

CHAPTER THREE

THERMODYNAMICS AND KINETICS OF POLYMERISATION

3.1. Thermodynamics of Polymerization

3.1.1. Significance of ΔG , ΔH , and ΔS

The thermodynamic characteristics (ΔG , ΔH , ΔS) of polymerization are important to an understanding of the effect of monomer structure on polymerization. Further, knowledge of ΔH allows one to maintain the desired R_p and X_n by appropriate thermal control of the process. The ΔG , ΔH and ΔS for a polymerization are the differences in free energy, enthalpy, and entropy, respectively, between 1 mol of monomer and 1 mol of repeating units in the polymer product. The thermodynamic properties of a polymerization relate only to the propagation step, since polymerization consists of single acts of initiation and termination and a large number of propagation steps.

Chain polymerizations of alkenes are exothermic (negative ΔH) and exoentropic (negative ΔS). The exothermic nature of polymerization arises because the process involves the exothermic conversion of p-bonds in monomer molecules into s-bonds in the polymer. The negative ΔS for polymerization arises from the decreased degrees of freedom (randomness) for the polymer relative to the monomer. Thus, polymerization is favorable from the enthalpy viewpoint but unfavorable from the entropy viewpoint.

Table 1: Enthalpy and Entropy of Polymerization at 25°C

Monomer	$-\Delta H$	$-\Delta S$
Ethylene ^c	93	155
Propene	84	116
1-Butene	83.5	113
Isobutylene	48	121
1,3-Butadiene	73	89
Isoprene	75	101
Styrene	73	104
α -Methylstyrene	35	110
Vinyl chloride	72	—
Vinylidene chloride	73	89
Tetrafluoroethylene	163	112
Acrylic acid	67	—
Acrylonitrile	76.5	109
Maleic anhydride	59	—
Vinyl acetate	88	110
Methyl acrylate	78	—
Methyl methacrylate	56	117

ΔH refers to the conversion of liquid monomer to amorphous or (slightly) crystalline polymer. ΔS refers to the conversion of monomer (at a concentration of 1 M) to amorphous or slightly crystalline polymer. The subscripts lc are often used with ΔH and ΔS to show the initial and final states (that is, ΔH_{lc} and ΔS_{lc}). The units of ΔH are kJ mol^{-1} of polymerized monomer; the units of ΔS are $\text{J K}^{-1} \text{mol}^{-1}$. c Data are for conversion of gaseous monomer to crystalline polymer.

ΔH values for various monomers. The ΔS values fall in a narrower range of values. The methods of evaluating ΔH and ΔS have been reviewed. These include direct calorimetric measurements of ΔH for the polymerization, determination by the difference between the heats of combustion of monomer and polymer, and measurements of the equilibrium constant for the polymerization. The overall thermodynamics of the polymerization of alkenes is quite favorable. The value of ΔG given by

$$\Delta G = \Delta H - T\Delta S$$

is negative because the negative $T\Delta S$ term is outweighed by the negative ΔH term.

The data in Table 1 clearly show the general thermodynamic feasibility for any carbon–carbon double bond. Although the relative thermodynamic feasibility of any one monomer varies depending on the substituents present in the monomer, ΔG is negative in all cases and polymerization is favored. However, thermodynamic feasibility does not indicate the experimental conditions that may be required to bring about the polymerization. Thus Table 1 showed that the kinetic feasibility of polymerization varies considerably from one monomer to another in terms of whether radical, cationic, or anionic initiation can be used for the reaction. In some instances thermodynamically feasible polymerizations may require very specific catalyst systems. This is the case with the α -olefins, which cannot be polymerized to high-molecular-weight polymers by any of the conventional radical or ionic initiators. The polymerization of these monomers was not achieved until the discovery of the Ziegler–Natta or coordination-type initiators.

3.1.1a. Effect of Monomer Structure

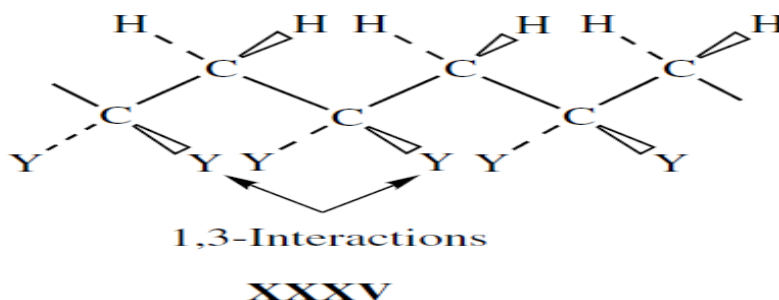
Consider the effect of monomer structure on the enthalpy of polymerization. The ΔH values for ethylene, propene, and 1-butene are very close to the difference ($82\text{--}90 \text{ kJ mol}^{-1}$) between the

bond energies of the p-bond in an alkene and the s-bond in an alkane. The ΔH values for the other monomers vary considerably. The variations in ΔH for differently substituted ethylenes arise from any of the following effects:

1. Differences in the resonance stabilization of monomer and polymer due to differences in conjugation or hyperconjugation.
2. Steric strain differences in the monomer and polymer arising from bond angle deformation, bond stretching, or interactions between nonbonded atoms.
3. Differences in hydrogen bonding or dipole interactions in the monomer and polymer.

