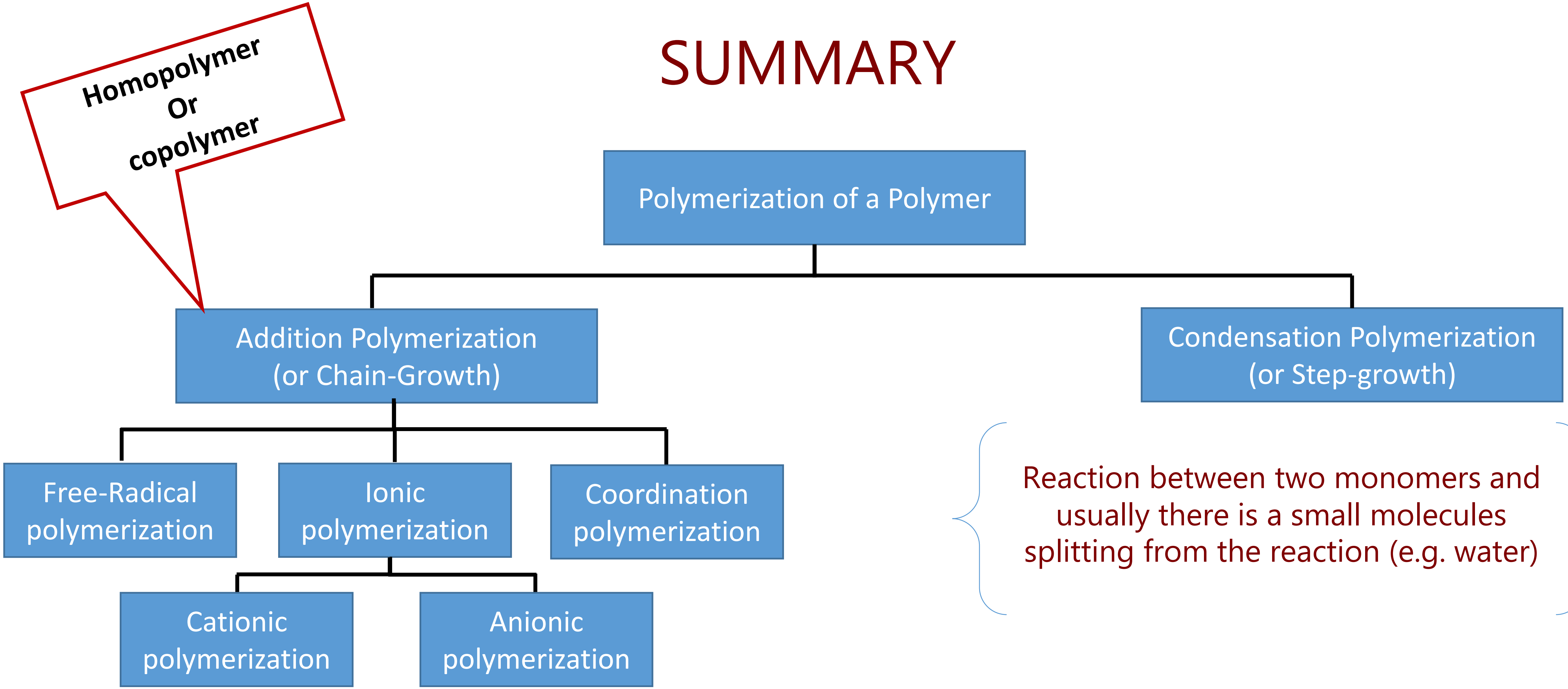
SUMMARY



- Polymerization of a Polymer
  - Addition Polymerization (or Chain-Growth)
    - Free-Radical polymerization
    - Ionic polymerization
      - Cationic polymerization
      - Anionic polymerization
    - Coordination polymerization
  - Condensation Polymerization (or Step-growth)

Homopolymer
Or
copolymer

Reaction between two monomers and usually there is a small molecules splitting from the reaction (e.g. water)

Usually, there is a single monomer and addition process occurs. However, note if there are more than two types of monomer reacting together by addition polymerization , the process is called “ copolymerization ” and the obtained polymer is called “ copolymer ”.

	Polymerization Mechanism[b]			
Monomer Type	Radical	Cationic	Anionic	Coordination
Ethylene	+	+	−	+
Propylene and α-olefins	−	−	−	+
Isobutylene	−	+	−	−
Dienes	+	−	+	+
Styrene	+	+	+	+
Vinyl chloride	+	−	−	+
Vinylidene chloride	+	−	+	−
Vinyl fluoride	+	−	−	−
Tetrafluoroethylene	+	−	−	+
Vinyl ethers	−	+	−	+
Vinyl esters	+	−	−	−
Acrylic and methacrylic esters	+	−	+	+
Acrylonitrile	+	−	+	+

[a] Lenz (1967).

