Condensation Polymeri+++++zation or Step-Growth Polymerization

2. Condensation Polymerization or Step-Growth Polymerization

2.1. Functionality Principle

Polymerization may be generally defined as intermolecular reaction between bifunctional or polyfunctional compounds (covering olefins and related compounds) avoiding formation of ring or cyclic structures and in a manner that makes the process functionally capable of proceeding to infinity. Functional groups or atoms, through disappearance of which polymerizations of different kinds take place are: reactive hydrogen atom (—H), hydroxyl group (—OH), carboxyl group (—COOH), amino group (—NH_2), halogen atom (—Cl, —Br), isocyanate group (—NCO), aldehyde group (—CHO), double bond $(C{=}C)$, etc.

According to the functionality principle and concept, for polymerization to take place, each of the reacting molecules must be at least bifunctional, giving average functionality for the system as 2. For reacting compounds containing two different kinds of functional groups, the average functionality is calculated on the basis of stoichiometric equivalence of the two kinds of functional groups. Thus, for reaction between a dicarboxylic acid and a trihydric alcohol, to strike stoichiometric equivalence of —COOH and —OH groups, the acid and the alcohol should be taken in a molar ratio 3 : 2, which would express the average functionality for the system as 12/5, i.e., 2.4. On this basis, any system consisting of a polyfunctional compound (functionality 3 or more) bearing a given kind of functional group (say, —OH) and a related monofunctional compound bearing a different kind of functional group (say, —COOH) would always give an average functionality less than 2. So, for any system, if one type of the reacting molecules is monofunctional, then the system would fail to produce polymer molecules. On consideration of functionality, a double bond $(C{=}C)$ is bifunctional, as on thermal or photoactivation, the π bond may open up to yield a diradical intermediate.

2.2. Types of Polymerization

It has been suggested in Chapter 1 that polymerization or growth of the polymer usually takes place by two basically different mechanisms. Depending on the mode of formation, one kind of polymerization is called condensation polymerization or step-growth polymerization, and the other kind is known as addition polymerization or chain-growth polymerization.[1] The physicochemical aspects of condensation polymerization will be the subject matter of this chapter.

2.3. Basic Characteristics of Condensation or Step-Growth Polymerization

Condensation polymerization takes place under suitable conditions allowing **bifunctional or polyfunctional molecules to condense intermolecularly** in a manner that **the growth of the molecule or chain extension takes place in controlled, distinguishable steps** and **the process is normally associated with the formation of condensed interunit chemical links** and **liberation of a small byproduct such as H_2O, HCl, etc, at each step of reaction.**[2] Formation of a polyester by condensation polymerization, or what may be alternatively termed as a polycondensation process between bifunctional monomers eliminating water as the byproduct of condensation, may be cited as a typical example.

2.3.1. Formation of a Polyester

Ist step

$$\underset{\text{(monomers)}}{\mathrm{HOROH + HOOCR'COOH}} \rightarrow \underset{\text{1st step reaction product}}{\mathrm{HOROOCR'COOH}} + \underset{\text{byproduct of condensation}}{\mathrm{H_2O}}$$

(2.1)

2nd step

$$\mathrm{HOROOCR'COOH + HOROH} \rightarrow \underset{\text{2nd step reaction product}}{\mathrm{HOROOCR'COOROH}} + \underset{\text{byproduct of condensation}}{\mathrm{H_2O}}$$

(2.2)

or

$$\mathrm{HOOCR'COOH + HOROOCR'COOH \rightarrow HOOCR'COOROOCR'COOH + H_2O}$$

(2.3)

The condensation process beyond the first step need not necessarily involve reaction with one of the monomers. Condensation products of all the successive steps retain the bifunctional character, and each bifunctional species formed and remaining into the system at any point of time or extent or reaction is capable of reacting with any other bifunctional species including another of its own size or an unreacted monomer molecule, and the elimination of a molecule of H_2O as a byproduct in each step remains a common feature. One more step of condensation results in the loss of one more bifunctional species and as a consequence two functional groups, one of each kind, are lost in each step. The formation of a long-chain molecule of degree of polymerization *n*, where *n* has a large value, may be expressed as follows, combining (2*n* – 1) successive steps of condensation:

$$n\ \mathrm{HOROH} + n\ \mathrm{HOOCR'COOH} \rightarrow \mathrm{HO{-}[{-}ROOCR'COO{-}]_{\mathit{n}}{-}H} + (2n - 1)\ \mathrm{H_2O}$$

(2.4)

The chain-growth process at any point of time may be represented by a general equation as follows:

$$\Sigma M_n + \Sigma M_m \rightarrow \Sigma M_{n+m} + \mathrm{H_2O}$$

(2.5)

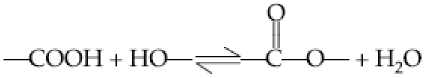
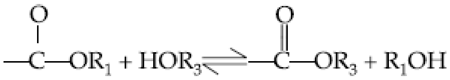
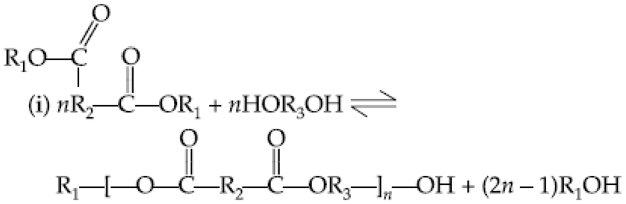
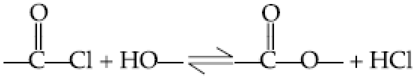
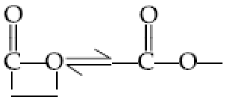
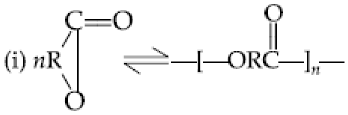
where *n* and *m* may have any integral value between 1 and *α*. For the monomer, the value of *n* or *m* is 1.