Many substituents stabilize the monomer but have no appreciable effect on polymer stability, since resonance is only possible with the former. The net effect is to decrease the exothermicity of the polymerization. Thus hyperconjugation of alkyl groups with the C=C lowers ΔH for propylene and 1-butene polymerizations. Conjugation of the C=C with substituents such as the benzene ring (styrene and α -methylstyrene), and alkene double bond (butadiene and isoprene), the carbonyl linkage (acrylic acid, methyl acrylate, methyl methacrylate), and the nitrile group (acrylonitrile) similarly leads to stabilization of the monomer and decreases enthalpies of polymerization. When the substituent is poorly conjugating as in vinyl acetate, the ΔH is close to the value for ethylene.

The effect of 1,1-disubstitution manifests itself by decreased ΔH values. This is a consequence of steric strain in the polymer due to interactions between substituents on alternating carbon atoms of the polymer chain



In XXXV the polymer chain is drawn in the plane of the text with the H and Y substituents placed above and below the plane of the text. The dotted and triangular lines indicate substituents

below and above this plane, respectively. Such interactions are referred to as 1,3-interactions and are responsible for the decreased ΔH values in monomers such as isobutylene, a methylstyrene, methyl methacrylate, and vinylidene chloride. The effect in α -methylstyrene is especially significant. The ΔH value of -35 kJ mol^{-1} is essentially the smallest heat of polymerization of any monomer.

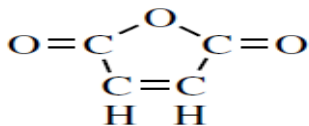
A contributing factor to the lowering of ΔH in some cases is a decrease in hydrogen bonding or dipole interactions on polymerization. Monomers such as acrylic acid and acylamide are significantly stabilized by strong intermolecular associations. The intermolecular associations are not as important in the polymer because its steric constraints prevent the required lining up of substituents.

The ΔH value for vinyl chloride is lowered relative to that for ethylene because of increased steric strain in the polymer and increased resonance stabilization of the monomer. However, it is not clear why ΔH for vinylidene chloride is not lower than that for vinyl chloride. The abnormally high ΔH for tetrafluoroethylene is difficult to understand. A possible explanation may involve increased stabilization of the polymer due to the presence of intermolecular association (dipole interaction).

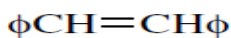
While the ΔH values vary over a wide range for different monomers, the ΔS values are less sensitive to monomer structure, being relatively constant within the range of $100\text{--}120 \text{ J K}^{-1} \text{ mol}^{-1}$. The $T\Delta S$ contribution to the ΔG of polymerization will be small as indicated earlier and will vary only within a narrow range. Thus the variation in the $T\Delta S$ term at 50°C for all monomers is in the narrow range $30\text{--}40 \text{ kJ mol}^{-1}$. The entropy changes that occur on polymerization have been analyzed for several monomers. The ΔS of polymerization arises primarily from the loss of the translational entropy of the monomer. Losses in the rotational and vibrational entropies of the monomer are essentially balanced by gains in the rotational and vibrational entropies of the polymer. Thus ΔS for polymerization is essentially the translational entropy of the monomer, which is relatively insensitive to the structure of the monomer.

3.1.1b. Polymerization of 1,2-Disubstituted Ethylenes

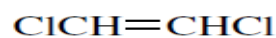
With some exceptions, 1,2-disubstituted ethylenes containing substituents larger than fluorine such as maleic anhydride, stilbene, and 1,2-dichloroethylene exhibit little or no tendency



Maleic anhydride



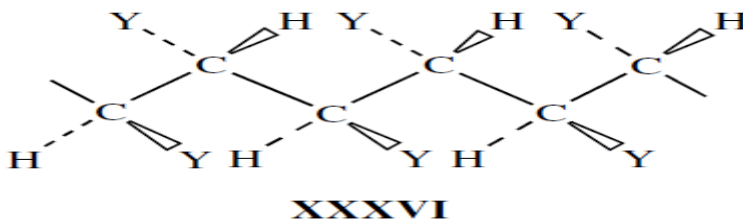
Stilbene



1,2-Dichloroethylene

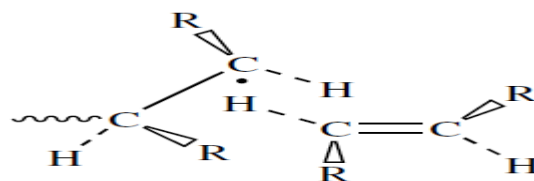
to undergo polymerization. Steric inhibition is the cause of this behavior, but the effect is different from that responsible for the low reactivity of 1,1-disubstituted ethylenes.