[b] + = high polymer formed; − = no reaction or oligomers only.

STEP-GROWTH (CONDENSATION) POLYMERIZATION

At the end of this lecture, you should be able to:

- Uunderstand what is the difference between condensation and condensation polymerization.
- List the similarities and differences between the step-growth and chain-growth polymerization
- Understand the kinetics of condensation polymerization.
- Understand molecular weight control in the step-growth polymerization
- Calculate the molecular weight average from the kinetics information.

1) What is meant by Condensation ?

Physically, condensation is a process in which a gas phase change to a liquid phase under certain conditions (i.e. temperature and pressure) and this phenomenon can be seen in nature many times.

In terms of chemical reaction, on the other hand, condensation is process in which two monomers react to form a larger molecule and eliminate a smaller molecule (usually water, ammonia, methanol or hydrogen chloride).

•As an example, the reaction of two monofunctional compounds, n-hexylamine and hexanoic acid gives one amide of molecular weight of 199

example: (with monofunctional molecules)

$$CH_3\boxed{NH_2 + HOOC}CH_2\text{-}CH_3 \Rightarrow CH_3\boxed{NH\text{-}CO}CH_2\text{-}CH_3 + H_2O$$

Amine + Acid = Amide + Water

NOTE: the same reaction can produce polymer if the reactants have two functional group ($NH_2\text{-}CH_2\text{-}NH_2$ & $HOOC\text{-}CH\text{-}CH_2\text{-}COOH$). Examples of polymers prepared by condensation reaction are Kevlar, nylon and Terylene.

2) Condensation (step-growth) polymerization

In this type of polymerization method, monomers with **di** or **multi-function** groups are necessary at least to form a polymer. A **difunctional monomer** or equal molar amounts of two different difunctional monomers can form a linear high molecular weight polymer.

In a step-growth polymerization, the molecular weight of the polymer chain builds up slowly and there is only one reaction mechanism for the formation of polymer. The distinct initiation, propagation, and termination steps of chain-growth polymerization are meaningless in step-growth polymerization. The polymerization reaction proceeds by individual reactions of the functional groups on the monomers. Thus, two monomers react to form a dimer.

Monomer + Monomer …………. Dimer + H_2O

The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer.

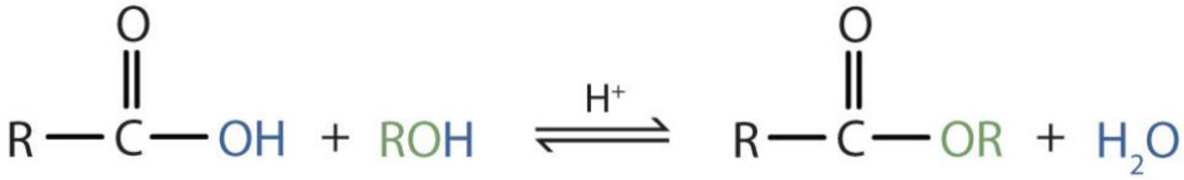
Monomer + Dimer…………………Trimer + H_2O

Dimer + Dimer………………………Tetramer + H_2O

This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively long period of time, a high molecular weight polymer is obtained.