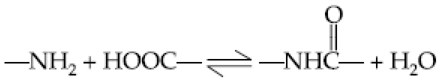
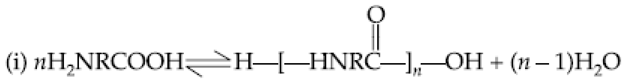
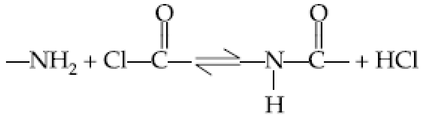
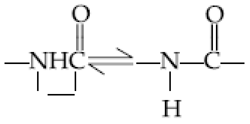
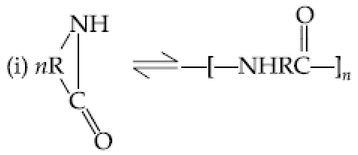
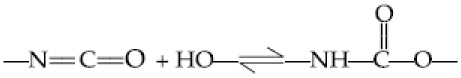
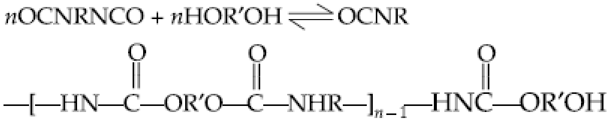
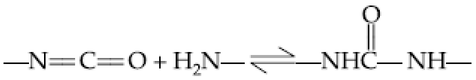
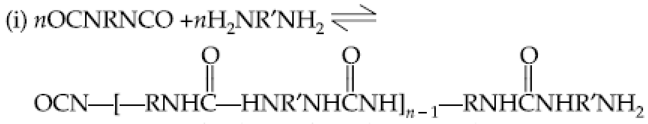
For a hydroxy acid, the reaction would be written as:

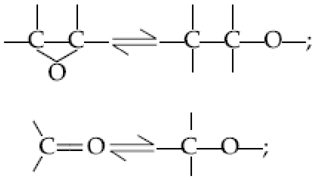
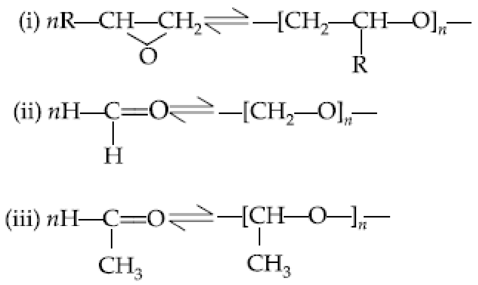
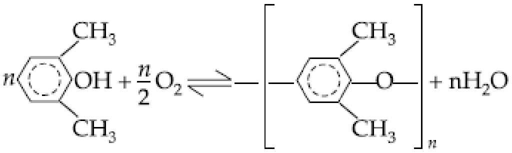
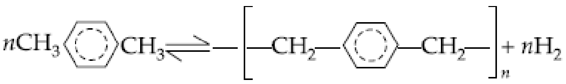
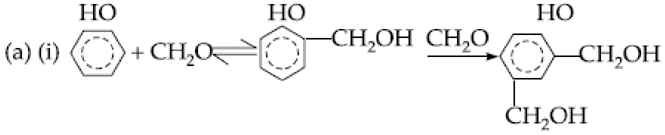
$$n\ \mathrm{HORCOOH} \rightarrow \mathrm{H}-[-\mathrm{ORCO}]_n-\mathrm{OH} + (n-1)\ \mathrm{H_2O}$$
(2.6)

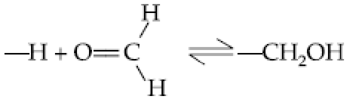
Examples of some step-growth polymerization are given in Table 2.1.

