Chapter 1

Theory of Copolymerization

1.1 Introduction[1]

Copolymerization may be defined as a process by which two or more monomers such as styrene and methyl methacrylate or, in general, M_1 and M_2, are joined to form a polymer chain, which may be represented as $\sim\sim M_1M_2M_1M_2\sim\sim$. This involved a definite chemical reaction between M_1 and M_2 and is not a simple mixing process of two different polymers, such as that used to produce polyblens, that is, $\sim\sim M_1M_1\sim\sim + \sim\sim M_2M_2\sim\sim$. The components of these mixtures may be separated by physical means, such as solvent extraction. The terms "interpolymer", "mixed polymer", and "heteropolymer" have all been used but IUPAC has selected the term "copolymer" to descripbe these versatile polymeric products.

The general term "copolymer" includes all polymeric products in which two or more monomers are present as integral parts. Hence, it included those produced by step-reaction, radical-chain, and ionic polymerization processes. Many naturally occuring polymers, such as cellulose, starch, and natural rubber, are homopolymers. However, proteins, which are the most important naturally occuring polymers, are complex copolymers of different amino acids.

Copolymers prepared by the anionic polymerization of mixtures of 2-methyl-1, 3-butadiene (isoprene) and 2, 3-dimethyl -1, 3-butadiene (isoprene) and 2, 3-dimethyl-1, 3-butadiene were investigated in the early 1920s. The art of bulk copolymerization of vinyl monomers was also practisedmany years before the theory of copolymerization was developed. However, the opportunity for the production of different copolymers in the 1920s was limited since only five vinyl monomers were available, viz., ethyl acrylate, methyl methacrylate, styrene, vinyl acetate, and vinyl chloride.

Nevertheless, many of the pioneer developments in the polymer field were associatedwith copolymers of vinyl chloride, butadiene, and isobutylene. The most widely used commercial polymers are homopolymers such as polyethylene, polystyrene, and poly (vinyl chloride). However, the utility of many other polymers is dependent on the copolymerization process. Butyl rubber (IIR) is an excellent example of the way in which copolymerization can bring about an improvement in properties.

The introduction of a copolymer reduces the tendency for crystallization. Copolymerization may also be used to introduce reactive groups, e.g., the addition of vinyl pyridine and maleic anhydride to a polymer chain. As was mentioned previously, the addition of a minor amount of a comonomer such as isoprene to isobutylene in the production of butyl rubber may have a substantial effect on the properties of the polymeric product. In a broad sense, most chainreaction polymers are copolymers since they contain free radical and telogen fragments. However, since these fragments represent less than 1 percent of the polymeric composition, they are overlooked in high-polymer chemistry. Of course, they are of considerable importance in oligomers and telomers.

The biochemist designates the relative content of aminoacids in a specific protein by the use of exponents, for example, $(\mathrm{gly}^{66}, \mathrm{ala}^{33})$. IUPAC suggests the insertion of "co" to indicate a copolymer such as poly (butadiene-co-styrene). The number of different monomers present in the chain is indicated by the terms bipolymer $(\sim\sim M_1M_2M_1M_2\sim\sim)$, terpolymer $(\sim\sim M_1M_2M_3M_1M_2M_3\sim\sim)$, quadripolymer $(\sim\sim M_1M_2M_3M_4M_1M_2M_3M_4\sim\sim)$, etc.

The following terms used to describe various types of copolymers are explained in the accompanying illustrations in the table 1.1.

1.2 Copolymer composition equation and reactivity ratio[2]

1.2.1 Copolymer composition equation

In 1936, Dostal made the first attack on the mechanism of copolymerization by assuming that the rate of addition of monomer to a growing free radical depends only on the nature of the end group on the radical chain. Thus,

Type of copolymer	
Alternating copolymers	$\sim\sim M_1M_2M_1M_2\sim\sim$
Random copolymers	$\sim\sim M_1M_1M_2M_1M_2M_2M_1\sim\sim$
Block copolymers	$\sim\sim M_1M_1M_1M_1M_2M_2M_2M_2\sim\sim$
Graft copolymers	$\sim\sim M_1M_1M_1M_1M_1M_1M_1M_1\sim\sim$ $\sim\sim M_2M_2M_2M_2M_2M_2M_2\sim\sim$

Table 1.1 Various types of copolymers are explained in the accompanying illustration.