Polymers from 1,2-disubstituted ethylenes (XXXVI) possess 1,3-interactions, but the steric strain is not as severe as in XXXV. Both XXXV and XXXVI possess the same number of 1,3-interactions but the distribution of the interactions is different. For XXXV, pairs of 1,3-carbons each have a pair of 1,3-interactions. No pair of 1,3-carbons in XXXVI has more than



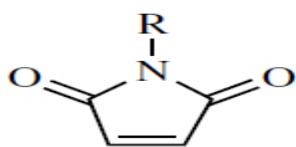
a single 1,3-interaction. Thus the ΔH value for maleic anhydride is -59 kJ mol^{-1} , which is favorable for polymerization compared to the value for some 1,1-disubstituted ethylenes.

The low tendency of 1,2-disubstituted ethylenes to polymerize is due to kinetic considerations superimposed on the thermodynamic factor. The approach of the propagating radical to a monomer molecule is sterically hindered. The propagation step is extremely slow because of steric interactions between the β -substituent of the propagating species and the two substituents of the incoming monomer molecule:

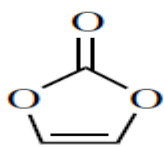


XXXVII

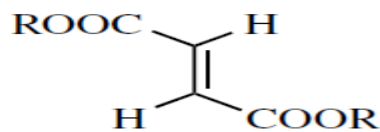
Some success has been achieved in polymerizing 1,2-disubstituted ethylenes, although the molecular weights are generally low. Maleic anhydride is very sluggish in polymerization. Only low-molecular-weight polymers are produced even when high initiator concentrations are used and the reaction proceeds in a complex manner with some loss of carbon dioxide. Various *N*-substituted maleimides, dialkyl fumarates (and fumaramides), and vinylene carbonate have been polymerized



N-Substituted
maleimide



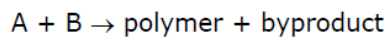
Vinylene
carbonate



Dialkyl
fumarate

to higher molecular weights, many in the 103–104 range with a few as high as 105. Dialkyl maleates have not been successfully polymerized, except when a base such as morpholine is present to isomerizes the maleate ester to fumarate ester prior to polymerization. The lack of polymerization for the maleate esters is a consequence of the *cis* placement of the substituents, which maximizes the steric problem. Steric hindrance is lowered when the *cis* substituents are part of a cyclic structure, as in maleic anhydride, maleimides, and vinylene carbonate. Fumarate esters polymerize because there is less steric hindrance when the substituents are *trans*. Both k_p and k_t are lowered in fumarate esters compared to monomers such as methyl acrylate or methyl methacrylate, but the decrease in k_t is much greater than the decrease in k_p , and polymerization is facilitated. The effect of decreased k_t relative to k_p and increased R_p is enhanced for larger sterically hindered groups such as *t*-butyl. Similar effects have been observed for dialkyl fumarates.

3.2. Kinetics of step-growth polymerization



R_p = rate of polymerization

$$R_p = \frac{-d[M]}{dt} = \frac{-d[a]}{dt} = \frac{-d[b]}{dt} = k[a][b]$$

Assume $r = 1$, where r is the stoichiometric ratio. $r = \frac{a}{b}$
 $[a] = [b]$

Terminology \bar{p}_n varies with $t \rightarrow \bar{p}_n = \frac{[a]_0}{[a]}$

(X_n) p. 50

$$\frac{-d[a]}{dt} = k[a]^2$$

$$\frac{-d[a]}{[a]^2} = kt$$

$$\frac{1}{[a]} - \frac{1}{[a]_0} = kt$$

$$\frac{[a]_0}{[a]} - 1 = [a]_0 kt$$

$$\pi = 1 - \frac{[a]}{[a]_0}$$

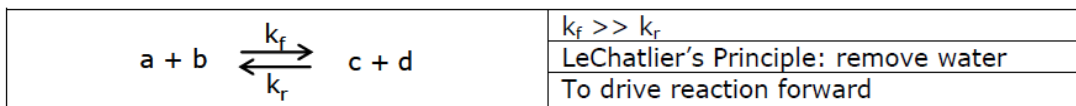
in book, $\pi = p$ (p. 46)

$$\frac{[a]_0}{[a]} = \frac{1}{1 - \pi}$$

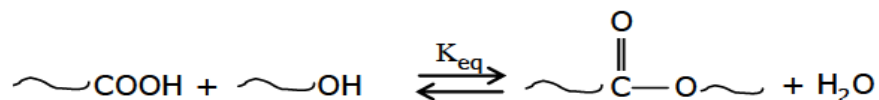
$$[a]_0 kt = \frac{1}{1 - \pi} - 1 = \bar{p}_n - 1$$

Notes:

1. $[M] \propto \frac{1}{t}$ as time \uparrow , concentration of monomer \downarrow
2. \bar{p}_n increases linearly with time



Making esters:



Ester can hydrolyze with water and go backwards (reverse rxn) \rightarrow drug delivery

$$K = \frac{1}{1-\pi} \cdot \frac{\pi}{1-\pi} \cdot \frac{[H_2O]_{eq}}{[M]_b}$$

$$\bar{p}_n = \frac{1}{1-\pi}$$

$$\frac{\pi}{1-\pi} = \frac{1}{1-\pi} - \frac{1-\pi}{1-\pi} = \frac{1}{1-\pi} - 1 = \bar{p}_n - 1$$