Table 2.1. Examples of some step-growth polymers

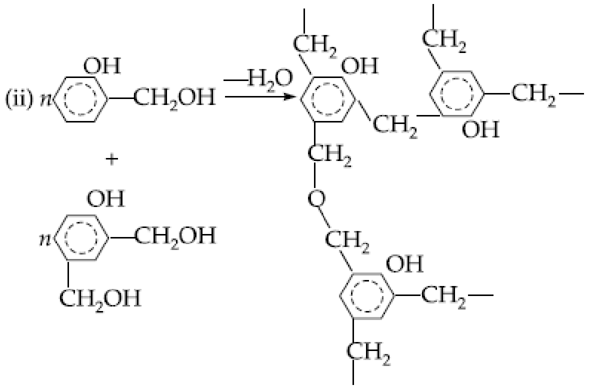
Polymer type (1)	*General reaction (showing interunit linkage formed and byproduct eliminated, etc.)* (2)	*Example (giving polymer structure)* (3)
Polyester	(a) Esterification (acid/alcohol)  $-\mathrm{COOH} + \mathrm{HO}- \rightleftharpoons -\overset{O}{\overset{\|}{C}}-O- + \mathrm{H_2O}$	(i) $n\mathrm{HORCOOH} \rightleftharpoons \mathrm{H}-[-\mathrm{ORCO}-]_n-\mathrm{OH} + (n-1)\mathrm{H_2O}$ (ii) $n\mathrm{HOOCRCOOH} + n\mathrm{HOR'OH} \rightleftharpoons \mathrm{HO}-[-\mathrm{OCRCOOR'O}-]_n-\mathrm{H} + (2n-1)\mathrm{H_2O}$
	(b) Ester interchange (ester/alcohol)  $-\overset{O}{\overset{\|}{C}}-OR_1 + HOR_3 \rightleftharpoons -\overset{O}{\overset{\|}{C}}-OR_3 + R_1OH$	 (i) $n\overset{R_1O-\overset{O}{\overset{\|}{C}}}{\overset{\|}{R_2}}-\overset{O}{\overset{\|}{C}}-OR_1 + nHOR_3OH \rightleftharpoons$ $R_1-[-O-\overset{O}{\overset{\|}{C}}-R_2-\overset{O}{\overset{\|}{C}}-OR_3-]_n-OH + (2n-1)R_1OH$
	(c) Esterification (acid chloride/alcohol)  $-\overset{O}{\overset{\|}{C}}-Cl + HO- \rightleftharpoons -\overset{O}{\overset{\|}{C}}-O- + HCl$	(i) $n\mathrm{ClOCRCOCl} + n\mathrm{HOR'OH} \rightleftharpoons \mathrm{Cl}-[-\mathrm{OCRCOOR'O}-]_n-\mathrm{H} + (2n-1)\mathrm{HCl}$
	(d) Ring opening polymerization of Lactone 	

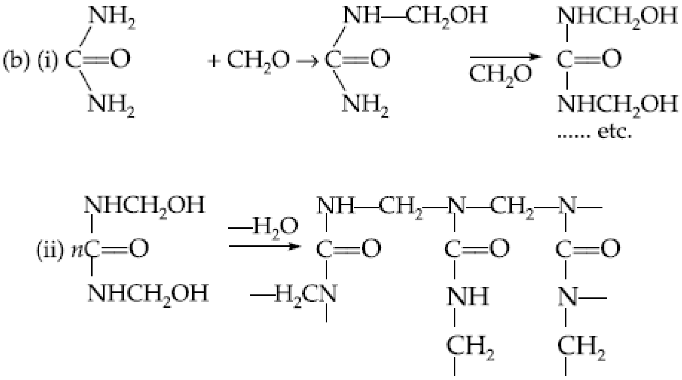
Polyamide	(a) Amidation (amine/acid)	
	 $—NH_2 + HOOC— \rightleftharpoons —NH\overset{\overset{O}{\Vert}}{C}— + H_2O$	 (i) $nH_2NRCOOH \rightleftharpoons H—[—HNR\overset{\overset{O}{\Vert}}{C}—]_n—OH + (n-1)H_2O$ (ii) $nH_2NRNH_2 + nHOOCR'COOH \rightleftharpoons$ $H—[—HNRNHCOR'CO—]_n—OH + (2n-1)H_2O$
	(b) Amidation (amine/acid chloride)	
	 $—NH_2 + Cl—\overset{\overset{O}{\Vert}}{C}— \rightleftharpoons —\underset{\underset{H}{\vert}}{N}—\overset{\overset{O}{\Vert}}{C}— + HCl$	(i) $nH_2NRNH_2 + nClOCR'COCl \rightleftharpoons$ $H—[—NHRNHCOR'CO—]_n—Cl + (2n-1)HCl$
	(c) Ring opening polymerization of lactam	
		
Polyurethane	Formation of urethane structure	
	 $—N{=}C{=}O + HO— \rightleftharpoons —NH—\overset{\overset{O}{\Vert}}{C}—O—$	 $nOCNRNCO + nHOR'OH \rightleftharpoons OCNR$ $—[—HN—\overset{\overset{O}{\Vert}}{C}—OR'O—\overset{\overset{O}{\Vert}}{C}—NHR—]_{n-1}—HN\overset{\overset{O}{\Vert}}{C}—OR'OH$ (no byproduct elimination)
Polyurea	Formation of urea structure	
	 $—N{=}C{=}O + H_2N— \rightleftharpoons —NH\overset{\overset{O}{\Vert}}{C}— NH—$	 (i) $nOCNRNCO + nH_2NR'NH_2 \rightleftharpoons$ $OCN—[—RNH\overset{\overset{O}{\Vert}}{C}—HNR'NH\overset{\overset{O}{\Vert}}{C}NH]_{n-1}—RNH\overset{\overset{O}{\Vert}}{C}NHR'NH_2$ (no byproduct elimination)

