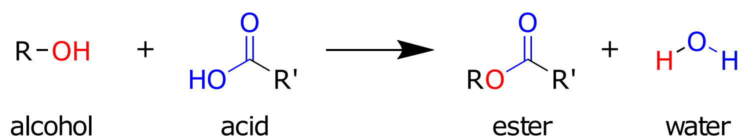
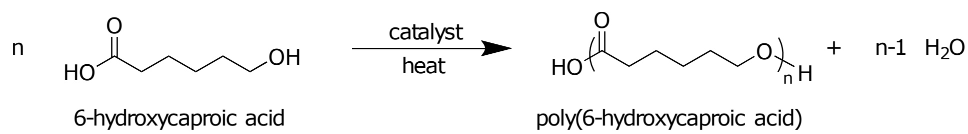
Chemistries of Step-Growth Polymerizations

Model 1: Synthesis of a Polyester

Esterification reactions are a common type of reaction used to produce polymers by step-growth polymerization. In a typical esterification reaction, an alcohol and a carboxylic acid react to form an ester bond:



One example of a polymerization reaction using this chemistry is the synthesis of poly(6-hydroxycaproic acid) from 6-hydroxycaproic acid monomers:



Critical Thinking Questions:

1. Consider the 6-hydroxycaproic acid monomer shown in Model 1:

   a) As drawn, what type of functional group is on the *left* side of the monomer?

   b) As drawn, what type of functional group is on the *right* side of the monomer?

Information:

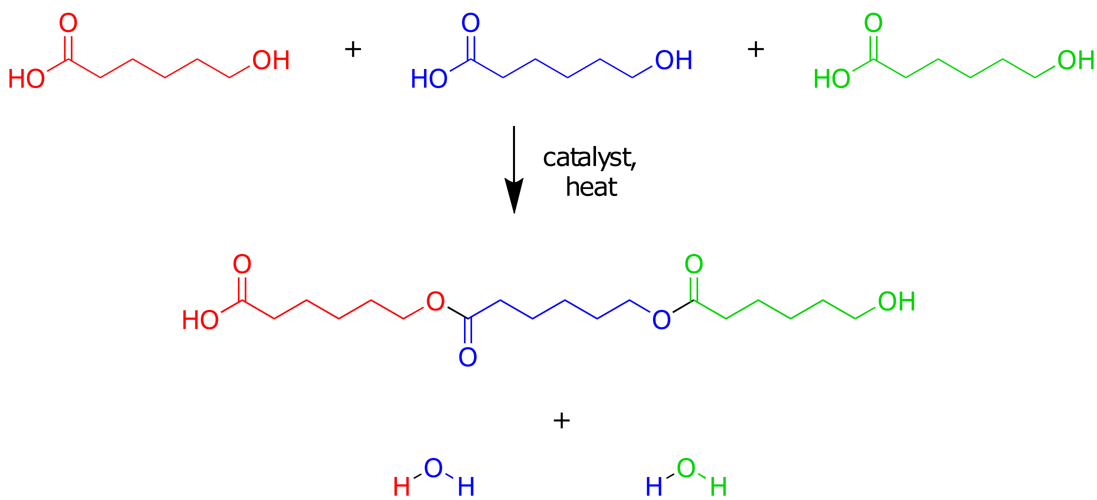
When a monomer used in a step-growth polymerization has different reactive functional groups on each end, it is called an "AB-type" monomer.

When a monomer used in a step-growth polymerization has the same reactive functional group on each end, it is called an "AA-type" or "BB-type" monomer.

Critical Thinking Questions:

2. Would you classify the poly(6-hydroxycaproic acid) monomer used in this synthesis as an AA-type monomer or an AB-type monomer? Briefly explain your answer in 1-2 complete sentences.

3. The synthesis of a short 6-hydroxycaproic acid oligomer from three monomers is shown explicitly, below:

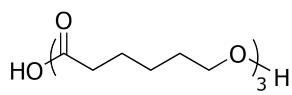


The molecules are color-coded so that you can see which atoms in the oligomer came from which monomer.

a) What type of bonds connect the different monomers in the polymer backbone?

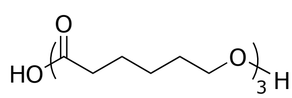
b) Explain, in one or two complete sentences, why you think we classify this polymer as a "polyester":

c) When we write the structure of this oligomer as

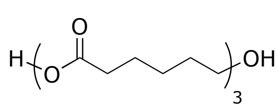


how many monomers make up each repeat unit in the polymer chain?