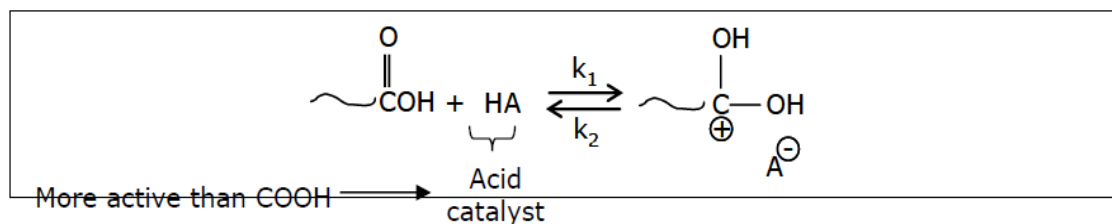
$$K = \bar{p}_n \cdot (\bar{p}_n - 1) \frac{[H_2O]_{eq}}{[M]_b}$$

$$[H_2O]_{eq} = \frac{[M]_b K}{\bar{p}_n (\bar{p}_n - 1)}$$

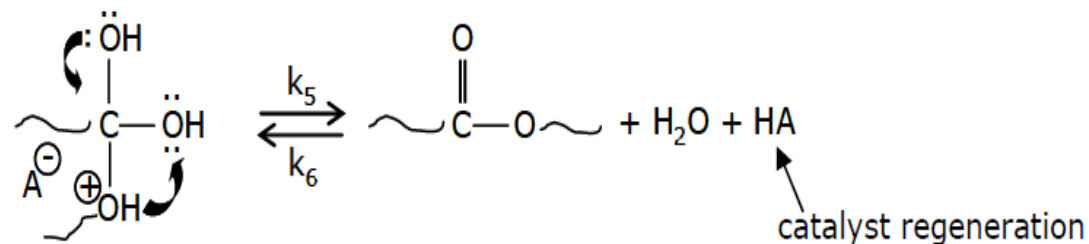
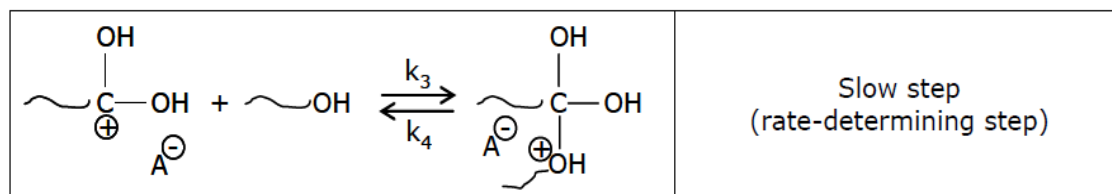
only get down to a certain water concentration

→ solve for best \bar{p}_n possible

Polyesterification Using Acid Catalysis



$$K_{12} = \frac{k_1}{k_2} = \frac{\left[\begin{array}{c} \text{OH} \\ | \\ \sim\text{C}-\text{OH} \\ \oplus \\ \text{A}^- \end{array} \right]}{[\text{HA}][\text{COOH}]}$$



$$R_p = \frac{-d[\text{COOH}]}{dt} \quad \text{Rate of disappearance of carboxylic monomer}$$

R_p	$= k_3 [C^+ (OH)_2][OH]$	(from previous page)
	$= k_3 K_{12} [HA][COOH][OH]$	
	From equilibrium expression	[HA] is constant because it's regenerated.

$$R_p = \frac{-d[\text{COOH}]}{dt} = k' [\text{COOH}][\text{OH}] \quad \text{where } k' = k_3 K_{12} [\text{HA}] \text{ constant}$$

Self-catalyzed: $[\text{HA}] = [\text{COOH}]$

$$R_p = \frac{-d[\text{COOH}]}{dt} = k'' [\text{COOH}]^2 [\text{OH}] \quad \text{where } k'' = k_3 K_{12}$$

$$R_p = \frac{-d[M]}{dt} = k'' [M]^3 \quad \text{separate and integrate}$$

$$2k''t = \frac{1}{[M]^2} - \frac{1}{[M]_0^2}$$

$$[M] = [M]_0 (1 - \pi)$$

$$\left(\frac{\pi}{1 - \pi}\right)^2 = \frac{1}{[M]_0^2} = 2[M]_0^2 k''t + 1$$

Much slower because of time-dependence (\sqrt{t})

That's why people add acid to drive reaction.

High Temperature

- increase k
- remove byproduct (evaporate H_2O)

Bulk or mass conditions (no solvent)

- $[M]_0$ is maximum
- no need to separate product
- viscosity η low until high π
- direct processing

Use solvent

- monomers are not miscible with each other but miscible with solvent
- allow high T
- dilute viscous media (carrier for viscous media)
 - improves processing
- improves heat and mass transfer

3.3. Kinetics of free radical polymerization

The polymerization of unsaturated monomers typically involves a chain reaction. It can be initiated by methods typical for simple gas phase chain reactions, including the action of ultraviolet light. It is susceptible to retardation and inhibition. In a typical chain polymerization, one act of initiation may lead to the polymerization of thousands of monomer molecules.