Polyacetal (acetal resins) (polyether)	Formation of acetal or ether structure 	(ii) $nH-\underset{H}{C}=O \rightleftharpoons -[CH_2-O]_n-$ (iii) $nH-\underset{CH_3}{C}=O \rightleftharpoons -[\underset{CH_3}{CH}-O-]_n-$ (no byproduct elimination)
Hydrocarbon polymer	Formation of hydrocarbon structure $-R-Br + 2Na + Br-R- \rightleftharpoons -R-R- + 2NaBr$;	$nBrRBr + 2nNa \rightleftharpoons -[-R-]_n + 2nNaBr$
Arylene polyether	Oxidative coupling (phenolic OH/active hydrogen of phenol) $-OH + \frac{1}{2}O_2 + H- \rightleftharpoons -O- + H_2O$	
Polyarylenes [e.g. poly (*p*-xylylene)	Pyrolytic oxidative coupling: (Pyrolytic dehydrogenation and spontaneous polymerization forming alkylene linkages)	
Phenolic or amino resins	Methylolation and subsequent condensation	..... etc.



$$-H + O{=}CH_2 \rightleftharpoons -CH_2OH$$





2.4. Relationship between Average Functionality, Extent of Reaction and Degree of Polymerization

W.H. Carothers derived a general expression, relating average functionality (*f*), extent of reaction (*p*) and average degree of polymerization ($\overline{X}_n$), for polycondensation reactions carried out for a time period *t*. The expression is commonly known as Carothers' Equation.

Let N_0 be the total number of reacting molecules initially present giving an average functionality for the system as *f*. The related functional groups (say, —OH and —COOH) are also considered to be present in stoichiometric equivalence. Let *N* be the number of molecules present at time *t* when the extent of reaction is *p*.

Then, number of molecules lost during the process over the time period *t* is ($N_0 - N$); for each molecule lost, the number of functional groups lost is 2 (one of each kind) and hence the total number of functional groups lost is $2(N_0 - N)$ against the initial total number of $N_0 f$ functional groups.

Hence, the extent of reaction $p = \dfrac{2(N_0 - N)}{N_0 f}$

or

$$p = \frac{2}{f}\left(1 - \frac{N}{N_0}\right)$$

(2.7)

The average degree of polymerization, $\overline{X}_n$, is defined as the average number of structural units per polymer molecule which can simply be expressed as:

$$\overline{X}_n = \frac{N_0}{N}$$

(2.8)

combining Eqs. (2.7) and (2.8), one obtains

$$p = \frac{2}{f}\left(1 - \frac{1}{\overline{X}_n}\right)$$

(2.9)

Equation (2.9), known as Carothers' Equation is very important for the understanding and control of the growth of polymers through polycondensation reactions. The critical extent of reaction p_c at the gel point (for $\overline{X}_n \rightarrow \alpha$) is given by:

$$p_c = \frac{2}{f}$$

(2.9a)

2.5. Bifunctional System

For a bifunctional system, $f = 2$, Eq. (2.9) reduces to:

$$p = \left(1 - \frac{1}{\overline{X}_n}\right)$$

(2.10)

for $p = 1$, $\overline{X}_n = \alpha$, which means that for complete reaction, the average degree of polymerization will be infinity; but short of complete reaction, the degree of polymerization is always a finite quantity. Polymer obtained in a bifunctional system is, under all practical situations, linear and hence soluble and fusible. The upper theoretical limit in the degree of polymerization is infinity and this can be attained only in the hypothetical condition of completion of reaction between the functional groups ($p = 1$). For bifunctional systems, Eq. (2.10) may be rearranged to express $\overline{X}_n$ as

$$\overline{X}_n = \frac{1}{(1-p)}$$

(2.11)

If the mean molecular weight of the repeat unit in the polymer molecules is M_0, then the average molecular weight $\overline{M}_n$ of the polymer system is expressed as

$$\overline{M}_n = \overline{X}_n \cdot M_0 = \frac{M_0}{(1-p)}$$

(2.12)

2.6. Polyfunctional System

A typical polyfunctional system in condensation polymerization is exemplified by the reaction between phthalic anhydride or phthalic acid and glycerol, i.e. by allowing a bifunctional acid to react with a trihydric alcohol. As discussed before, this system is characterized by an average functionality of 2.4.

For this system, Eq. (2.9) will assume the form:

$$p = \frac{2}{2.4}\left(1 - \frac{1}{\overline{X}_n}\right)$$

(2.13)

We may now easily find out the critical extent of reaction, p_c at which gelation or cross-linking would commence, i.e. at which point $\overline{X}_n$ would first assume a value of infinity; the calculated value of p_c, according to Eq. (2.9a), will be 2/2.4 = 0.83.

Thus, it is clearly seen that at the point of a theoretical extent of reaction $p = 0.83$, i.e. when the reaction is 83% complete, the polymer being formed in the polycondensation system gets cross-linked and, hence, turns into an insoluble, infusible gelled mass. Technically, such a condensation polymerization cannot and should not be allowed to proceed beyond this point (83% completion), or otherwise the reaction mass would turn into an unusable product. In fact, it is advisable to arrest the reaction nearly 10–15% earlier in p to avoid damage of the reaction kettle and to collect a good quality product which would be useful and which could be easily manipulated in subsequent steps.