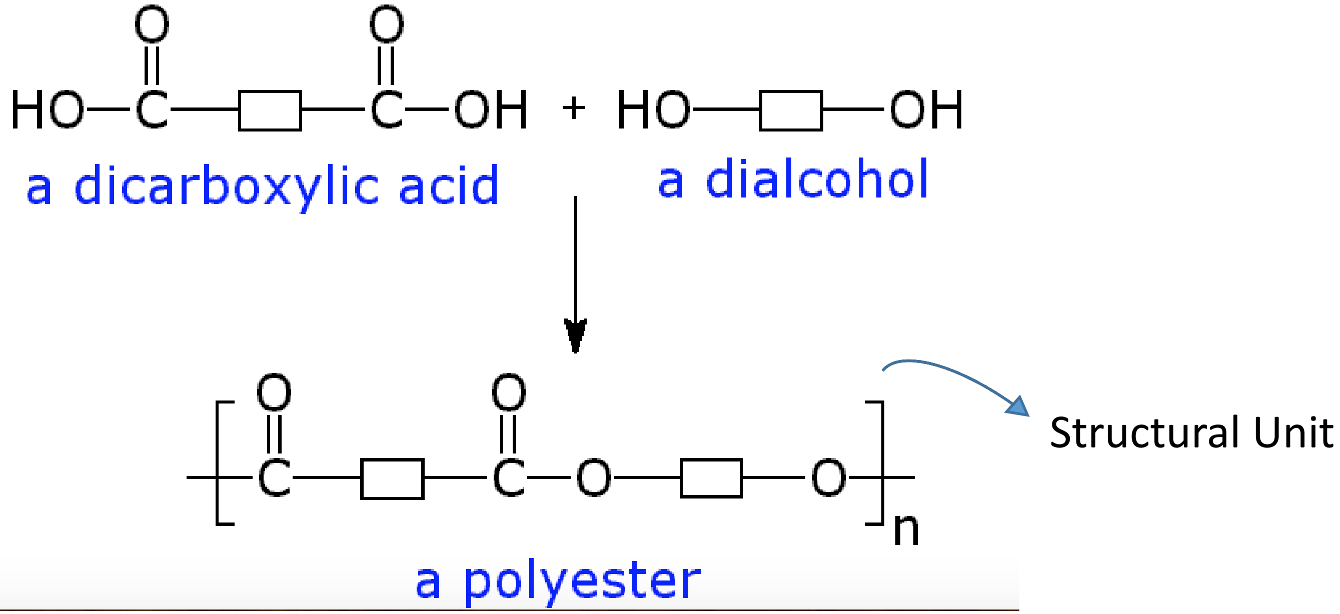
Monofunctional condensation reaction Vs. Difunctional condensation polymerization

Monofunctional condensation reaction: you can recall that making an ester requires a Carboxylic Acid, an Alcohol and an Acid catalyst.

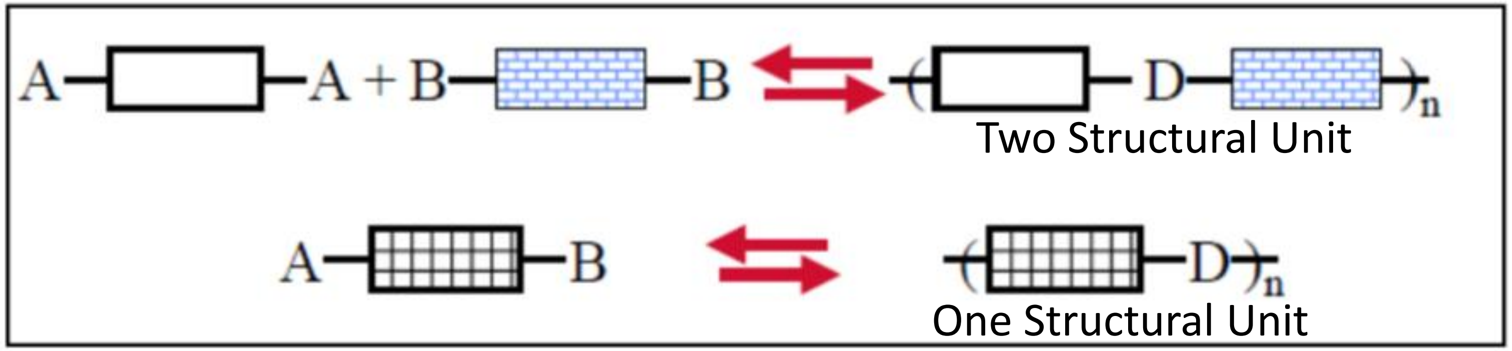


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + ROH \xrightleftharpoons{H^+} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + H_2O$$

Difunctional condensation polymerization: If we started with a ***diol*** (a molecule with two alcohol groups HO-R-OH instead of a normal alcohol ROH), and reacted it with a ***dicarboxylic acid*** (HOOC-R-COOH) then the esterification could happen at either end of the molecule forming a long molecule containing multiple ester linkages.