The characteristics of chain polymerization suggest that the active center responsible for the growth of the chain is associated with a single polymer molecule through the addition of many monomer units. Thus polymer molecules are formed from the beginning, and almost no species intermediate between monomer and high-molecular-weight polymer are found.

The concept of vinyl polymerization as a chain mechanism is not new, dating back to Staudinger's work in 1920. In 1937 Flory showed conclusively that radical polymerization proceeds by the three steps of initiation, propagation, and termination typical of chain reactions in low-molecular-weight species.

The carbon-carbon double bond is, because of its relatively low stability, particularly susceptible to attack by a free radical. The reaction of the double bond with a radical proceeds well for compounds of the type $\text{CH}_2=\text{CHX}$ and $\text{CH}_2=\text{CXY}$, called vinyl monomers (Monomers in which fluorine is substituted for hydrogen may be included in this class).

Not all vinyl monomers yield high polymer as a result of radical polymerization. Aliphatic hydrocarbons other than ethylene polymerize only to oils, and 1,2-disubstituted ethylenes not at all. Among compounds of the type $\text{CH}_2=\text{CXY}$, those in which both groups are larger than CH_3 polymerize slowly, if at all, by radical mechanisms.

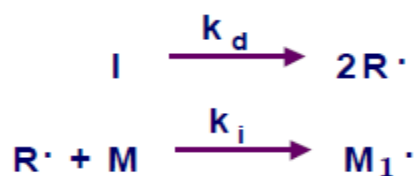
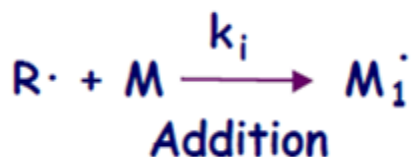
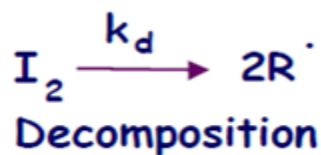
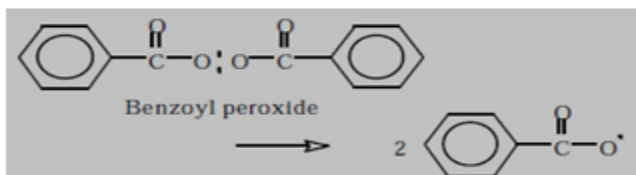
Generation of Free Radicals. Many organic reactions take place through intermediates having an odd number of electrons and, consequently, an unpaired electron. Such intermediates are known as free radicals. They can be generated in a number of ways, including thermal decomposition of organic peroxides or hydroperoxides (Mageli 1968) or azo or diazo compounds (Zand 1965).

Two reactions commonly used to produce radicals for polymerization are the thermal or photochemical decomposition of benzoyl peroxide,

We need to consider the following steps

- Initiation
- Propagation
- (Chain transfer)
- Termination

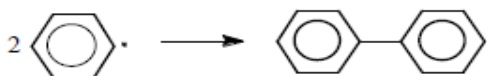
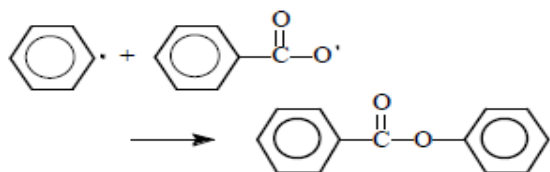
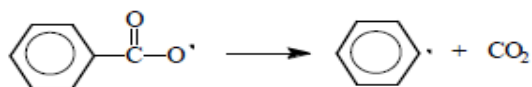
INITIATION



Assume decomposition is the rate limiting step then we should only have to consider

i.e. $k_i \gg k_d$ Then we should only have to consider k_d

$$\text{i.e. } -\frac{d[I]}{dt} = \frac{1}{2} \frac{d[M_1^\cdot]}{dt} = k_d [I] \quad \text{But, only a fraction } f \text{ of radicals initiates chain growth}$$

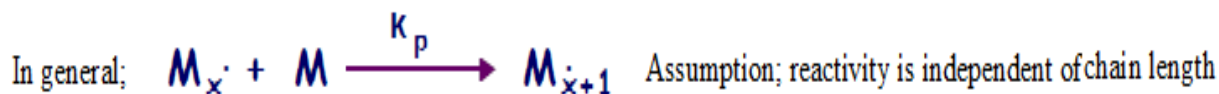


$$r_i = \frac{d[\text{M}_i]}{dt} = 2 f k_d [\text{I}]$$

PROPAGATION

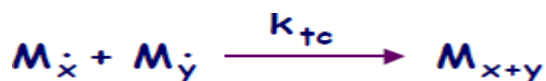
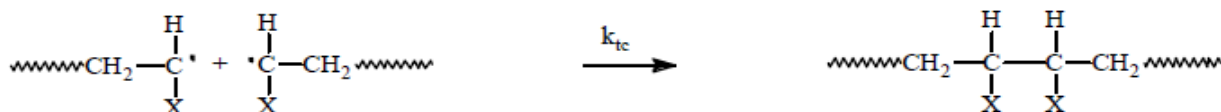


