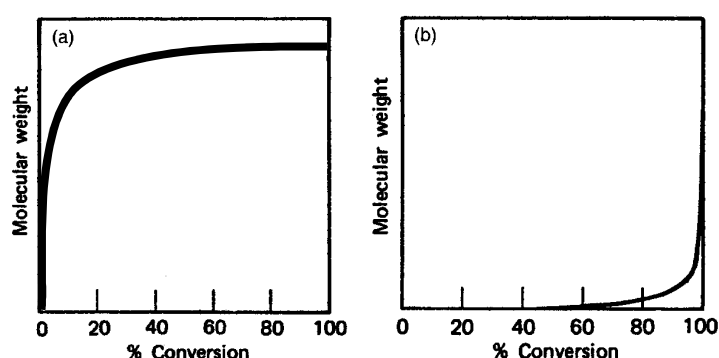


Polymer chemistry and macromolecular engineering
Fall 2024
HW 2-Solutions

- 1) a. Draw an (idealized) molecular weight vs monomer conversion curve for chain polymerization and step polymerization.
b. Briefly explain why they look different.
c. How can we control the molecular weight of a condensation polymer?

(a)

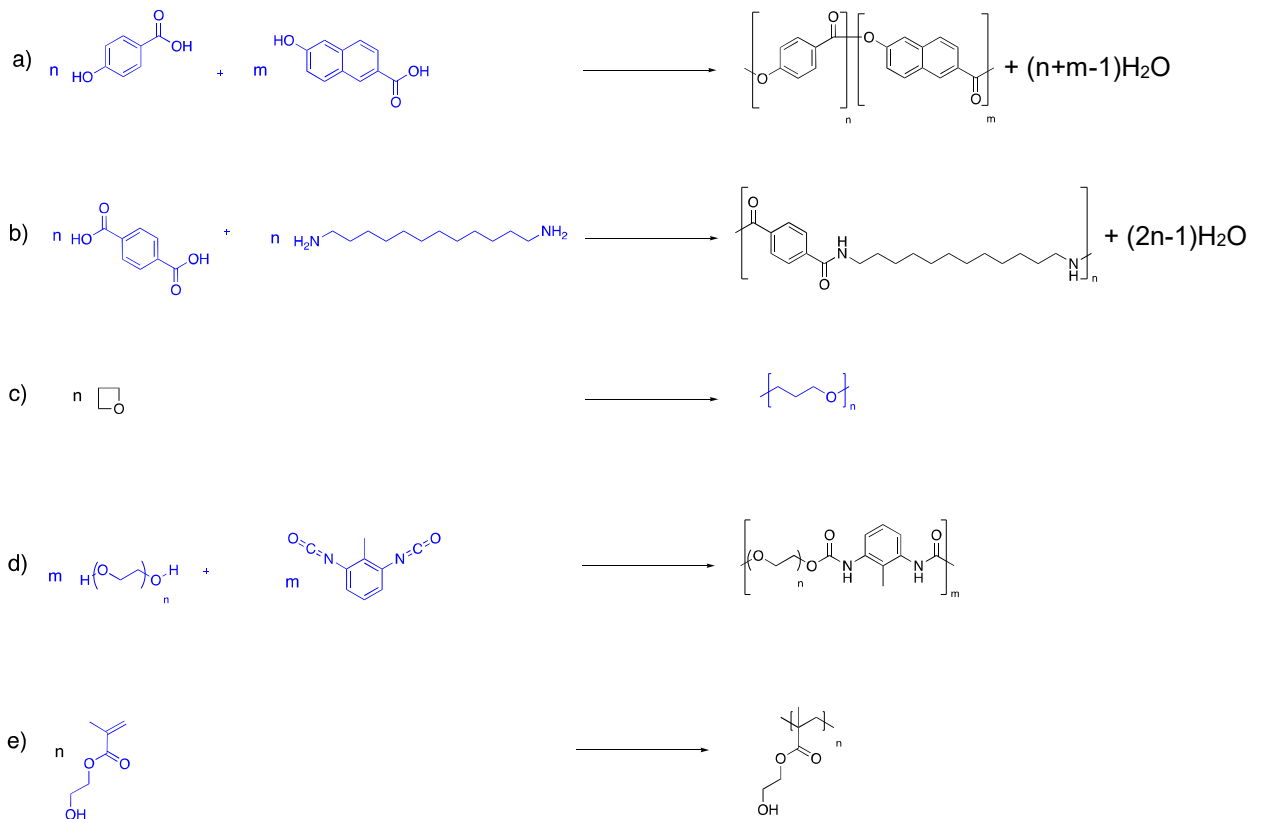


(b) In chain polymerization, only a few chains grow at a time to their full length which is a very fast process. Hence, high molecular weight chains are formed from the very beginning. In step polymerization monomers form oligomers first before forming high molecular weight polymers at high monomer conversions.

(c) The molecular weight can be controlled by using the following methods:

- Controlling concentration of the side-product e.g. water, controlling reaction time; quenching the polymerization, e.g. by decreasing temperature
- Non-stoichiometry
- Addition of a monofunctional monomer (chain stopper)

- 2) Draw the missing structures in the polymerization reactions below and state if the polymer is an addition or a condensation polymer and if the polymerization is proceeding via a step growth or chain growth mechanism.



