MSE 214 (Polymers)
Exercise 2 — Synthesis (I)
24th September 2025

Question 1.

What are some characteristics of step-growth polymerization? (Think in terms of mechanism, molecular weight, and conversion).

Question 2.

For the synthesis of a polyamide from stoichiometric quantities of a diacid (A-A) and a diamine (B-B), calculate the conversion necessary to achieve a number average degree of polymerization of 90. Give your answer to three decimal places.

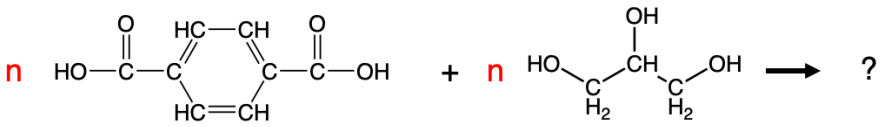
Question 3.

Discuss two strategies for controlling the molecular weight of polymers in step polymerization?

Question 4.

In the lecture, we only discussed syntheses with bifunctional monomers. Let's think a little about going beyond that.

a) Given that a carboxylic acid (COOH) reacts with an alcohol (OH) to form an ester, draw an oligomer that can be formed from the system below at low conversions (show 10 monomers in the molecule):



You are free to abstract the molecules into something that is easier to draw, e.g.: A-A
Note: Oligomers are formed from the polymerization of a few monomers. Polymers are formed from the polymerization of a large number of monomers.

b) Describe the architecture of the oligomer that you've drawn. How would you classify this polymer if the reaction was allowed to proceed to high conversions?

c) Let's discuss a system where the monomers have 2 or more functionalities (such as the monomers shown above in part a)) BUT their functionalities are present in equal amounts, i.e. the two functional groups A and B are present in equivalent amounts. We can define the average functionality of the polymerization system as such, f_{avg} :

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i}$$

Where N_i is the number of moles of monomer i with functionality f_i, and the summations are over all the monomers present in the system. Functionality refers to the number of functional groups on the monomer that can partake in the polymerization reaction. f_{avg} represents the

average number of functional groups per monomer molecule for all types of monomer molecules.

Calculate f_{avg} for a system consisting of 2 mol of glycerol and 3 mol of phthalic acid.

(Hint: Look up the structures of these molecules, what are the functional groups that can be used to make polymers?)

d) Let us now try to derive the equation for conversion for such stoichiometric multifunctional systems:

For a system containing an equivalent number of A and B groups, what is the total number of functional groups present initially?

Hint:Assume that the number of monomer molecules present initially is N_0 and the average functionality of the system is f_{avg}.

e) If each polymerization step results in the formation of an AB linkage, then every time a new linkage is formed, the reaction mixture will contain one less molecule. Thus, when the number of molecules (polymer + monomer) in the system is N (at some time t), the number of AB linkages which has been formed has to be $N_0 - N$. With this information, what is the equation for conversion, p, as a function of N_0, N, and f_{avg}?

Hint: $p = \frac{Number\ of\ functional\ groups\ reacted}{Number\ of\ functional\ groups\ initially}$

f) Using the equation for p that you derived in part e, derive the equation for the number average degree of polymerization ($\bar{X}_n$) as a function of p and f_{avg}.

Hint: The number average degree of polymerization ($\bar{X}_n$) is the average number of monomers in each polymer.

g) In the case where $f_{avg} = 2$, i.e. the cases we discussed in the lecture with bifunctional monomers, what does $\bar{X}_n$ simplify to?

Hint: You should get back the same equation we obtained in the lecture.

h) Rearrange the equation you derived in part f) such that p is now a function of $\bar{X}_n$ and f_{avg}. Using this equation, determine the equation for the critical extent of reaction p_c at the gel point.

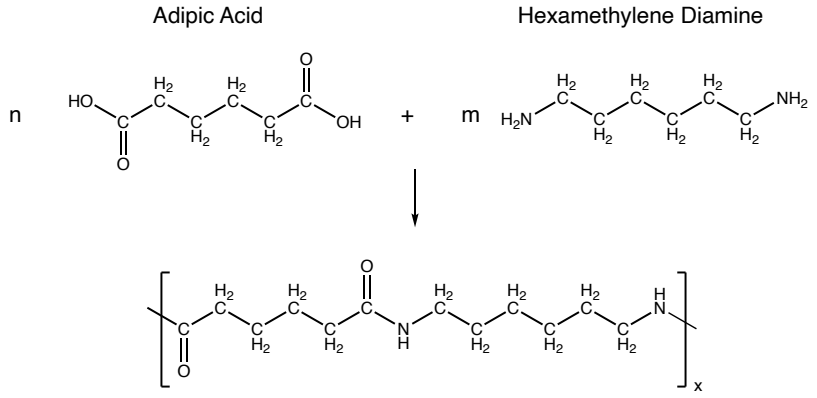
Hint: At the gel point, the polymer can be thought of as having an “infinite molecular weight”

i) For the system described in part c) (2 mol of glycerol and 3 mol of phthalic acid), what is the critical extent of reaction required to reach the onset of gelation?

Question 5.

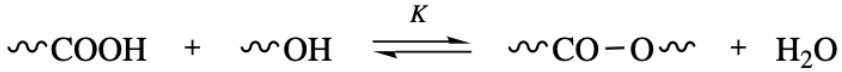
Calculate the ratio of adipic acid (146.14 g/mol) and hexamethylene diamine (116.21 g/mol) that should be used to obtain a polyamide of approximately 15'000 g/mol (number average molecular weight) at 99.5% conversion? (Express your answer to 4 decimal places)

Hint 1: What is the degree of polymerization needed to reach this number average molecular weight? Remember that degree of polymerization is with respect to the monomeric unit!
Hint 2: The repeat unit of the polymer that is formed from reacting adipic acid and hexamethylene diamine is shown below:



Question 6.

Many of the step reactions covered in the lecture are actually equilibrium reactions, i.e., it is more accurate to depict them as such:



(Carboxylic acid) (Hydroxyl group) (Ester)

where *K* is the equilibrium constant of the reaction

a) Knowing that these reactions are equilibrium reactions, why is it important to remove the byproduct of these step reactions?

b) It is often difficult to remove the byproduct of these reactions, especially at higher conversions. Why do you think this is so?

c) What is one important sustainability implication of the fact that these reactions are in an equilibrium?