$$r_p = \frac{d[\text{M}]}{dt} = k_p [\text{M}] [\text{M}\cdot]$$

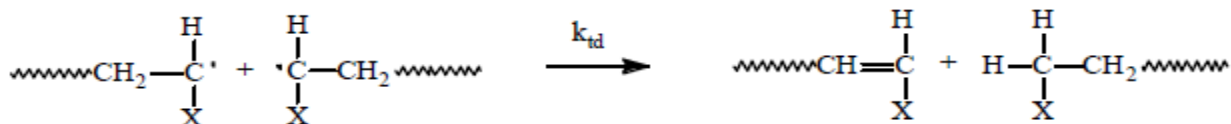


TERMINATION

Combination



Disproportionation



Rate of termination

$$r_t = -\frac{d[\text{M}\cdot]}{dt} = 2 k_t [\text{M}\cdot][\text{M}\cdot] \quad \text{Where} \quad k_t = k_{tc} + k_{td}$$

Obtained from:

- Both reactions are second order
- Rate of removal of chain radicals = sum of the rates of the two termination reactions

Summary

$$r_i = \frac{d[M_i]}{dt} = 2fk_d[I]$$

$$r_p = \frac{d[M]}{dt} = k_p[M][M\cdot]$$

$$r_t = -\frac{d[M\cdot]}{dt} = 2k_t[M\cdot][M\cdot]$$

3.4. Free radical copolymerisation–Reactivity ratios

Although the polymerization of organic compounds has been known for over 100 years, the simultaneous polymerization (*copolymerization*) of two or more monomers was not investigated until about 1911, when *copolymers* of olefins and diolefins were found to have rubbery properties and were more useful than *homopolymers* made from single monomers.

In the 1930's it was found that monomers differed markedly in their tendencies to enter into copolymers. Staudinger (1939) fractionated a vinyl chloride-vinyl acetate copolymer made from a mixture of equimolar quantities of the two monomers. He found no polymer containing equal amounts of each monomer but, instead, found vinyl chloride: vinyl acetate ratios of 9: 3, 7: 3, 5: 3, and 5: 7 among the fractions.

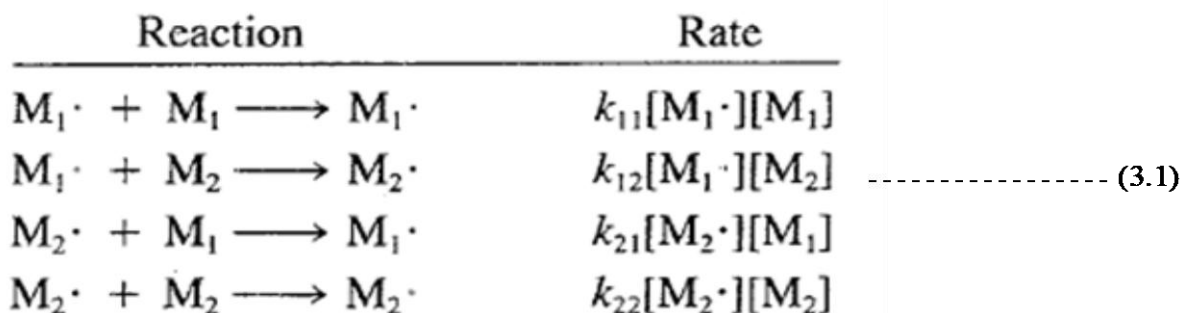
At about the same time, acrylic esters were found to enter copolymers with vinyl chloride faster than did the second monomer. The first polymer formed was rich in the acrylate; later, as the amount of acrylate in the monomer system was depleted, the polymer became richer in vinyl chloride. Maleic anhydride and other monomers that homopolymerize with great difficulty were found to copolymerize readily with such monomers as styrene and vinyl chloride. Pairs of monomers, such as styrene-maleic anhydride and isobutylene-fumaric ester, in which neither monomer polymerizes alone, readily gave high-molecular-weight copolymers in which the monomers appeared in a 1 : 1 ratio, no matter which was in excess in the monomer feed.

More recently, the ability to produce polymers containing long sequences of two or more different monomers (*block* and *graft copolymers*) has led to new products with unique and valuable properties

The kinetic scheme for chain-reaction copolymerization is developed for radical reactions; extension to ionic systems is straightforward.