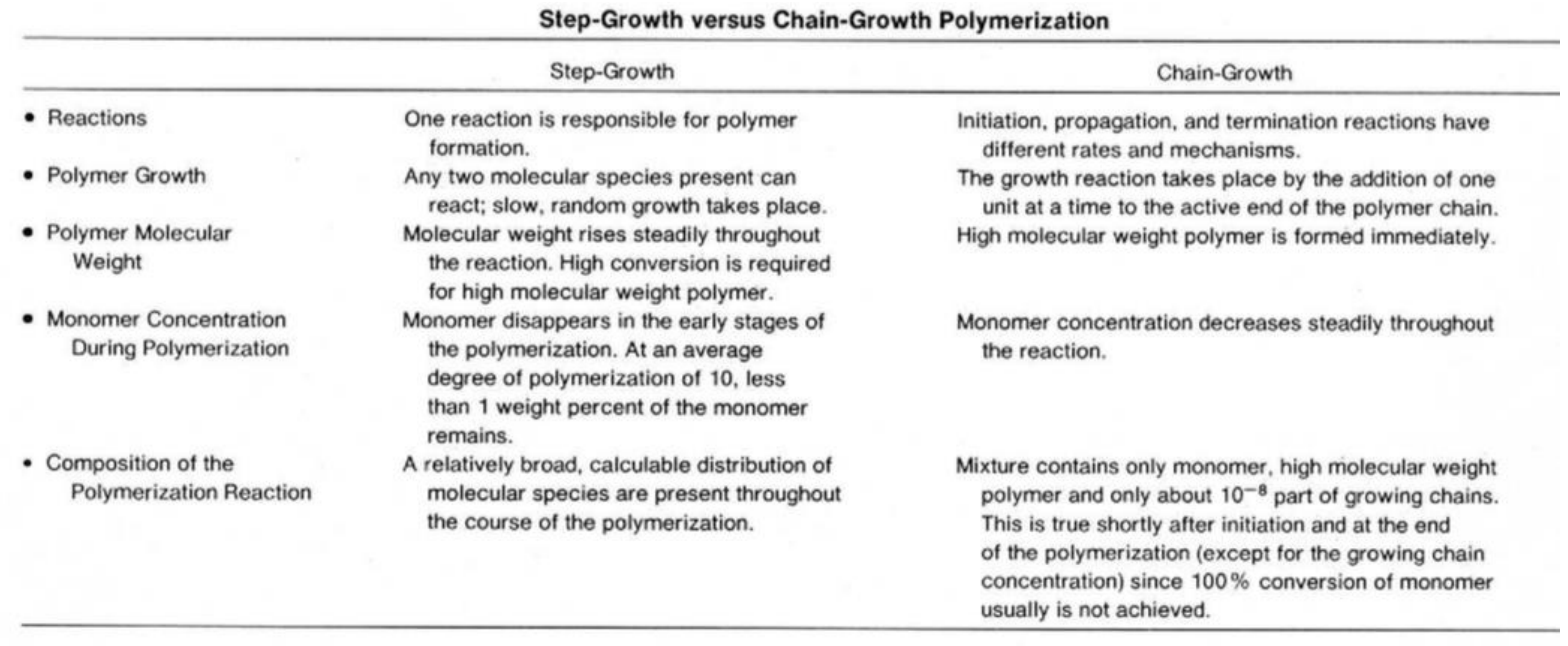


The formation of polyesters, polyamides and polyurethane represent a typical condensation polymerization. These reactions can be written in a general from as:



- Polyesters: D = -COO-
  A = -COOH, -COCl, -COOR, -COOOC- and B = -OH
- Polyamides: D = -CONH-
  A = -COOH, -COCl, -COOR, -COOOC- and B = $-NH_2$
- Polyurethanes: D = -NHCOO-
  A = -NCO and B = -OH

Some of the similarities and differences in the step-growth and chain-growth polymerization are listed in the Table below*