monomers M_1 and M_2 lead to radicals of types M_1 and M_2. There are four possible ways in which co-monomer can add:

$$\begin{array}{ll} \text{Reaction} & \text{Rate} \\ M_1^{\bullet} + M_1 \longrightarrow M_1^{\bullet} & k_{11}\,[M_1^{\bullet}]\,[M_1] \\ M_1^{\bullet} + M_2 \longrightarrow M_2^{\bullet} & k_{12}\,[M_1^{\bullet}]\,[M_2] \\ M_2^{\bullet} + M_1 \longrightarrow M_1^{\bullet} & k_{21}\,[M_2^{\bullet}]\,[M_1] \\ M_2^{\bullet} + M_2 \longrightarrow M_2^{\bullet} & k_{22}\,[M_2^{\bullet}]\,[M_2] \end{array} \qquad (1)$$

Since four independent rate constants were involved, Dostal made no attempt to test his assumption experimentally.

After several unsuccessful approaches, the kinetics of copolymerization were elucidated in 1944 by Alfrey, Mayo, Simha, and Wall. As an extension of basic reaction scheme, they additionally assumed that a steady state condition could be applied to each radical type separately, i.e., with the concentrations of $M_1^{\bullet}$ and $M_2^{\bullet}$ each remaining constant. It follows from this that the rate of conversion of $M_1^{\bullet}$ to $M_2^{\bullet}$ must equal that of $M_2^{\bullet}$ to $M_1^{\bullet}$:

$$\text{i.e.,} \quad k_{21}\,[M_2^{\bullet}]\,[M_1] \quad = \quad k_{12}\,[M_1^{\bullet}]\,[M_2] \qquad (2)$$

The rates of disappearance of the two types of monomer are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^\bullet][M_2] + k_{22}[M_2^\bullet][M_2] \qquad (3)$$

By difining the respective monomer reactivity ratios, r_1, r_2, as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and combining Eqs. (2) and (3), it can be shown that the composition of copolymer being formed at any instant is given by

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left[\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right] \qquad (4)$$

This is known as the copolymer composition equation ; it has been verified by many experimental investigations of copolymer composition.

The monomer reactivity ratios r_1 and r_2 are each defined as the ratio of the rate constant for a given radical adding its own monomer to that for its adding the other monomer. Thus, $r_1 > 1$ means that the radical $M_1^\bullet$ prefers to add M_1 ; $r_1 < 1$ means that it prefers to add M_2. In the system styrene (M_1)-methyl methacrylate (M_2), for example, $r_1 = 0.52$ and $r_2 = 0.46$; i.e., each radical adds the other monomer about twice as fast as its own.

Since the rate constants for initiation and termination do not appear in Eq. (4), the composition of the copolymer is independent of the overall reaction rate and initiator concentration. The reactivity ratios are unaffected in most cases by the presence of inhibitors, chain transfer agents, or solvents. Even in heterogeneous systems they remain unchanged unless the availability of the monomers is altered by their distribution between phases. A change from a free radical to an ionic mechanism, however, changes r_1 and r_2 markedly.

A few typical values of monomer reactivity ratios are given in Table 1.2. An extensive compilation is given by Mark (1966)[3].

1.2.2 Types of Copolymerization

(a) Ideal

A copolymerization system is said to be ideal when each of the two radicals show the same preference for adding one of the monomers over the other : $k_{11}/k_{12} = k_{21}/k_{22}$, or $r_1 = 1/r_2$, or $r_1 r_2 = 1$. In this case the end group on the growing chain has no influence on the rate of addition, and the two types of units are arranged at random along the chain in relative amounts determined by the composition of the feed and

Monomer 1	Monomer 2	r_1	r_2	T(°C)
Acrylonitrile	1, 3-Butadiene	0.02	0.30	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.20	0.05	50
	Vinyl chloride	2.70	0.04	60
1, 3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.80	0.035	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20.00	0.015	60
	Vinyl chloride	10.00	0.10	68
Styrene	Vinyl acetate	55.00	0.01	60
	Vinyl chloride	17.00	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

Table 1.2 Typical monomer reactivity ratios.

the relative reactivities of the two monomers. The copolymer composition equation then reduces to $d[M_1]/d[M_2] = r_1 [M_1]/[M_2]$.

(b) Alternating.

Here each radical prefers to react exclusively with the other monomer : $r_1 = r_2 = 0$. The monomers alternate regularly along the chain regardless of the composition of the monomer feed. The copolymer composition equation then simplifies to $d[M_1]/d[M_2] = 1$.

