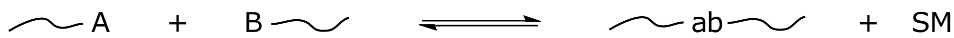
Equilibrium in Condensation Polymerizations

Model 1: Equilibria in Condensation Reactions

So far, we have written all reactions as unidirectional, proceeding only from *reactants* to *products*. However, in reality, the reactions used to produce polymers by step-growth polymerization are typically reversible, and proceed under equilibrium conditions.

This issue is particularly important for condensation reactions, which produce a small-molecule byproduct. Consider the reaction of an "A" functional group with a "B" functional group to produce an "ab" bond:



Here, we have included the small molecule byproduct, "SM" on the right side of the reaction. We have also written the reaction arrow as a double arrow ($\leftrightharpoons$) to indicate that the reaction is reversible.

Critical Thinking Questions:

1. Write an expression for the equilibrium constant for this reaction, K_{eq}, in terms of the concentrations of A groups ([A]), B groups ([B]), ab bonds ([ab]), and released small molecules ([SM]):

2. Suppose we start with v_A^0 A groups. If the reaction is stoichiometrically balanced, that means we also start with v_A^0 B groups.

   Using this information, complete the following ICE table:

	A	**B**	**ab**	**SM**
Initial	v_A^0	v_A^0	0	0
Change	$-x$			
Equilibrium		$v_A^0 - x$		

3. Plug your values from the equilibrium line of this table into your expression from question 5 to find an expression for K_{eq} in terms of v_A^0 and x.

   Note: your expression from question 5 is written in terms of concentrations, while the values in the table in question 2 are written in terms of numbers of molecules. In this problem, however, it turns out that everything cancels such that you can just plug the values from question 2 into the expression from question 5 directly.

4. When the extent of reaction is equal to p, the number of A groups that have reacted is pv_A^0, so $x = pv_A^0$. Using this information, rewrite K_{eq} only in terms of p.

   Hint: to make question 5 easier, leave the denominator in the form $(1-p)^2$ *instead of multiplying it out.*

5. Solve for p in terms of K_{eq}.

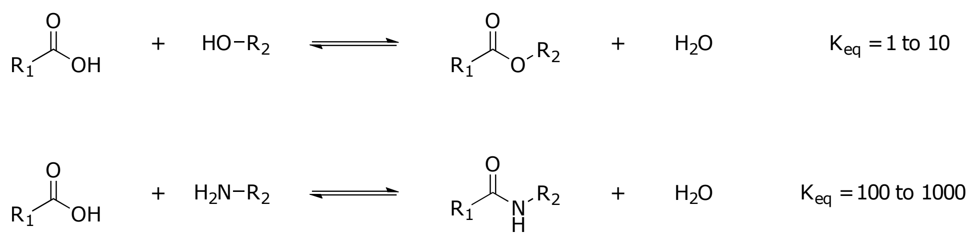
   Hint: start by taking the square root of both sides of the equation.

6. Finally, recalling that the number-average degree of polymerization is related to p by $N_n = \frac{1}{1-p}$, find an expression for N_n in terms of K_{eq}.

Model 2: Equilibrium in Condensation Polymerizations

Polyesters and polyamides are two important classes of polymers formed by condensation polymerization.

Shown below are the bond-forming reactions and range of equilibrium constants for typical esterification and amidation reactions:



Critical Thinking Questions:

7. Calculate the range of N_n values you would expect for a polyester synthesized under equilibrium conditions.

8. Calculate the range of N_n values you would expect for a polyamide synthesized under equilibrium conditions.

Information:

Commercial applications of polyesters and polyamides typically require degrees of polymerization of 100 or more.

Critical Thinking Questions:

9. Can commercial polyesters and polyamides be produced under equilibrium conditions? Why or why not?

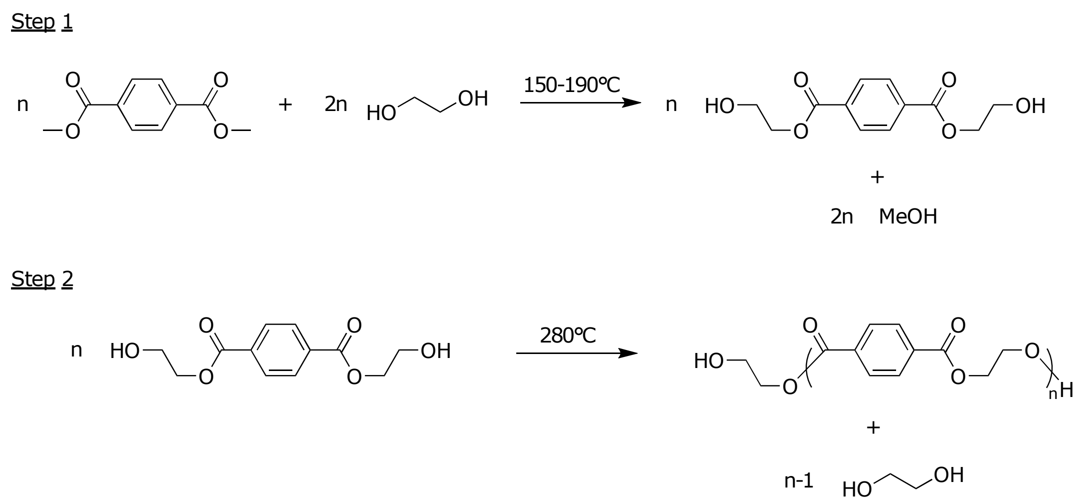
10. Propose at least one way that you could increase the degree of polymerization for polymers produced using the reactions shown in Model 2. Explain your proposed solution in 2-3 complete sentences.

    Hint: you will probably want to think about this question in the context of Le Chatelier's principle.

Model 3: Synthesis of Polyethylene Terephthalate

One commercially-important polyester produced by condensation polymerization is polyethylene terephthalate, or PET. PET is produced in quantities of more than 9 billion pounds per year, and is used in drink bottles, plastic films, and many other products.

PET is produced in a two-step transesterification process, as shown below:



Critical Thinking Questions:

11. What small molecule is released in the transesterification reaction shown in Step 1?

12. What small molecule is released in the transesterification reaction shown in Step 2?

Information:

The boiling point of methanol is 64.7°C.

The boiling point of ethylene glycol ($HOCH_2CH_2OH$) is 196°C.

Critical Thinking Questions:

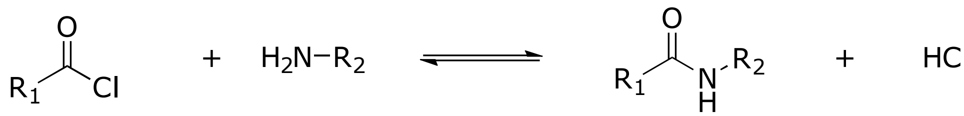
13. Why is the reaction in Step 1 carried out between 150 and 190°C? Briefly explain your answer in 1-2 complete sentences.

14. Why is the reaction in Step 2 carried out at 280°C? Briefly explain your answer in 1-2 complete sentences.

15. If we attempted to run the reaction in Step 1 at 280°C, would we form the desired polymer? Why or why not?

Exercises:

1. Both of the reactions shown in Model 2 produced water (H_2O) as the small-molecule byproduct. However, if we had started with acid chloride reagents, we might instead produce HCl as the small-molecule byproduct:



Explain why, in this case, adding a stoichiometric amount of triethylamine should help promote formation of high molecular weight products.

2. Explain, in complete sentences, why the reactions shown in Model 3 are both referred to as "trans-esterification" reactions.

Hint: what types of bonds are broken in each reaction, and what types of bonds are formed? How does this differ from the other esterification reactions you have studied in this class?

3. Why does the first reaction in Model 3 (i.e. "Step 1") produce only a small oligomer rather than a large polymer chain? Explain your answer in terms of the reaction stoichiometry.

4. The reactions in Model 3 produce PET by transesterification of AA and BB-type monomers.

Propose alternate monomers that could be used to produce the same polymer by...

a) ... esterification of AA and BB-type monomers:

b) ... transesterification of an AB-type monomer:

c) Both the AA+BB-type trans-esterification shown in Model 3 and the AA+BB-type esterification you drew in part (a) of this problem are used commercially to produce PET. However, PET is never (or only rarely) produced from AB-type monomers. Why do you think this is true?

5. Although our focus in this exercise was on how to increase the degree of polymerization by removing the small-molecule byproduct, it is sometimes advantageous to push the equilibrium in the other direction.

If you were to take a sample of PET and heat it in the presence of a large excess of water, what products would you expect to result? Propose at least one application in which this process might be useful.