The usefulness of Carothers' Equation lies in the linking of p, f and $\overline{X}_n$ in one expression, and in the fact that it can be used to predict gelation in polyfunctional systems. The limitation of the equation is that practically gelation starts even at earlier stages than predicted by the equation because of uncontrolled local conditions in the hot viscous reaction mass. Moreover, this equation is applicable to polycondensation reactions only, and it loses relevance in the context of addition or chain growth polymerization.

2.7. Molecular Weight Control: Quantitative Effect of Stoichiometric Imbalance on Maximum Attainable Molecular Weight

Condensation polymerization being an equilibrium step process and endothermic in nature in most cases, control of molecular weight can be readily achieved by allowing the reaction to die down at a desired point by withdrawing heat supply or by cooling and further, by allowing the byproduct of condensation to accumulate in the medium. But in any event, the intermediate product may not be adequately stable toward further heating under a favourable condition with respect to further chain extension and gain in molecular weight. Control of molecular weight can be more precisely attained by striking a calculated stoichiometric imbalance of the two types of reacting functional groups. This may be clearly illustrated considering a bifunctional system having monomers of the A–A and B–B types and giving the numbers of A and B functional groups as N_A and N_B respectively, such that $(N_A/N_B) = r$, where r is either equal to 1 or less than 1, i.e. B groups are present in the system in molar excess, if there is stoichiometric imbalance. The total number of molecules initially present, N_0 is then given by $(N_A + N_B)/2$, or $N_A(1 + 1/r)/2$.

Let us now find out the total number of molecules N left into the system after a specific time period of reaction when extent of reaction for A groups is p, i.e. p is the fraction of A groups which have reacted. The fraction of B groups which have reacted by that time is then given by rp.

The total number of unreacted A and B groups are then expressed as $(N_A - N_A p)$, i.e. $N_A(1 - p)$ and $N_B - N_B rp$, i.e. $N_B(1 - rp)$ respectively. The total number of polymer chain ends is thus, given by [N_A(1

– p) + $N_B(1 - rp)$], i.e. [$N_A(1 - p) + N_A(1 - rp)/r$]. The value of N, being one half this number, is given by $N = N_A[(1 - p) + (1 - rp)/r]/2$.

Then,

$$\overline{X}_n = \frac{N_0}{N} = \frac{N_A(1+1/r)/2}{N_A[(1-p)+(1-rp)/r]/2}$$

or

$$\overline{X}_n = \frac{1+r}{1+r-2rp}$$

(2.14)

and

$$\text{Lt } p \rightarrow 1,\ \overline{X}_n = \frac{1+r}{1-r}$$

(2.15)

For equimolar proportions of A and B groups, i.e. for $r = 1.0$ $\overline{X}_n = 1/(1 - p)$, which is the same as given by Eq. (2.11). The maximum theoretically attainable degree of polymerization for $r = 1.0$ is α. But for $r \neq 1.0$, and with only, say one mole per cent excess of B groups taken into the system (by taking excess of the related bifunctional compound in calculated amount), and taking the help of Eq. (2.15), the maximum attainable $\overline{X}_n$ becomes:

$$\overline{X}_n = \frac{1+(100/101)}{1-(100/101)} = 201$$

This consideration clearly establishes the importance of stoichiometric equivalence or balance of the reacting functional groups (A and B groups) for attaining high degrees of polymerization, or of introduction of stoichiometric imbalance in order to limit the maximum attainable degree of polymerization to a desired lower level. Figure 2.1 shows how $\overline{X}_n$ varies with variation in stoichiometric imbalance, i.e., variation in the value of r.

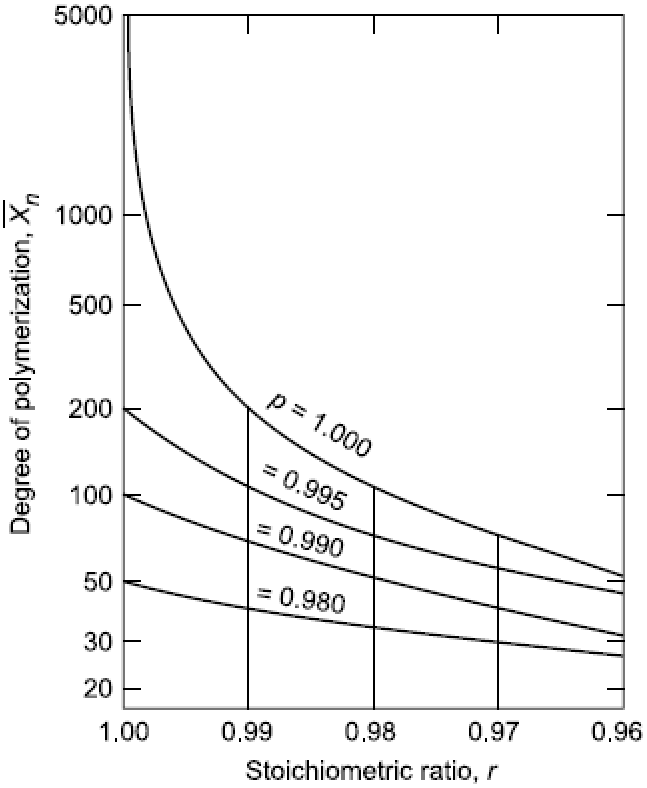


Figure 2.1. Trend of variation of number average degree of polymerization X-macr$_n$ with stoichiometric ratio r for different extents of reaction, p in the polycondensation involving A–A and B–B type monomers