Most practical cases lie between the ideal and the alternating systems $0 < r_1 r_2 < 1$. A third possibility, with both r_1 and r_2 greater than unity, corresponds to the tendency to form block copolymer. This has been observed, However, in only a few cases.

1.2.3 Instantaneous composition of feed and polymer

Let F_1 and F_2 be the mole fractions of monomers 1 and 2 in the polymer being formed at any instant:

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d([M_1] + [M_2])} \qquad (5)$$

If f_1 and f_2 similarly represent mole fractions in the monomer feed,

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \qquad (6)$$

the copolymer composition equation can be re-written as:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \qquad (7)$$

It is apparent that in general F_1 does not equal f_1 and F_1 change as the polymerization proceeds. The polymer obtained over a finite range of conversion consists of many increments, each differing in composition.

Equation (7) may be used to plot curves of feed v.s instantoneous polymer composition for various monomer reactivity ratios. Such curves for a series of ideal copolymerizations ($r_1 r_2 = 1$) are shown in Fig. 1.1. Except for pairs of monomers having very similar reactivities, only a small range of feeds gives copolymers containing appreciable amounts of both components.

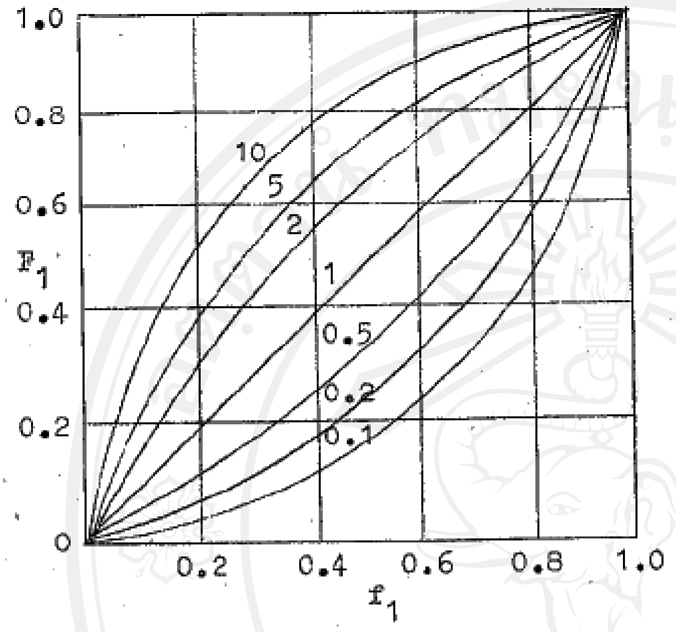


Fig. 1.1 Instanteneous composition of copolymer (mole fraction F_1) as a function of monomer composition (mole fraction f_1) for ideal copolymers with the values of $r_1 = 1/r_2$ indicated.

Several curves for non-ideal cases are shown in Fig. 1.2. These curves shows the effect of increasing tendenccy toword alternation. As alternation increases, more and more feeds yield a copolymer contaning a good deal of each components. This tendency makes practical the preparation of many important copolymers.

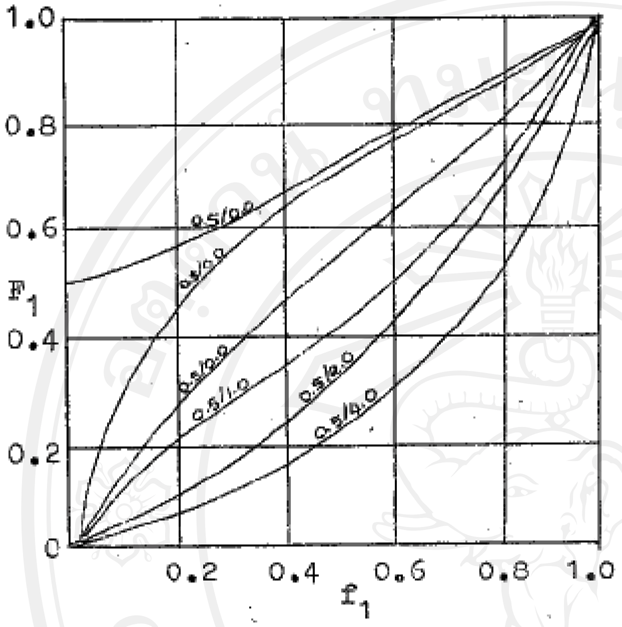


Fig. 1.2 Instanteneous composition of copolymer F_1 as a function of monomer composition f_1 for the values of the reactivity ratios r_1/r_2 indicated.