Step-Growth versus Chain-Growth Polymerization

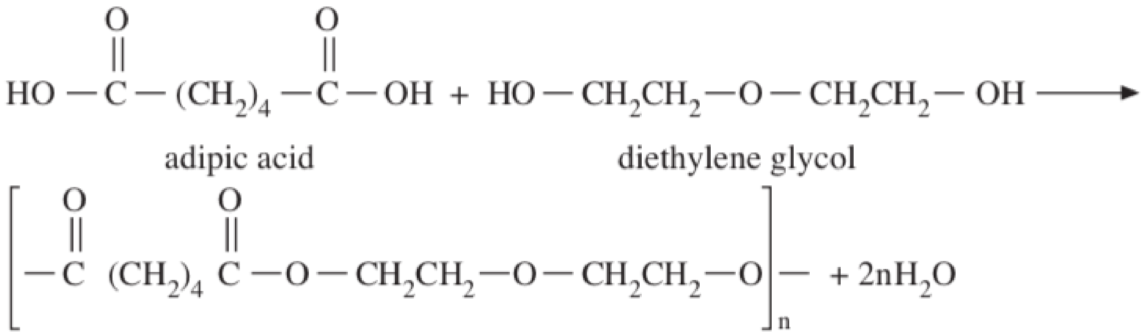
	Step-Growth	Chain-Growth
• Reactions	One reaction is responsible for polymer formation.	Initiation, propagation, and termination reactions have different rates and mechanisms.
• Polymer Growth	Any two molecular species present can react; slow, random growth takes place.	The growth reaction takes place by the addition of one unit at a time to the active end of the polymer chain.
• Polymer Molecular Weight	Molecular weight rises steadily throughout the reaction. High conversion is required for high molecular weight polymer.	High molecular weight polymer is formed immediately.
• Monomer Concentration During Polymerization	Monomer disappears in the early stages of the polymerization. At an average degree of polymerization of 10, less than 1 weight percent of the monomer remains.	Monomer concentration decreases steadily throughout the reaction.
• Composition of the Polymerization Reaction	A relatively broad, calculable distribution of molecular species are present throughout the course of the polymerization.	Mixture contains only monomer, high molecular weight polymer and only about 10^{-8} part of growing chains. This is true shortly after initiation and at the end of the polymerization (except for the growing chain concentration) since 100% conversion of monomer usually is not achieved.

*****J. K. Stille, *Step-growth polymerization, Colorado State University*, Fort Collins, CO 80523, 1981.

3) KINETICS OF CONDENSATION POLYMERIZATION

Flory has greatly simplified the complicated kinetic analysis of condensation polymerization which has been validated on mechanistic and experimental grounds . Flory proposes that all steps in a condensation polymerization have equal rate constants. Depending on this principle, we can discuss the condensation polymerization kinetics by considering two cases:

Case 1: Polymerization without Added Strong Acid: Consider esterification — the formation of a polyester from a glycol and a dibasic acid. The progress of reaction is easily followed by titrating the unreacted carboxyl groups in samples removed from the reaction mixture. This polyesterification and other simple esterifications are acid-catalyzed. In the absence of an added strong acid, a second molecule of the acid being esterified acts as the catalyst.



$$HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + HO-CH_2CH_2-O-CH_2CH_2-OH \longrightarrow$$

$$\left[-\overset{\overset{O}{\|}}{C}\ (CH_2)_4\ \overset{\overset{O}{\|}}{C}-O-CH_2CH_2-O-CH_2CH_2-O\right]_n- + 2nH_2O$$

The rate of polyesterification process can therefore be written:

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

where concentrations (written in square brackets) are expressed as equivalents of the functional groups. As written here the above equation assumes that the rate constant k is independent of molecular size of reacting species and is the same for all functional groups.

If the concentration, C, of the unreacted carboxyl and hydroxyl groups at time t are equal, the rate equation may be rewritten as:

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

On integration, this yields ***the third-order reaction expression***

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

NOTE 1: the constant can be found by applying $C = C_o$ at $t = 0$ where C_o =initial concentration of one of the reactants. This gives the constant = $1/(C_o)^2$,

Now, let us introduce the *extent of reaction* (conversion), p, defined as the fraction of the functional group that has reacted at time t. That is,

$$p = \frac{C_o - C}{C_o}$$

As defined, C_o= initial concentration of one of the reactants. Now from the above equation:

$$C = C_o(1 - p)$$

Hence, on substitution, ***the third-order reaction expression*** becomes

$$2C_o^2kt = \frac{1}{(1-p)^2} - 1$$

Case II: Polymerization with Added Strong Acid: The kinetic expression can be greatly simplified if the polyesterification is carried out in the presence of a small amount of strong acid, e.g., *p*-toluene sulfonic acid. With the catalyst concentration kept constant throughout the process, the rate expression becomes

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

where k′ = k [catalyst] and where the alcohol and carboxylic acid concentrations are kept constant. Integrating this second-order rate equation and inserting the extent of reaction, p, we have:

$$C_o k't = \frac{1}{1-p} - 1$$

NOTE: The presence of catalyst gives a linear relation between time and 1/ (1-p) while a polymerization without catalyst the relation is time ∝ $1/(1-p)^2$.

4) Degree of polymerization (Xn or DP)

In the case of condensation polymerization, X_n is given by the ratio of the initial number of molecules to the final number of molecules, i.e.,

$$\overline{X}_n = \frac{\text{original number of molecules}}{\text{final number of molecules}}$$

$$= \frac{C_o}{C_o(1-p)} = \frac{1}{1-p}$$

From the definition of X_n, it follows that the number-average molecular weight will be given by the expression:

$$\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1-p}$$

where M_o = average molecular weight of the **structural unit**.

