\left(\frac{[M_1]}{[M_2]}\right)_{\text{feed}} = \frac{1-r_2}{1-r_1}$$

(4.21)

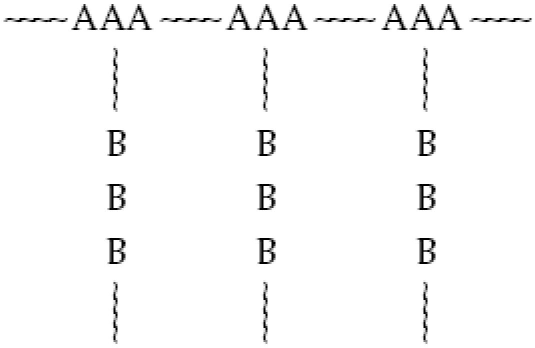
Block and Graft Copolymers

The probability of finding long sequences of one monomer in an ordinary random copolymer is very remote except in the trivial case where one monomer is present in a large excess. Methods of synthesis of polymer containing such long sequences of specific monomer units are of great interest, since they often lead to polymers with properties widely different from those of the two homopolymers or the corresponding random copolymers or their blends. Polymers with long sequences of two monomers can have two distinctive arrangements of chains:

i. *"Block copolymers"*—where the sequences follow one another along the polymer chain axis:

$\sim\sim\sim$ AAABBB $\sim\sim\sim$ BBBAAA $\sim\sim\sim$ AAABBB $\sim\sim\sim$

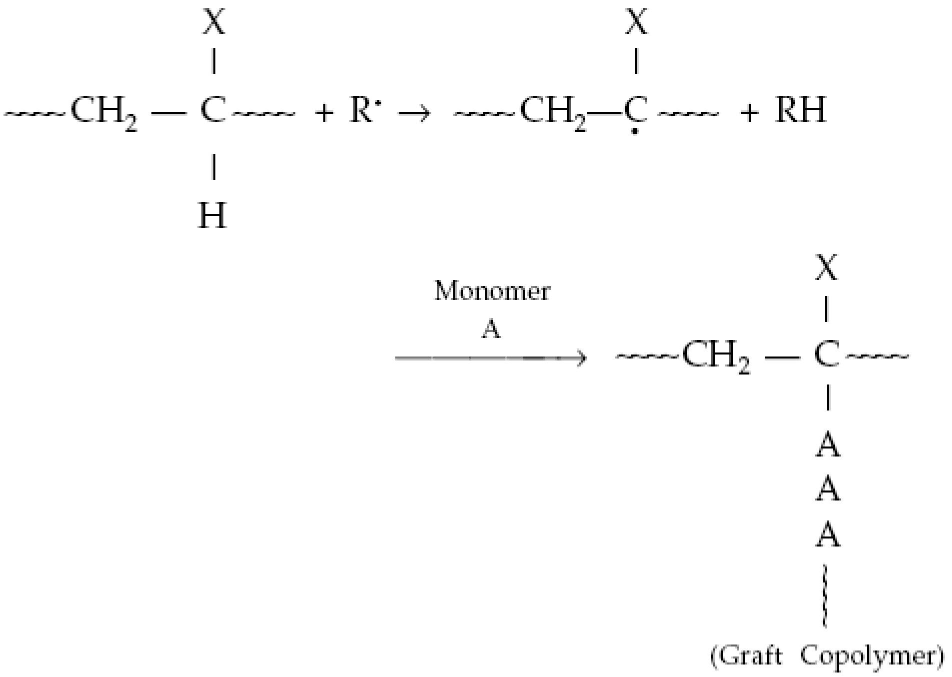
ii. *"Graft copolymer"*—where long or short sequences of one monomer appear as grafted or pendent chains linked to a "backbone" of long sequences of another monomer:



The ultimate aim in preparing a graft or block copolymer is to obtain the desired copolymer free from homopolymers as far as practicable. Although the copolymer structures resulting from the graft and block copolymerization processes are quite different, the former being a chain-branching process and the latter a chain extension process, both may be considered as a chain modification process differing only in direction. They are usually prepared by polymerizing a second monomer in presence of the preformed polymer of a different kind of monomer, and the process generally depends on the presence of labile sites particularly sensitive to radical attacks at different points along the chain axis or at chain ends of the reactant macromolecule. Reactive groups, according to their presence as end groups or as side groups along the chain may also lead to formation of block or graft copolymers by appropriate design of the overall process. Polymer–polymer reaction through selected functional groups present or incorporated on them may also lead to block or graft copolymer structure.

Studies of block copolymers are very much limited in comparison with those of graft copolymers because formation of block copolymers solely depends on the presence of reactive groups or labile atoms at chain ends of linear polymers. The physical properties of high polymers containing blocks of two or more repeat units with two, three or many blocks in a chain have not been studied and examined extensively, even though modification of polymers to block copolymer structures is being used commercially. A commercial product commonly known as "thermoplastic elastomer" is a triblock copolymer containing a middle block of polybutadiene or polyisoprene linked in a linear fashion to two end blocks of polystyrene and is prepared by anionic polymerization. Formation of polyurethane rubbers by chain extensions of different polyesters or polyethers as depicted by Eq. (4.2) also involves an approach to block copolymerization.

Graft copolymerization usually involves polymerization of a monomer onto a different polymer backbone; the various reactions associated with polymerization processes can be utilized for the synthesis of graft copolymers. Most graft copolymers are formed by free radical polymerization, and often the major activation involves chain transfer. The reaction shown involves generation of a radical site on the preformed polymer by a chain-transfer mechanism and then growth of a new polymer structure from that new radical site:



$$\sim\!\sim CH_2-\underset{\displaystyle H}{\overset{\displaystyle X}{C}}\sim\!\sim \;+\; R^{\bullet} \rightarrow \;\sim\!\sim CH_2-\overset{\displaystyle X}{\underset{\bullet}{C}}\sim\!\sim \;+\; RH$$

$$\xrightarrow{\text{Monomer A}} \;\sim\!\sim CH_2-\underset{\displaystyle \begin{matrix} | \\ A \\ A \\ A \\ \wr \end{matrix}}{\overset{\displaystyle X}{C}}\sim\!\sim$$