If one of the monomers is very much more reactive than the other, the initial copolymer formed contains mostly the more reactive monomer. However, as the copolymerization proceeds, this monomer gradually becomes used up, such that the copolymer formed during the latter stages consists mainly of the less reactive monomer. Styrene and vinyl acetate form such a system.

For cases in which both r_1 and r_2 are less than unity (or, hypothetically, greater than unity), the curves of Fig. 1.2 cross the line representing $F_1 = f_1$. At the point of intersection polymerization proceeds without a change in the composition of feed or polymer. This is known as azeotropic copolymerization. Solution of Eq. (4) with d $[M_1]$ / $[M_2]$ gives the critical composition for the azeotrope:

$$\frac{[M_1]}{[M_2]} = \frac{1-r_2}{1-r_1}$$

or form Eq. (7),

$$(f_1)_c = \frac{1-r_2}{2-r_1 - r_2} \qquad (8)$$

1.2.4 Evaluation of monomer reactivity ratios.

The usual experimental determination of r_1 and r_2 involves polymerization to low conversion for a variety of feed compositions. The polymers are isolated and their compositions measured. Elemental analysis, chemical analysis for reactive groups, or physical analysis (e.g., by refractive index when styrene is one of the components) may be used.

Four methods of analysing the data are available:

(i) Direct curve fitting on polymer-monomer composition plots. This is a poor method, since the composition curve is rather insensitive to small changes in r_1 and r_2.

(ii) Plots of r_1 v.s r_2. The copolymer equation may be solved for one of the reactivity ratios:

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{d\,[M_2]}{d\,[M_1]} \left(1 + \frac{[M_1]}{[M_2]}\, r_1 \right)^{-1} \right] \qquad (9)$$

Each experiment with a give feed gives a straight line ; the intersection of several of these allows the evaluation of r_1 and r_2 (Fig. 1.3). If the experimental errors are high, the lines may not intersect in a single point ; the region within which the intersections occur gives information about the precision of the experimental results.

(iii) Plots of F_1 v.s f_1. Equation (7) can be rearranged to

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1^2\,(F_1-1)}{(1-f_1^2)F_1}\, r_1 \qquad (10)$$

This is the equation of a straight line with slope r_1 and intercept r_2. Each experiment gives one point on the line. The least-squares treatment of a series of such points gives the best values of r_1 and r_2 in a straight forward way.

(iv) Analysis of data giving the copolymer composition as a function of conversion using the integrated form of the copolymer equation given as follows.

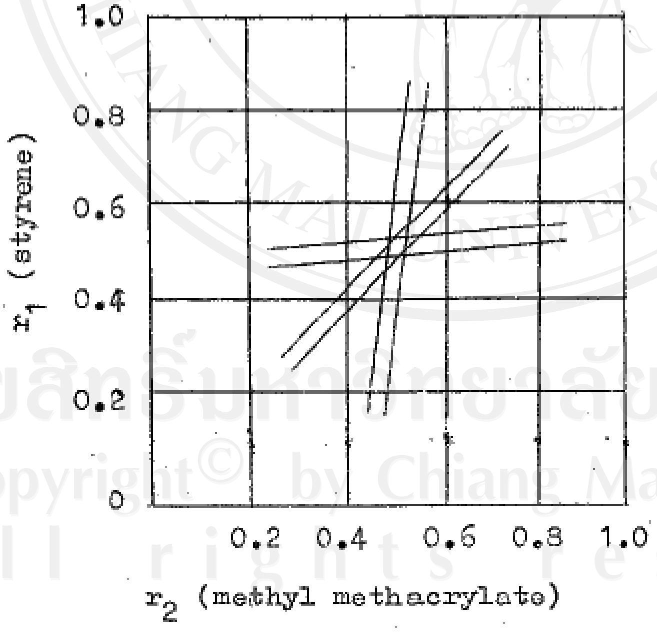


Fig. 1.3 Evaluation of monomer reactivity ratios by graphical solution of the copolymer equation.