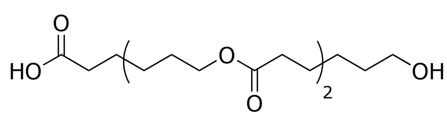
d) Explain, in one or two complete sentences, why we generally abbreviate the product of this reaction as



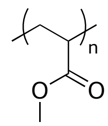
rather than as



or



4. Consider the following polymer:



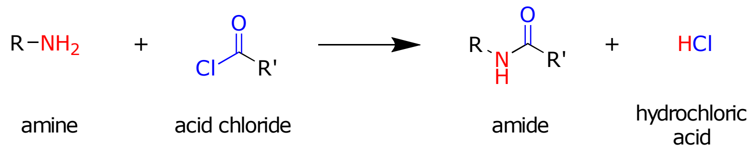
a) Does this polymer have ester bonds in the polymer backbone?

b) Would you be able to produce this polymer by esterification reactions of small molecules? Why or why not?

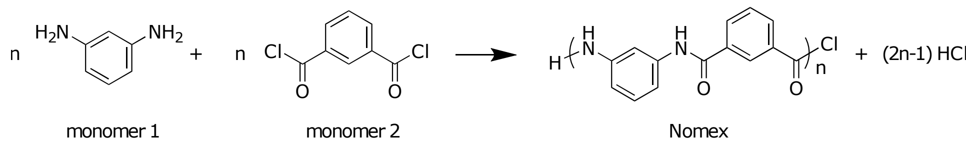
c) Based on your answers to the previous two questions, would you classify this polymer as a polyester? Why or why not?

Model 2: Synthesis of a Polyamide

Amidation reactions are another type of reaction used to produce polymers by step-growth polymerizations. For example, acid chlorides can be reacted with primary amines to form an amide bond:



Commercially, this reaction is used to produce Nomex, a heat-resistant polymer used in oven mitts and firefighters' protective clothing, among other applications. A reaction scheme for the synthesis of Nomex is shown below:



Critical Thinking Questions:

5. Why is this polymer classified as a polyamide?

6. What functional groups does monomer 1 have? Would you classify this monomer as an AA-type monomer or an AB-type monomer?

7. What functional groups does monomer 2 have? Would you classify this monomer as an AA-type monomer or an AB-type monomer?

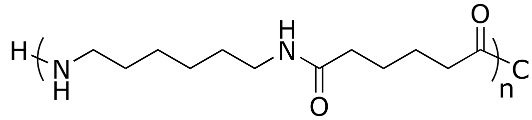
8. Explain, in one or two complete sentences, why we might describe this reaction as an “AA+BB”-type polymerization:

9. How many monomers make up each repeat unit?

10. A very similar reaction can be used to make Kevlar, the high-strength polymer used in bulletproof vests and cut-resistant gloves. Given that Kevlar is produced from the following two monomers,

predict the structure of the Kevlar polymer:

11. A similar chemistry can also be used to prepare nylon-6,6, a polymer used in many consumer goods. The structure of nylon-6,6 is shown below:



What two monomers would you need to combine to make this polymer?

Information:

A polymerization reaction is called a *condensation* polymerization if the reaction produces a small-molecule byproduct that is not part of the polymer chain.

Critical Thinking Questions:

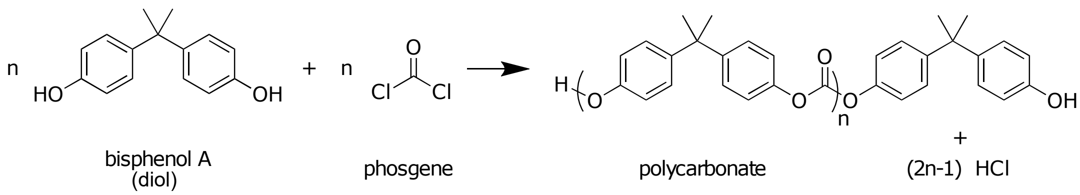
12. Is the esterification reaction in Model 1 a condensation polymerization? If so, what is the small-molecule byproduct that is produced?

13. Is the amidation reaction in Model 2 a condensation polymerization? If so, what is the small-molecule byproduct that is produced?