Considering a bifunctional system and Eqs. (2.11) and (2.15) applicable to it, it is clearly realized that the step-growth polymerization must always be carried out to very high conversions, at least to 98%, since a degree of polymerization >50 is normally required for a polymer to be widely useful. Higher conversions and lesser deviation from stoichiometric balance are required for higher degrees of polymerization. The interdependence of $\overline{X}_n$ on *p* and *r* is given by Eq. (2.14) and Fig. 2.1. Closer adherence to stoichiometric equivalence is required for obtaining higher degrees of polymerization. The effect of stoichiometric imbalance is much more pronounced in the very high conversion zone (>98%) than in the lower conversion zones.

2.8. Kinetics of Step-Growth Polymerization

A powerful tool for a good understanding of any chemical reaction is the study of its kinetics. Kinetic analysis of a reaction helps in the understanding of the mechanism of the reaction.

2.8.2. Rate of Step-growth Polymerization

a. ***Self-catalyzed Polyesterification*** With the idea of equal reactivity of specific functional groups independent of molecular size, the consideration of rate of step-growth polymerization becomes easy. The formation of a polyester from a dicarboxylic acid and a diol may again be taken as an example, for simplicity. This reaction is prone to catalysis by mineral acids. But in the absence of an added mineral acid such as H_2SO_4 or HCl, the reactant carboxylic acid itself acts as a catalyst; for each step of reaction between a —COOH group

$$\text{—COOH} + \text{HO—} \xrightarrow[\text{(catalyst)}]{\text{— COOH}} \text{—COO—} + \mathrm{H_2O}$$

(2.16)
and an alcohol (—OH) group, a second COOH group from the reactants acts as a catalyst. The rate of the reaction can be measured by measuring the rate of disappearance of the carboxyl groups:

$$-\frac{d[\text{COOH}]}{dt} = k\,[\text{COOH}]^2\,[\text{OH}]$$

(2.17)
Here, *k* is the rate constant of the reaction given by equation (2.16). Considering equimolar presence of carboxyl and hydroxyl groups, and *c* giving the concentration of each group at a given point,

$$-\frac{dc}{dt} = kc^3$$

(2.18)
or

$$-\frac{dc}{c^3} = k\,dt$$

(2.19)
on integration, Eq. (2.19) gives:

$$2kt = \frac{1}{c^2} - \text{constant}$$

(2.20)
If c_0 is the initial concentration of each kind of functional group and *p* is the extent of reaction, i.e. fraction of a given functional group that has reacted at time *t*, then

$$c = c_0(1 - p)$$

(2.21)
By combining Eqs. (2.21) and (2.20), we get

$$2c_0^2kt = \frac{1}{(1-p)^2} - \text{constant}$$

(2.22)
Equation (2.22) prescribes linearity of the plot of $1/(1 - p)^2$ vs time. In the case of self catalyzed polycondensation (polyesterification) of diethylene glycol and adipic acid at 166°C, as studied by Flory,[4] the linearity is found to be strictly followed only over the range of nearly 80–94%. Below or above this range of extent of reaction, the experimental points deviated from the third order plot (Fig. 2.2). Equation (2.22) actually shows a linear relationship between square of the average degree of polymerization, $(\bar{X}_n)^2$ with time of polycondensation.

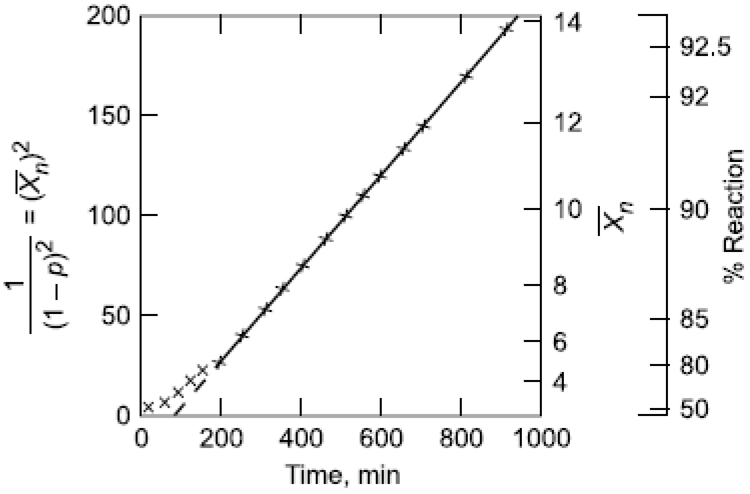


Figure 2.2. Plot showing $1/(1 – p)^2$ or (X-macr$_n$) vs time for self catalyzed polyesterification of diethylene glycol with adipic acid at 166°C (Flory, 1939; ***Courtesy****, American Chemical Society, Washington)*

It may be mentioned here that the initial nonlinearity is not limited to polyesterification; the initial deviation from the third order linear plot is characteristic of esterification in general.

