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.

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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:

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

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 = $N_A (1-P_A) + N_B - N_A P_A \qquad 2$

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

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

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

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

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

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

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

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

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:

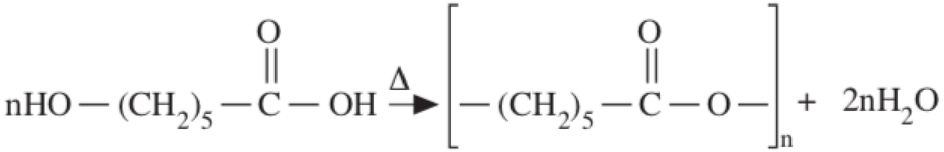
$$P_x = p^{x-1}(1-p)$$

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

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

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:

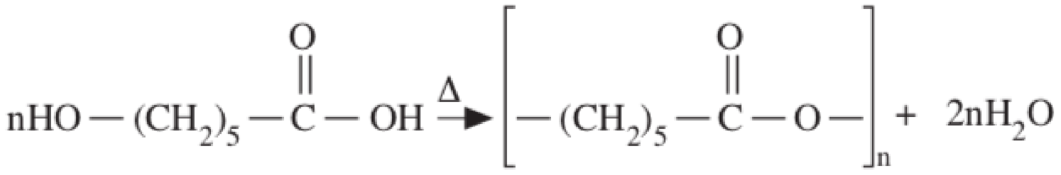


$$nHO-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{\Delta} \left[-(CH_2)_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right]_n + 2nH_2O$$

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:



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

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

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
FOR YOUR LISTENING