The Copolymer 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 monomers M_1 and M_2 lead to radicals of types $M_1\cdot$ and $M_2\cdot$. There are four possible ways in which monomer can add:



The kinetics of copolymerization was more fully elucidated in 1944 by Alfrey, Mayo, Simha, and Wall. To Dostal's reaction scheme they added the assumption of the steady state applied to each radical type separately, that is, the concentrations of $M_1\cdot$ and $M_2\cdot$ must each remain constant. It follows that the rate of conversion of M_1 to M_2 must equal that of conversion of M_2 to M_1 :

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \text{ ----- 3.2}$$

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

$$\begin{aligned}
 -\frac{d[M_1]}{dt} &= k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \\
 -\frac{d[M_2]}{dt} &= k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]
 \end{aligned}
 \tag{3.3}$$

By defining $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and combining Eqs. 3.2 and 3.3, it can be shown that the composition of copolymer being formed at any instant is given by

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] [M_1] + r_2 [M_2]}
 \tag{3.4}$$

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

Monomer Reactivity Ratios

The *monomer reactivity ratios* r_1 and r_2 , are the ratios of the rate constant for a given radical adding its own monomer to the rate constant for its adding the other monomer. Thus $r_1 > 1$ means that the radical $M_1\cdot$ 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 $r_2 = 0.46$; 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. 3.4, the composition of the copolymer is independent of 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 3.1. An extensive compilation is given by Young (1975a)

TABLE 3.1 Typical Monomer Reactivity Ratios^a

Monomer 1	Monomer 2	r_1	r_2	$T(^{\circ}\text{C})$
Acrylonitrile	1,3-Butadiene	0.02	0.3	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
1,3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.8	0.035	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.015	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
	Vinyl chloride	17	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

^aYoung (1975a).

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

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 equation simplifies to $d[M_1] / d[M_2] = 1$

Most actual 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 copolymers.

Free-Radical Copolymerization

The order of reactivity of monomers toward free radicals not only is a function of the reactivity of the monomers, but also depends on the nature of the attacking radical. This is illustrated by the tendency of many monomers to alternate in a copolymer chain. The two factors, general reactivity and alternating tendency, are predominant in determining the behavior of monomers in copolymerization.

The reactivity of monomers and radicals in copolymerization is determined by the nature of the substituents on the double bond of the monomer. These substituents influence reactivity in three ways: They may activate the double bond, making the monomer more reactive; they may

stabilize the resulting radical by resonance; or. they may provide steric hindrance at the reaction site.

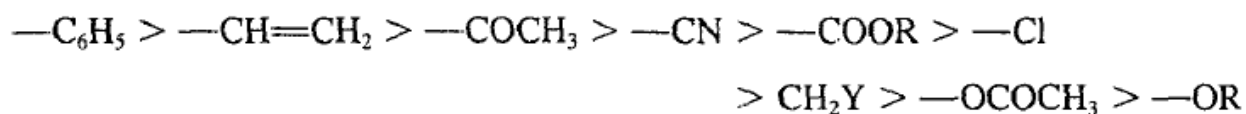
Reactivity of Monomers. The relative reactivities of monomers to a reference radical can be derived from the monomer reactivity ratio. The inverse of this ratio is the rate of reaction of the reference radical with another monomer, relative to that with its own monomer. If the latter rate is taken as unity, relative monomer reactivities can be examined. A few such rates are listed in Table 3.2; more extensive tabulations are given in the General References. As a different reference point is

TABLE 3.2 Relative Reactivities of Monomers to Reference Radicals at 60°C

Monomer	Reference Radical				
	Styrene	Methyl Methacrylate	Acrylonitrile	Vinyl Chloride	Vinyl Acetate
Styrene	(1.0)	2.2	25	50	100
Methyl methacrylate	1.9	(1.0)	6.7	10	67
Acrylonitrile	2.5	0.82	(1.0)	25	20
Vinylidene chloride	5.4	0.39	1.1	5	10
Vinyl chloride	0.059	0.10	0.37	(1.0)	4.4
Vinyl acetate	0.019	0.05	0.24	0.59	(1.0)

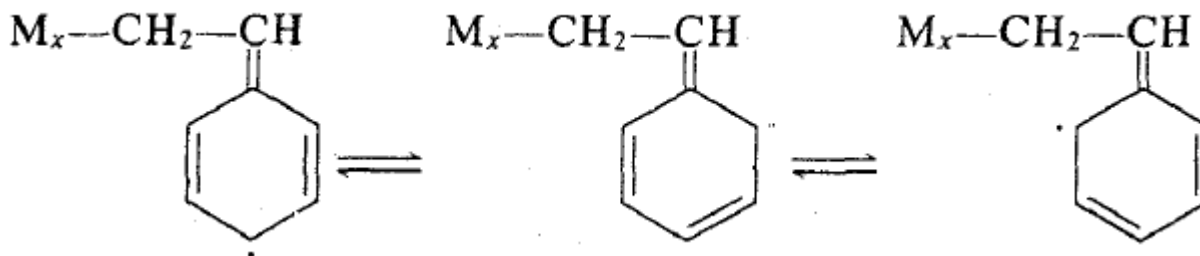
taken for each radical, values in different columns are not comparable, although ratios of values can be compared from column to column.

Although there are some exceptions, the effectiveness of substituents in enhancing the reactivity of the monomer lies in about the order



The effect of a second substituent on the same carbon atom is usually additive.