To avoid confusion, it is necessary to reemphasize the definition of structural unit — the residue from a glycol or from a dibasic acid. This means that the number of structural units equals the total number of bifunctional monomers initially present. Thus the repeating unit of a chain derived from A–A/B–B type monomers consists of two structural units, while the repeat unit in the case of type A–B monomers is the same as the structural unit.

NOTE: A closer look at M_n equation reveals that in condensation polymerization, a high molecular weight product is obtained only when the extent of reaction is almost 100% as shown in Table 1 below. Polymers, by definition, derive their unique properties from their high molecular weights. Thus, commercially useful condensation polymers are obtained only under the rather stringent condition of almost quantitative reaction. This means that in addition to **high conversion**, a step-growth polymerization requires **high yield** and **high monomer(s) purity**.

$$\boxed{\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1 - p}}$$

TABLE 1 *High Molecular Weight Achieved Only by High Conversion*

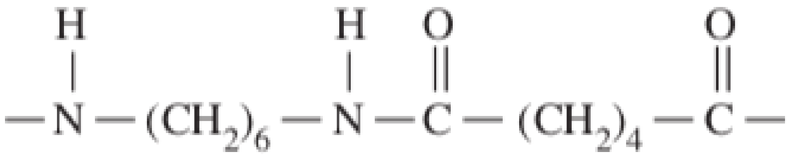
P	0	0.5	0.8	0.9	0.95	0.99	0.999	0.9999	1.0
$\overline{M}_n$	1	2	5	10	20	100	1,000	10,000	∞

Example 1: A 21.3 g sample of poly(hexamethylene adipamide) is found to contain 2.5 x 10^{-3} mol of carboxyl groups (-COOH) by both titration with base and infrared spectroscopy. From these data calculate

a. The number-average molecular weight.

b. The extent of reaction.

What assumption is made in your calculations?

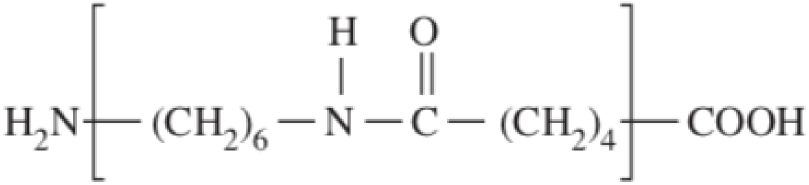


$$-\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_6-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}-$$

(MW = 226)

SOLUTION:

Assumption is that each polymer molecule contains one –COOH group, i.e.,



$$H_2N\left[-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\right]COOH$$

$$\overline{M}_n=\frac{\sum W_i}{\sum N_i}=\frac{W}{N}=\frac{21.3}{2.5\times10^{-3}}=8520 \text{ g/g mol}$$

$$\overline{X}_n=\frac{1}{1-p}=\frac{\overline{M}_n}{M_o}$$

where M_o = average molecular weight of residue = $\frac{226}{2}$ = 113.

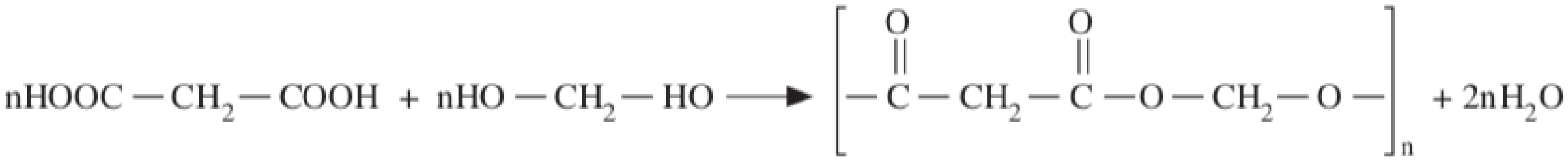
Now,

$$\overline{X}_n=\frac{1}{1-p}=\frac{8520}{113}=75.40$$

$$1-p=0.013$$

$$p=98.7\%$$

Example 2: For condensation polymerization between a dibasic acid and a glycol, show that M_o is the average molecular weight of the structural units where the structural unit is the residue from each monomer.



$$nHOOC-CH_2-COOH + nHO-CH_2-HO \longrightarrow \left[-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-O-\right]_n + 2nH_2O$$

SOLUTION:

Assume that we start with 10 moles of each monomer and suppose that the extent of reaction at a time t equals $p = 0.5$. By definition

$$p = \frac{N_i - N}{N_i}$$

N_i = initial number of moles
N = number of moles at time t

At time t,

$$\begin{aligned} N &= N_i\,(1 - p) \\ &= 20\,(1 - 0.5) \\ &= 10 \end{aligned}$$

Now

$$\overline{X}_n = \frac{1}{1-P} = \frac{1}{1-0.5} = 2$$

$$\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1-P} = 2M_o$$

M_o = molecular weight of structural unit

Three cases have to be considered.