1.2.5 Integration of the copolymer composition equation.

The direct integration of the copolymer composition equation gives a result which is not convenient for calculations. The most convenient method for calculating copolymer composition and distribution involves the use of Eq.(7). For a system in which $F_1 > f_1$, when dM moles of monomer have polymerized, the polymer contains F_1 dM moles of monomer 1 and the feed contains $(f_1-df_1)(M-dM)$ moles of monomer 1. For a material balance,

$$Mf_1-(M-dM)(f_1-df_1) = F_1 dM \qquad (11)$$

combining this with Eq.(7) gives

$$\frac{dM}{M} = \frac{df_1}{F_1-f_1} \qquad (12)$$

which can easily be integrated by numerical or graphical means to give the desired composition of polymer as a function of conversion. One convenient closed-form result of this integration is :

$$\log\frac{M}{M_0} = \frac{r_2}{1-r_2}\log\frac{f_1}{(f_1)_0} + \frac{r_1}{1-r_1}\log\frac{f_2}{(f_2)_0} + \frac{1-r_1r_2}{(1-r_1)(1-r_2)}\log\frac{(f_1)_0-\varepsilon}{f_1-\varepsilon} \qquad (13)$$

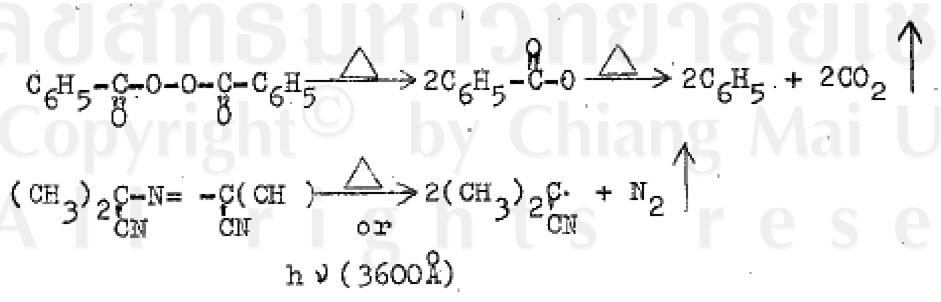
where $\varepsilon = (1-r_2)/(2-r_1+r_2)$.

1.3 Free radical copolymerization[4]

1.3.1 Introduction

Vinyl compounds are characterized by unusual activity because of the π-orbitals which result from incomplete overlapping of the p-orbitals. The reactivity of these π-bonds, which are 60 percent as strong as the δ-bonds, is well-covered in introductory organic chemistry textbooks. The chain-reaction polymerization reactions of π-bonds may involve free radicals (i.e., atoms or molecules with unpaired electrons) or ions (charged atoms or molecules).

The initiation of free radical reactions is usually dependent on unimolecular homolytic dissociation of weak bonds by irradiation or heat. Organic peroxides, such as benzoyl peroxide, and azo compounds, such as azo-bis-isobutyronitrile(AZBN), readily dissociate to form free radicals (R^{o}), as shown in the following equations:



$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow{\Delta} 2C_6H_5-\overset{\overset{O}{\|}}{C}-O \xrightarrow{\Delta} 2C_6H_5 + 2CO_2 \uparrow$$

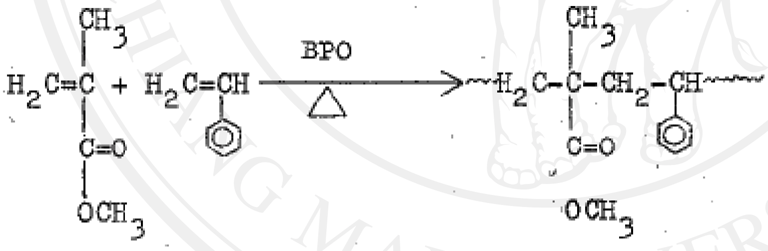
$$(CH_3)_2\underset{CN}{C}-N= -\underset{CN}{C}(CH\ ) \xrightarrow[\text{or } h\nu\,(3600\text{Å})]{\Delta} 2(CH_3)_2\underset{CN}{C}\cdot + N_2 \uparrow$$

or in general,

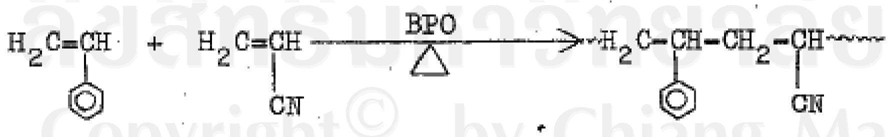
$$R \cancel{-} R \longrightarrow 2R\cdot$$