This order of reactivity corresponds to the resonance stabilization of the radical formed after the addition. In the case of styrene the radical can resonate among forms of the type



The radical is stabilized with a resonance energy of about 80 kJ/mole. At the other extreme, substituents that have no double bonds conjugated with the ethylenic double bond give radicals having very low resonance energies (5-15 kJ/mole), since only polar or unbonded forms can contribute to the resonance.

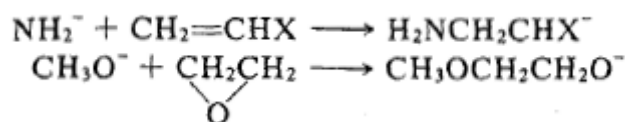
Substituents that stabilize the product radical tend also to stabilize the monomer, but the amount of stabilization is much smaller than for the radical; in styrene the monomer is stabilized to the extent of about 12 kJ/mole. Thus the stabilizing effect of a substituent on the product radical is compensated for only to a limited extent by stabilization of the monomer.

3.5. Kinetics of Ionic Polymerization

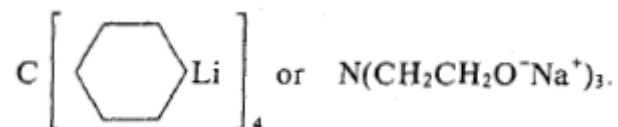
Anionic polymerization was carried out on a commercial scale for many years before the nature of the polymerization was recognized, in the production of the buna-type synthetic rubbers in Germany and Russia by the polymerization of butadiene with sodium or potassium as the catalyst. The first anionic chain reaction to be so identified was the polymerization of methacrylonitrile by sodium in liquid ammonia at -75°C . In modern times, the growth of commercial products of anionic polymerization has been phenomenal. Most of these polymerizations are based on the use of organometal catalyst systems, which allow unprecedented control over polymer structure.

3.5.1. Mechanism of Ionic Polymerization

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

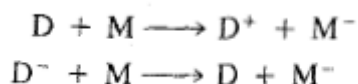


(In the equations of this section the counterions are omitted; however, their role is essentially the same as in cationic polymerization..) Simultaneous growth from more than one center can be obtained from polyvalent ions such as those derived from

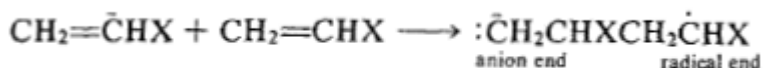


The more basic the ion, the better it serves to initiate chains Thus OH⁻ will not initiate the anionic polymerization of styrene, NH₂⁻ initiates fairly well, but O⁻CH₂⁻ is powerful Similarly, more acid monomers require less basic ions, with the acidity of the monomer depending on the strength of the X---M-bond formed in initiation and the stability of the resulting ion.

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, or



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



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

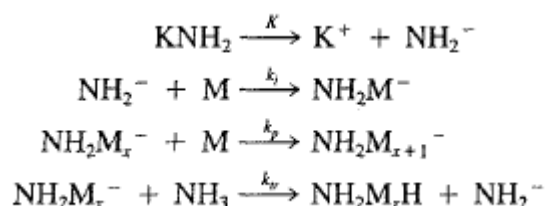
Propagation in anionic polymerization may be conventional or may be more complex, as in the elimination of CO₂ from N-carboxyanhydrides In contrast to radical polymerization, the β (unsubstituted) carbon atom at the end of the growing chain is the site of addition of the next monomer.

As in cationic polymerization, termination is always unimolecular, usually by transfer The recombination of a chain with its counterion or the transfer of a hydrogen to give terminal unsaturation, frequent in cationic polymerization, is unlikely in anionic mechanisms, as may be recognized by considering the small likelihood of transferring 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 is described below under "Living" Polymers.

The kinetics of anionic polymerization may be illustrated by the polymerization of styrene with potassium amide in liquid ammonia.



The usual kinetic analysis leads for high degree of polymerization to

$$v_p = \frac{Kk_p k_i}{k_t} \frac{[\text{NH}_2^-]}{[\text{NH}_3]} [\text{M}]^2$$

And

$$\bar{x}_n = \frac{k_p[\text{M}]}{k_t[\text{NH}_3]}$$

"Living" Polymers

Since the termination step usually involves transfer to some species not essential to the reaction, anionic polymerization with carefully purified reagents may lead to systems in which termination is lacking. The resulting species, called "living" polymers (Henderson 1968; Szwarc 1968b), can be prepared, for example, by polymerizing styrene with sodium naphthalene. Kinetic analysis shows that the polymer can have an extremely narrow distribution of molecular weight and for all practical purposes be essentially monodisperse; if initiation is rapid compared to propagation, the molecular-weight distribution is the Poisson function for which $\bar{X}_w/\bar{X}_n \approx 1/\bar{X}_n$. The polymer can be "killed" by addition of a terminating agent, for example, water, at the end of the reaction.

The living polymer technique provides an unique opportunity for the preparation of block copolymers.