Over the initial 50–80% conversion range, a very significant change takes place in the reaction medium, although the average growth in size of the molecules remains far too low. A large change in the polarity of the reaction mixture, however, takes place due to the disappearance of a large fraction of the polar carboxyl groups resulting in the formation of less polar ester linkages. This definite change in polar nature of the reaction medium has a major role to play in causing the deviation in question. But the exact manner or mechanism in which the rate of esterification is affected as a consequence of this polarity change is not very well understood.

The deviation from linearity in the high conversion region (>94%), however, arises as a consequence of other factors including loss of reactants through degradation or volatilization, or even cyclization and other side reactions. Such losses of reactants are likely to be of much less importance in the initial stages. Difficulty in removal of the byproduct of condensation (water) from the reaction medium due to the very high viscosity it assumes in the later stages, is also an important contributing factor in decreasing the reaction rate with increasing extent of reaction beyond 94% conversion.

b. ***Polyesterification using Strong Acids as Catalysts*** The direct or self-catalyzed polyesterification is slow and sluggish, considering slow increase in molecular weight or average degree of polymerization and this is understood to be a consequence of the third order kinetics. A better result and a faster rate of chain growth is, however, achieved by adding a small amount of a strong acid such as sulphuric acid, *p*-toluenesulphonic acid, etc. as a catalyst, which remains undepleted in the system with progress of the reaction. The rate of disappearance of COOH groups can then be expressed as

$$-\frac{d[\mathrm{COOH}]}{dt} = k' \ [\mathrm{COOH}] \ [\mathrm{OH}]$$

(2.23)

For stoichiometric equivalence of the two functional groups and taking *c* as the concentration of either group, the Eq. (2.23) may be written as

$$-\frac{dc}{dt} = k'c^2$$

(2.24)

where *k*′ is the overall rate constant. On integration, and making use of Eq. (2.21), the following expressions, relating extent of reaction *p* or degree or polymerization $\overline{X}_n$ with time of reaction, *t*, are obtained:

$$c_0k't = \frac{1}{(1-p)} - \text{constant}$$
(2.25)

or

$$c_0k't = \overline{X}_n - \text{constant}$$
(2.26)

A plot of $1/(1-p)$, i.e. $\overline{X}_n$ vs time, would be linear according to Eqs (2.25) and (2.26). Data relating to polymerization of diethylene glycol and adipic acid catalyzed by *p*-toluenesulphonic acid as observed by Flory[4], are shown in Fig. 2.3. The plot shows the experimental variation of $\overline{X}_n$, the average degree of polymerization with time of polycondensation at a given temperature.[5] Comparison of Figs 2.2 and 2.3 clearly shows that the polyesterification process is much more readily and economically accomplished when an external strong acid catalyst is used. Not only the linearity of $\overline{X}_n$ vs time plot is very closely maintained, particularly in the more important high conversion zone, but also the rate of increase of $\overline{X}_n$ with time of reaction is much higher. The second order kinetics find good experimental support up to nearly 98.9% conversion, corresponding to $\overline{X}_n$ value of approximately 90 or a molecular weight of nearly 10,000. This approach of kinetic analysis, however, shows that the reactivities of the carboxyl and hydroxyl groups remain practically unchanged despite growth of the chain molecules to a fairly big average molecular size and a big increase in medium viscosity as a consequence.

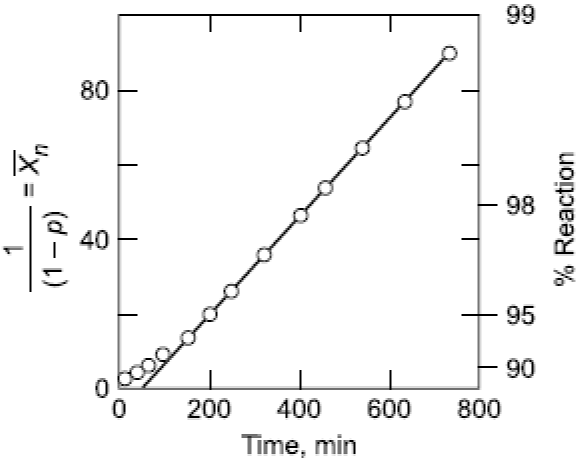
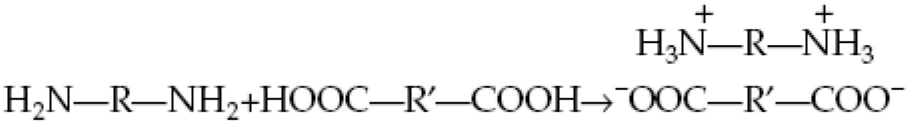


Figure 2.3. Plot showing 1/(1 – ***p****) or X-macr$_n$ vs time for polycondensation of diethylene glycol and adipic acid at 109°C using 0.4 mole % p-toluene sulphonic acid as the catalyst*[4, 5] *(Flory, 1939; Solomon, 1967;* ***Courtesy****, American Chemical Society, Washington)*

Step-growth polymerization other than polyesterification may proceed at desired rates in presence of external acidic or basic catalysts or as uncatalyzed reactions. Irrespective of the approach and situation prevailing, the basic and overall kinetics will be much the same as detailed above for polyesterification. For stoichiometric proportions of the two types of reacting functional groups, say A and B groups, Eq. (2.25) would be useful to reasonably describe and analyze the kinetics in the respective systems. Whether or not the reacting monomers are of the A–A and B–B types or simply of the A–B types, the observed kinetics will be the same.