1.3.2 Equation for synthesis of free radicals.

Free radicals (R•) may be produced when a labile organic compound (initiator) is decomposed by heat, light, or particulate radiation. When styrene, methyl methacrylate or acrylonitrile is heated, free radicals are readily formed. Example of free radical copolymerization can be represented by the following equations:



Methyl methacrylate — Styrene — Methyl methacrylate-Styrene Copolymer



Styrene — Acrylonitrile — Acrylonitrile-Styrene Copolymer

1.4 Ionic Copolymerization.

Ionic or polar polymerization may either be anionic when electron-withdrawing groups, such as chloride, are present in the monomer or cationic when electro-donating groups, such as methyl, are present.

Anionic (carbanion) polymerization and cationic (carbonium) polymerization are more complex but more versatile than free-rodical chain polymerization. These polar reactions are characterized by the rapid production of high molecular-weight polymers at very low temperatures.

1.4.1 Anionic Polymerization.

Anionic polymerzation was carried out on a commercial scale for many years, before the nature of the polymerization was recognized, in the production of the buna-type synthetic rubbers in Germany and Russia by the polymerization of butadiene with sodium or potassium as the catalyst. The first anionic chain reaction to be so identified was the polymerization of methacrylonitrile by sodium in liquid ammonia at -75°C.

Typical catalysts for anionic polymerization include the alkali metal alkali metal amides, alkoxides, alkyls, aryls, hydroxides, and cyanides.

The conventional method of ionic initiation of polymer chains involves the addition of a negative ion to the monomer, with the opening of a bond or ring, and growth at one end:

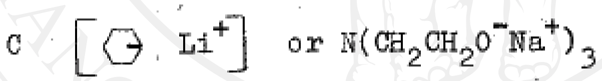
e.g.,

$$NH_2^- + CH_2{=}CHX \longrightarrow H_2NCH_2CHX^-$$

$$CH_3O^- + CH_2CH_2O \longrightarrow CH_3OCH_2CH_2O^-$$

$$Bu^-Li^+ + CH_2{=}CHX \xrightarrow[\text{benzene}]{} BuCH_2CHX^-Li^+$$

Simutaneous growth from more than one center can be obtained from polyvalent ions such as those derived from



$$C\left[\bigcirc\ Li^+\right] \text{ or } N(CH_2CH_2O^-Na^+)_3$$

The more basic the ion, the better it serves to initiate chains. Thus, although OH^- will not initiate the anionic polymerization of styrene, NH_2^- initiates it fairly well, whilst ⬡ CH_2^- is quite powerful. Similarly, more acid monomers require less basic ions, with the acidity of the monomer depending on the strength of the $X{-}M^-$ bond formed on initiation and the subsequent stability of the resulting carbanion.

Initiation can also occur by the transfer of an electron to a monomer of high electron affinity. If D or D^- is an electron donor,

$$D + M \longrightarrow D^+ + M^-$$

or

$$D^- + M \longrightarrow D + M^-$$

Presumably, M^- is less reactive than a true carbanion or a free radical but the addition of a monomer to M^- gives a species which contains one radical end and one anion end:

$$CH_2{=}C^-HX \;+\; CH_2{=}CHX \longrightarrow :C^-H_2CHXCH_2\dot{C}HX$$

anion end radical end

This species can add monomer from the two ends by different mechanism. Two radical ends may dimerize, however, leaving a divalent anion to propagate.

Propagation in anion polymerization may be conventional or may be more complex, as in the elimination of CO_2 from N-carboxyanhydrides. In contrast to radical polymerization, the β (unsubstituted) carbon atom at the end of the growing chain is the site of addition of the next monomer.