Case 1:

M_o = molecular weight of repeating unit
= 116 kg/kg mol
$\overline{M}_n = 2M_o = 232$ kg/kg mol
Mass of polymer = 232 × 10 = 2320 kg

Case 2:

M_o = average molecular weight of starting monomers
$= \frac{104 + 48}{2} = 76$
$M_n = 2M_o = 152$
Mass of polymer produced at t = 152 × 10 = 1520 kg

Case 3:

M_o = average molecular weight of structural units where structural unit equals residue from each monomer
$= \frac{116}{2} = 58$
$\overline{M}_n = 2 \times 58 = 116$
Mass of polymer produced = M_n × 10 = 1160 kg

To establish which of the above definitions of M_o is correct, we need to carry out a simple mass balance:

Initial mass = sum of masses of reactants = 104 × 10 + 48 × 10 = 1520 kg
Mass of product = mass of polymer + mass of H_2O split off
Mass of water split off = $2nH_2O$ = 2 × 10 × 18 = 360

Case 1: mass of product = 2320 + 360 = 2680 kg
Case 2: mass of product = 1520 + 360 = 1880 kg
Case 3: mass of product = 1160 + 360 = 1520 kg

From mass balance, it is obvious that only Case 3 gives a correct mass balance.

5) Molecular Weight Control

From the previous lecture, it is obvious that in addition to high conversion, a step-growth polymerization requires **high yield** and **high monomer quality (purity)** to obtain a polymer of high molecular weight. High yield means the absence of any side reactions that could deactivate the polymerization process. For example, any side reactions that would lead to monofunctional units that are incapable of further reaction would limit the formation of high molecular weight of A–A/B–B or A–B type polymers.

In general, depression of molecular weight can be brought about by:

- Nonequivalence of reactants.
- Monofunctional ingredients introduced as impurities formed by side reaction.
- Unbalance in stoichiometric proportions. Example: $H_2 + 1/2\ O_2 \longrightarrow H_2O$

Now, suppose an excess of a functional group is obtained by the addition of reactant designated B+B. In this case the two types of polymerizations discussed above become:

Case I: A–B + little B+B

Case II: A–A + B–B + little B+B

Then let,

N_A = total number of A groups initially present

N_B = total number of B groups initially present

Therefore, total number of monomers = $(N_A+N_B)/2$ used initially in the polymerization and the ratio of the total number of A groups to the group B can be expressed as:

$$r = \frac{N_A}{N_B} < 1 \text{ i.e., } N_A < N_B \qquad \text{———} \quad 1$$

Now, consider that P_A is fraction of A groups that have reacted at a given time of the reaction (i.e. extent of reaction for monomer A).

Knowing P_A, one can easily find the amount of unreacted groups at any time throughout the polymerization:

Thus,

The total number of unreacted groups = $N_A(1-P_A) + N_B - N_A P_A \qquad \text{———} \quad 2$

Now, the degree of polymerization can be determined from Eqs 1 and 2:

$$\bar{X}_n = \frac{\text{original no. of molecules}}{\text{final no. of molecules}}$$

$$\bar{X}_n = \frac{N_A + N_B}{N_A\,(1-P_A) + N_B - N_A P_A}$$

Re-arrange the above equation and use Eq. 1, the following equation can be obtained:

$$\bar{X}_n = \frac{1 + r}{r\,(1-P_A) + 1 - rP_A}$$

$$\boxed{\bar{X}_n = \frac{1 + r}{1 + r - 2rP_A}}$$

For r = 1 (for stoichiometric amounts of A and B)

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

For p = 1, i.e., degree of polymerization is maximum.

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

By playing around with Equation 6.14 we see how the degree of polymerization and hence the molecular weight of the product is influenced by a proper control of the purity of reactants and prevention of extraneous reactions. In practice the molecular weight of nylons can be stabilized by the deliberate addition of a predetermined amount of a monofunctional monomer like acetic acid.