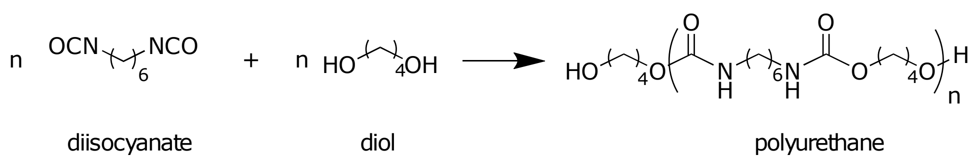
Model 3: Other Chemistries used for Step-Growth Polymerization

Shown below are synthetic schemes for a variety of other commercially-important polymers produced by step-growth polymerization:

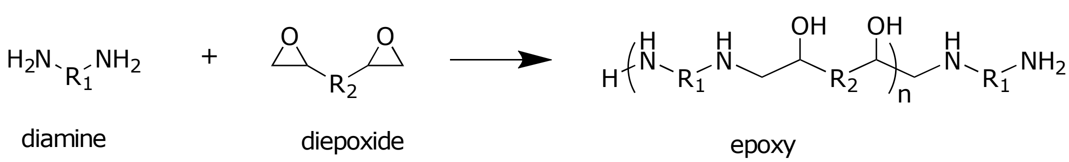
a) polycarbonate (high transparency and impact resistance; used in DVDs, glasses, etc.)



b) polyurethanes (foams; thermoplastic elastomers, e.g. spandex)



c) epoxies (adhesives; coatings)



Critical Thinking Questions:

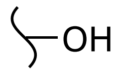
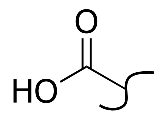
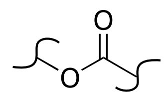
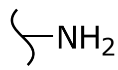
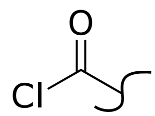
14. Classify each of the reactions in the above Model as either an “AB-type” or “AA+BB-type” polymerization:

    a)

    b)

    c)

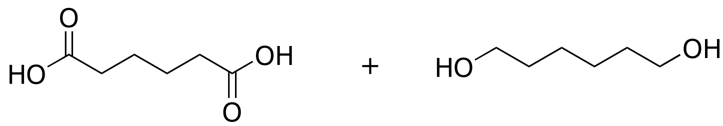
15. Complete the following table for the polymerizations depicted in Models 1-3:

Polymer	"A" reactive group	"B" reactive group	"ab" bond formed	Small Molecule Byproduct
Polyester				
Polyamide				HCl
Polycarbonate				
Polyurethane				
Epoxy				

16. Which of the above polymerization reactions would you classify as condensation polymerizations? Briefly explain your answer in 1-2 complete sentences.

Exercises:

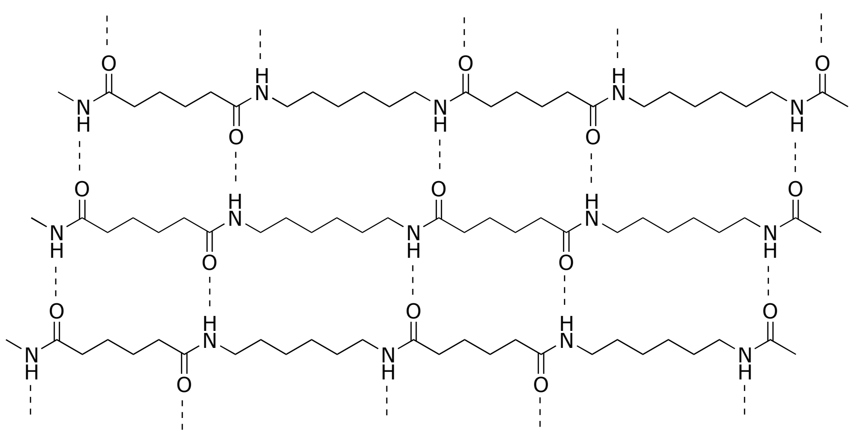
1. Although the polymers formed by AB-type and AA+BB-type step-growth polymerizations are similar, there are some subtle but important differences. Consider the synthesis of a polyester from the following two monomers:



   a) Draw the structure of the polymer that would be formed from this pair of monomers.

   b) Compare this structure to the polymer produced from the AB-type monomer in Model 1 (hint: you may find it useful to explicitly draw out a few repeat units). Are they the same, or different? If they are different, briefly describe what is different about the two structures.

2. One of the reasons that polyamides have such useful properties is that the amide groups can form hydrogen bonds between chains, as shown below:



   These inter-chain hydrogen bonds significantly improve the mechanical properties (e.g. stiffness, resilience, etc.) of the material.

   Draw an analogous structure for the AA+BB-type polyester that you drew in Exercise 1. Can this polymer form inter-chain hydrogen bonds? Briefly explain your answer, and discuss how you expect the physical properties of the polyester to compare to those of the polyamide.

3. The epoxidation reaction shown in Model 3 formed a linear polymer with secondary amines. However, secondary amines can also attack epoxides. Draw out the polymer structure that you would expect to generate if this occurs. How would you describe this polymer architecture?