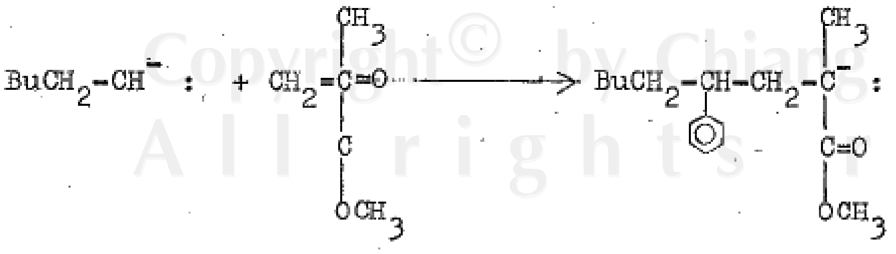
As in cationic polymerization, termination is always unimolecular, usually by transfer. The recombination of a chain with its counterion or the trasfer of a hydrogen to give terminal unsaturation, frequent in cationic polymerization, is unlikely in anionic mechanisms, as may be recognized by considering the small likehood of transffering H^- when the counterion is Na^+. Thus, in anionic polymerization, termination usually involves transfer and the kinetic chain is broken only if the new species is too weak to propagate.

This leads to the unique situation in which, by careful purification to eliminate all species to which transfer can occur, the termination step is effectively eliminated and the growing chains remain active indefinitely. This case leads to what are generally referred to as "living polymer".

An example of anionic copolymerization is given as follows:

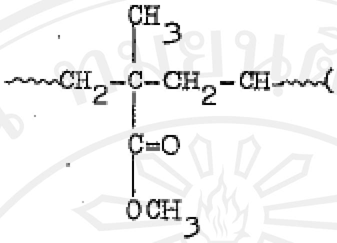
$$\mathrm{Bu^-Li^+ + CH_2{=}CH \xrightarrow{Benzene} BuCH_2{-}CH^- + Li^+}$$

Butyl Lithium Styrene



$$\mathrm{BuCH_2{-}CH^- : + CH_2{=}C(CH_3){-}C({=}O)OCH_3 \longrightarrow BuCH_2{-}CH{-}CH_2{-}C^-(CH_3)(C{=}O)OCH_3 :}$$

Methyl methacylate

The product obtained is 

$$\sim\sim CH_2-\underset{\underset{\displaystyle OCH_3}{|}}{\underset{\displaystyle C=O}{\underset{|}{\overset{\overset{\displaystyle CH_3}{|}}{C}}}}-CH_2-CH\sim\sim$$

(Methyl methacrylate-Styrene copolymer).

1.4.2 Cationic Polymerization.

Typical catalysts for cationic polymerization are lewis acids and Friedel-Crafts catalysts such as $AlCl_3$, $AlBr_3$, BF_3, $SnCl_4$, H_2SO_4, and other strong acids. All these are strong electron acceptors. Most of them, with the possible exception of the strong protonic acids, require a co-catalyst to initiate polymerization, usually a Lewis base or other donor of a proton, which is presumed to be the effective initiator.

High rate of polymerization at low temperatures is a characteristic of ionic polymerizations. It is often difficult to establish uniform reaction conditions before the reactants are consumed. The polymerization of isobutylene by $AlCl_3$ or BF_3 takes place within a few seconds at -100°C, producing polymer of molecular weight up to several million. Both rate and molecular weight are much lower at room temperature.

The most satisfactory theory cationic polymerizaation involves the carbonium ion as the chain carrier. For example, in the polymerization of isobutylene with boron trifluoride catalyst, the step is the reaction of the catalyst and aco-catalyst, for example water, to form a catalyst-co-catalyst complex.

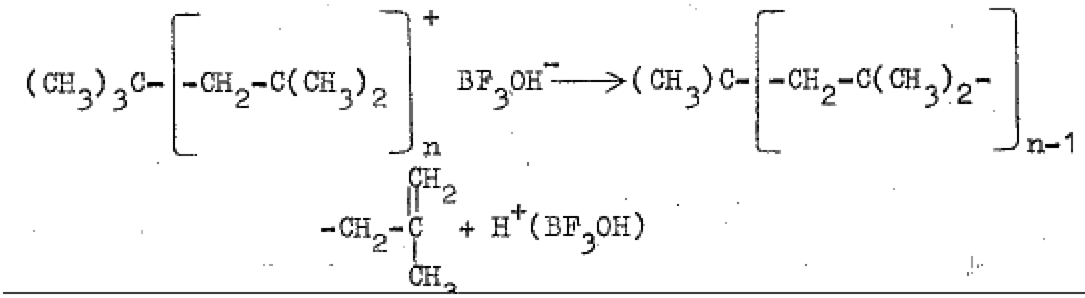
$$BF_3 + H_2O \rightleftharpoons H^+(BF_3OH)^-$$