2.14. Interfacial Polymerization

Polycondensation reactions such as the amidation between diacids and diamines have been studied widely in melt condition (in bulk), in solution and even in the solid state. Stoichiometric balance between the reactive functional groups is easily obtained by precipitating the 1 : 1 ammonium salt in alcoholic medium.



$$H_2N—R—NH_2 + HOOC—R'—COOH \rightarrow \overset{H_3\overset{+}{N}—R—\overset{+}{N}H_3}{{}^{-}OOC—R'—COO^{-}}$$

The ammonium salt is commonly called the nylon salt. The salt/polymer equilibrium is favourable more toward polymer for polyamide formation than for the formation of polyesters by ester-interchange step polymerization, such as in the case involving dimethyl terephthalate and ethylene glycol. These reactions are usually carried out at high temperatures (>200°C) in two successive stages, each culminating into a melt polymerization system in the final stage.

Formation of polyesters and polyamides can be accomplished at much lower temperatures, often under the room temperature conditions starting with the more reactive acid chlorides (Table 2.1) and employing a solution polymerization technique. A special technique known as interfacial polymerization has been developed for the formation of polyamides, polyesters, polycarbonates and polyurethanes. The technique is so designed as to permit polymerization at the interface between two immiscible solutions one of which contains one of the dissolved monomers while the second monomer is dissolved in the other.

By the interfacial technique, polyamidation is usually performed at or near room temperature using a set up as given in Fig. 2.11, showing formation of the polyamide at the interface between a layer of aqueous solution of a diamine over a solution of the diacid chloride in an organic solvent layered below. The reactant monomers diffuse to and transform into the polymer at the interface.[16] The polymer gets precipitated which can be taken out or withdrawn from the interface in the form of a continuous filament or film. The rate of polycondensation is determined by the rates of diffusion of the reacting monomers in the two phases to the interface. The monomers diffusing to the interface, however, react with the polymer chain ends. Thus, the mechanism involved in interfacial polycondensation is different from the usual step-growth polymerization in that the new reactants taking part late in the process contribute to chain extension by reacting with existing chains rather than interacting to form fresh chains. A much higher molecular weight usually results in the interfacial process as a consequence of this difference.

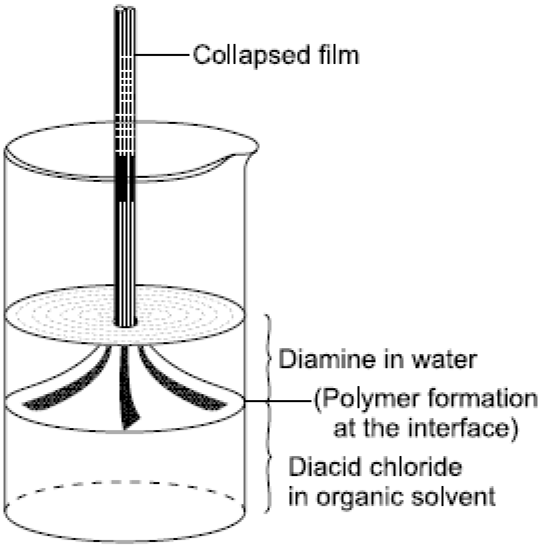


Figure 2.11. Interfacial polymerization

The byproduct of condensation, HCl (using diacid chlorides in the organic layer) is usually neutralized by dissolving an inorganic base in the aqueous layer in order to prevent lowering of reaction rate due to formation of unreactive amine hydrochloride salt. The likelihood of hydrolysis of the acid chloride to the much less reactive or unreactive acid in the presence of an aqueous inorganic (strong) base is avoided or kept to a minimum in view of very low water solubility of the acid chloride and also in view of high rates of polymer formation at the interface thus preventing or putting hindrance to the diffusion of the acid chloride into the aqueous layer through the polymer layer at the interface.

The selection of organic solvent plays a significant role in determining the properties of the polymer formed, particularly the molecular weight. Premature precipitation due to poor solvent action of a selected solvent limits molecular weight of the product and prevents formation of products of high degree of polymerization. The biphasic system and the nonsolvent action of water in interfacial polycondensation lead to molecular weight distributions[17, 18] far different from the most probable distributions [Eq. (2.30)] derived by Flory[2].

From many considerations, the biphasic interfacial polycondensations are more advantageous than the polycondensation done in homogeneous solution or under melt conditions. The impurity of the reactants is of much less consequence as their adverse effect is insignificant or of much lower dimension at the much lower temperature of polymerization for the interfacial system. Stoichiometric equivalence of the reactants in the two phases is not a prerequisite as stoichiometry is automatically struck at the interface where only the polycondensation proceeds. Attainment of high molecular weight for the product is not dependent on p or the extent of reaction. Low temperature of polymerization makes the process more stable toward occurrence of undesired side reactions. Final products in the form of films, fibres and fibrous particles may be formed by direct polymerization. The major demerit of the interfacial process which stands in the way of its commercial development is the unfavourable economy for the high cost of the acid chloride, handling of large amount of solvents and their recovery, etc.