- a) Step polymerization; condensation polymer
- b) Step polymerization; condensation polymer
- c) Ring-opening polymerization; condensation polymer
- d) Step polymerization; condensation polymer
- e) chain polymerization; addition polymer

3) Increasing the conversion from 96 % to 98 % of an external catalyzed step polymerization took 90 minutes. Calculate the time needed to reach 95% conversion

$$\text{we know that } tk[M_o] = \frac{1}{1-p} - 1$$

$$\text{rearranging } tk[M_o] = \frac{p}{1-p} \quad \text{hence, } t = \frac{p}{k[M_o](1-p)}$$

$$t_{96\%} = \frac{0.96}{k[M_o](1-0.96)} = \frac{24}{k[M_o]}$$

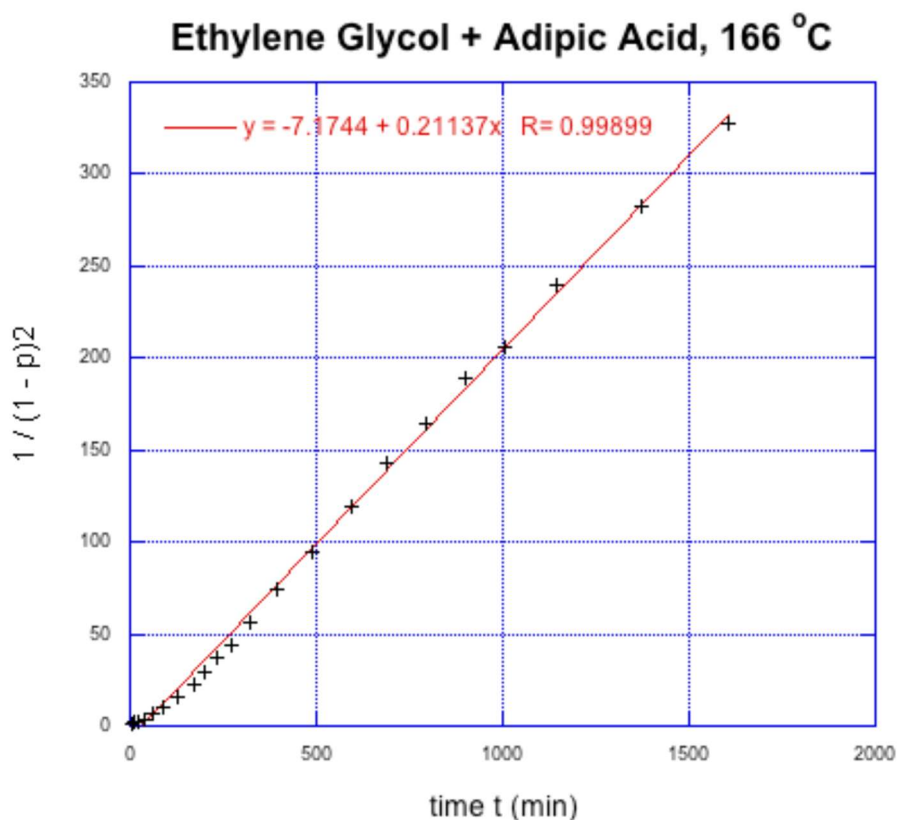
$$\text{likewise } t_{98\%} = \frac{0.98}{k[M_o](1-0.98)} = \frac{49}{k[M_o]}$$

The time needed from 96 to 98% conversion $t_{98\%} - t_{96\%} = \frac{49}{k[M_o]} - \frac{24}{k[M_o]} = 90 \text{ minutes}$

$$k[M_o] = 0.28/\text{min}$$

The time needed to reach 95% conversion is, $t_{95\%} = \frac{p}{k[M_o](1-p)} = \frac{0.95}{k[M_o](1-0.95)} = 67.8 \text{ minutes}$

- 4) a. Given an initial alcohol group concentration $[M]_0 = 17 \text{ M}$, determine the rate constant from Flory's data in $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$.



- b. The following data were obtained during externally catalysed condensation of 12-hydroxyl stearic acid (MW ~ 300) at 433.5 K. $[\text{COOH}]$ was determined for each sample by titrating with ethanolic sodium hydroxide. How long it would take to build a M_n of 30,000 (ignore the end group molecular weight)?

t (h)	$[\text{COOH}]$ (mol L ⁻¹)
0	3.10
2	0.48
3	0.34

- a. Equation for straight line is $y = mx + c$
Slope of the graph is m in units of y/x

$$\text{Also } \frac{1}{(1-p)^2} = 2[M_o]^2 kt + 1$$

Equating above two equations we get, $m = 2[M_o]^2 k = 0.21137 \text{ min}^{-1}$

By solving the above equation, we get, $k = 6.09 \times 10^{-6} \text{ L}^2 \text{mol}^{-2} \text{s}^{-1}$

$$\text{b. } X_n = \frac{\text{Original monomer concentration}}{\text{Remaining monomer concentration}} = \frac{[M_o]}{[M]} = 3.10/0.34 \sim 9$$

Degree of polymerization of 12-hydroxyl stearic acid after 3 h is 9.

$$\text{Now we know that } X_n = [M_o]kt + 1$$

$$9 = (3.10 \text{ mol L}^{-1} \times k \times 3 \text{ h}) + 1$$

$$k = 8/9.3 \text{ mol}^{-1} \text{ L h}^{-1} = 0.86 \text{ L mol}^{-1} \text{ h}^{-1}$$

For M_n of 30,000, X_n will be approximately 100 (ignoring the end group molecular weight)

Therefore, once again using $X_n = [M_o]kt + 1$ and substituting the values we get

$$100 = (3.10 \text{ mol L}^{-1} \times 0.86 \text{ L mol}^{-1} \text{ h}^{-1} \times t) + 1$$

Rearranging and solving for t we get,

$$t \sim 37 \text{ h}$$