which donates a proton to an isobutylene molecule to give a carbonium ion,

$$H^+ + (CH_3)_2C=CH_2 \longrightarrow (CH_3)_3C^+$$

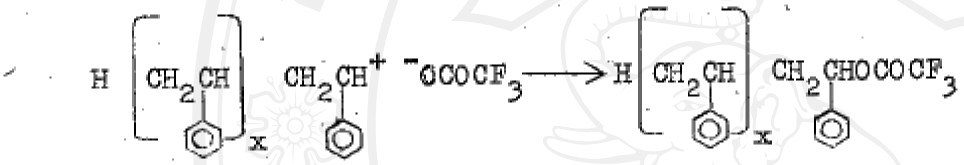
This ion then reacts with monomer with the reformation of a carbonium ion at the end of each step. The "head-to-tail" addition of monomer to ion is the only one possible for energetic reasons. Since the reaction is, in general, carried out in a hydrocarbon medium of low dielectric constant, the anion can not be separated from the growing cationic end to any appreciable distance ; rather, they form an "ion pair".

The termination reaction can take place by the rearrangement of the ion pair to yield a polymer molecule with terminal unsaturation, plus the original complex,

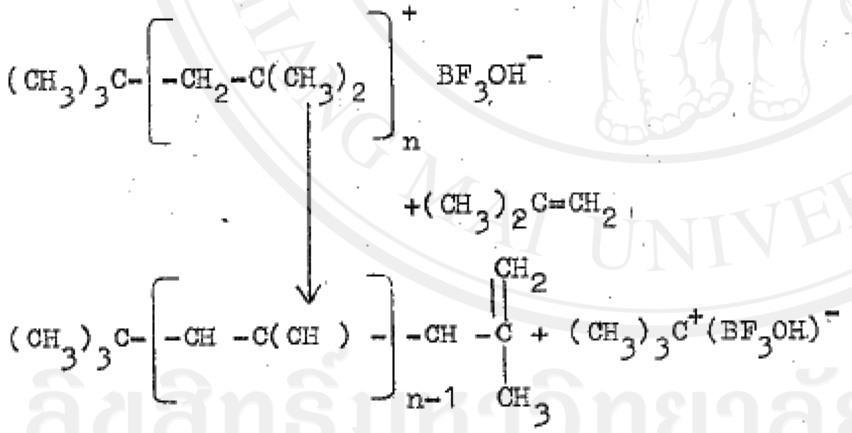


$$(CH_3)_3C-\left[-CH_2-C(CH_3)_2\right]_n^+ \; BF_3OH^- \longrightarrow (CH_3)C-\left[-CH_2-C(CH_3)_2-\right]_{n-1} -CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2}{\overset{\|}{C}}} + H^+(BF_3OH)$$

Here the catalyst-co-catalyst complex is regenerated ; hence, many kinetic chains can be produced from each catalyst-co-catalyst species. An alternative mechanism, in which the catalyst or co-catalyst combines with the growing chain, is unlikely in this example but can take place when a covalent bond is formed, as in the polymerization of styrene using trifluoroacetic acid:



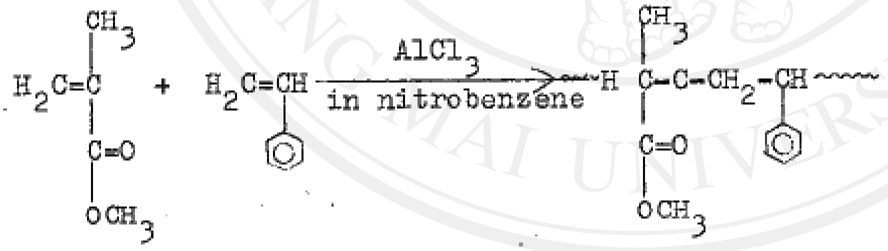
Chain transfer to monomer can also take place:



Chain transfer to polymer is also known and leads to branched polymers.

The efficiency of the catalyst is dependent on the acid strength of the catalyst-co-catalyst complex. Also, the efficiency of the catalyst as a terminator should be related to the base strength of the complex anion. Thus, the more active a molecule is as a catalyst, the less active it is as a terminate. Although the requirements of the isobutylene-BF_3 system are fully satisfied by the mechanism just given, generalization of the scheme should be applied with caution. The experimental data on other systems, for example, do not conclusively prove the necessity of a co-catalyst.

An example of cationic copolymerization is given as follows:



Methyl methacrylate   Styrene   Methyl methacrylate-Styrene copolymer