Note: The equation in the previous slide (in the red box) can be used to evaluate the degree of polymerization in a system containing bifunctional reactants and a small amount of monofunctional species provided r is defined as

$$r = \frac{N_A}{N_A + 2N_{B+}}$$

6) Molecular Weight Averages

Measuring the molecular weight of a polymer experimentally has been discussed in the previous lectures. Here, there are some useful relations that can predict what the amount of the polymer molecular weight based on the kinetic information:

1) Number-average molecular weight

$$\overline{X}_n = \frac{1}{1-p} \longrightarrow \overline{M}_n = \frac{M_o}{1-p}$$

2) Weight- average molecular weight

$$\overline{X}_w = \frac{1+p}{1-p} \longrightarrow \overline{M}_w = M_o \overline{X}_w$$

$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + p$$

NOTE: The total probability (P_x)that a given polymer molecule contains X units can be predicted using the following equation:

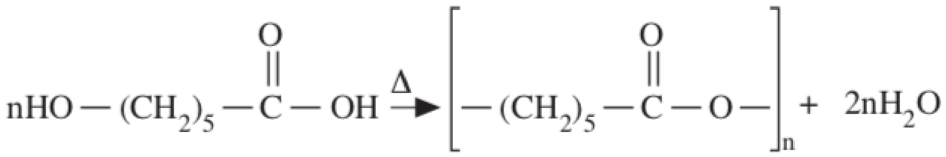
$$P_x = p^{x-1}\left(1-p\right)$$

And the weight fraction of molecule contains X units also can be predicted by:

$$W_x = X\left(p^{x-1}\right)\left(1-p\right)^2$$

EXAMPLE (4):

(a) Polyester fibers for “lace” material can, in principle, be produced from ω-hydroxycaproic acid. If the initial 100 moles of the hydroxyacid are reduced to 2 moles after 10 h reaction time, calculate:

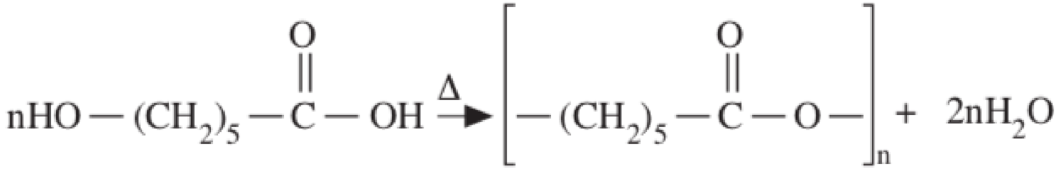


$$n\mathrm{HO}-(\mathrm{CH_2})_5-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OH} \xrightarrow{\Delta} \left[-(\mathrm{CH_2})_5-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\right]_n + 2n\mathrm{H_2O}$$

1. The number average molecular weight M_n
2. The weight average molecular weight M_w
3. The probability that the reaction mixture contains tetramers
4. The weight fraction of these tetramers.

(b) As a result of extraneous reactions of the hydroxyl groups, a 5% excess of the carboxylic acid is present in the reaction mixture. Calculate the number-average molecular weight for the same extent of reaction in a.

SOLUTION:



$$nHO-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{\Delta} \left[-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right]_n + 2nH_2O$$

$$\text{Extent of reaction } p = \frac{C_o - C}{C_o} = \frac{100-2}{100} = 0.98$$

1. $\overline{M}_n = \overline{X}_n M_o = \dfrac{M_o}{1-p} = \dfrac{114}{0.02} = 5700$

2. $\overline{M}_w = X_w M_o = M_o\left[\dfrac{1+p}{1-p}\right] = 114\left[\dfrac{1.98}{0.02}\right] = 11{,}286$

3. $P_x = p^{x-1}(1-p)$

   $= (0.98)^{4-1}\,(1-0.98) = 0.019$

4. $W_x = X\left(p^{x-1}\right)(1-p)^2$

   $= 4(0.98)^3\,(0.02)^2 = 1.51 \times 10^{-3}$

b. $$\overline{X}_n = \frac{1+r}{2r(1-p)+1-r}$$

$$r = \frac{100}{105} = 0.95$$

$$\overline{X}_n = \frac{1+0.95}{2(0.95)(1-0.98)+1-0.95} = 22.16$$

$$\overline{M}_n = \overline{X}_n M_o = 2526$$

Notice the depression in $\overline{M}_n$ as a result of stoichiometric imbalance.

THANK YOU