POGIL Polymers

Guided-Inquiry Activities
for Polymer Chemistry and Polymer Physics

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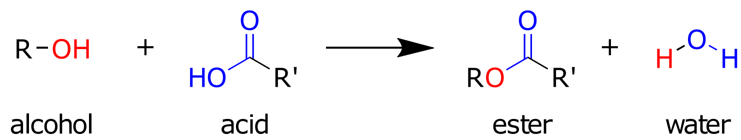
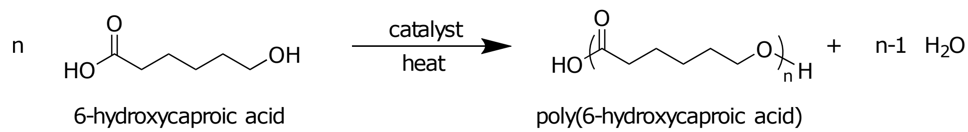
Activity 1: Chemistries of Step-Growth Polymerizations

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:

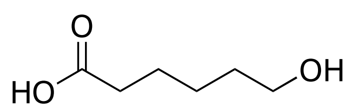


One example of a polymerization reaction using this chemistry is the synthesis of poly(6-hydroxycaproic acid) from 6-hydroxycaproic acid monomers:



Critical Thinking Questions:

1. The 6-hydroxycaproic acid monomer is shown below:



   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:

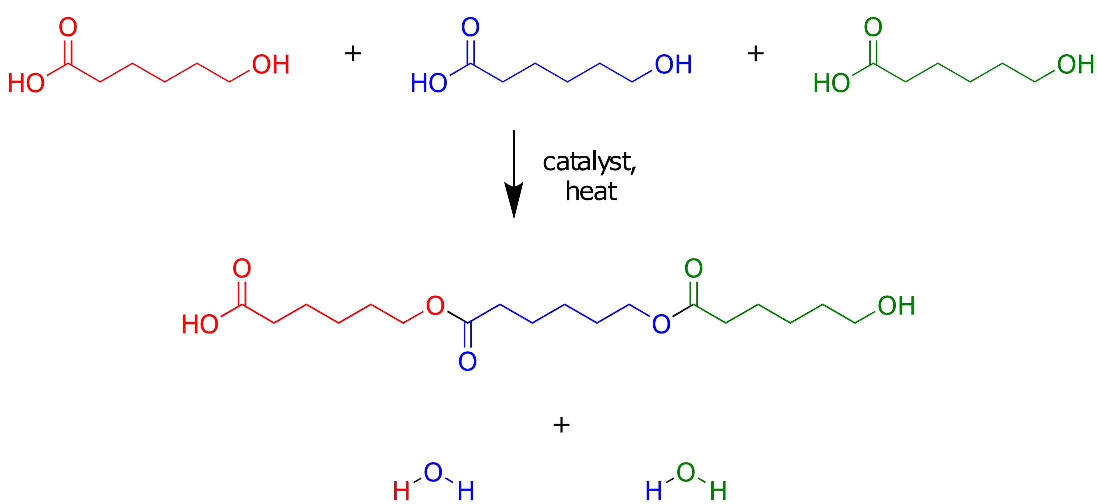
When a monomer used in a step-growth polymerization has different reactive functional groups on each end, it is called an "AB-type" monomer.

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.

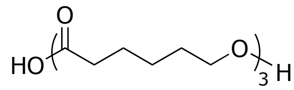
3. The synthesis of a short 6-hydroxycaproic acid oligomer from three monomers is shown explicitly, below:



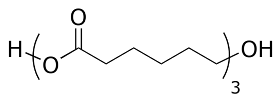
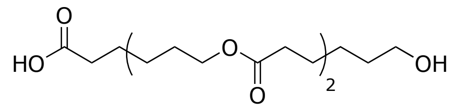
The molecules are color-coded so that you can see which atoms in the oligomer came from which monomer.

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

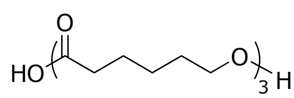
b) Explain, in one or two complete sentences, why we generally abbreviate the product of this reaction as



rather than as

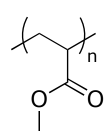
 or 

c) When we write the structure of this oligomer as



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

4. Consider the following polymer:

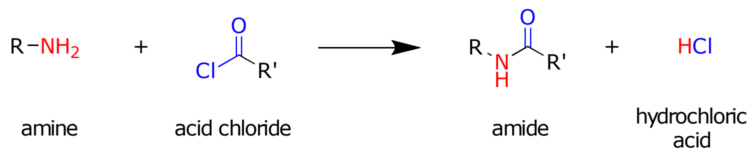


a) Would you be able to produce this polymer by esterification reactions of small molecules? Why or why not?

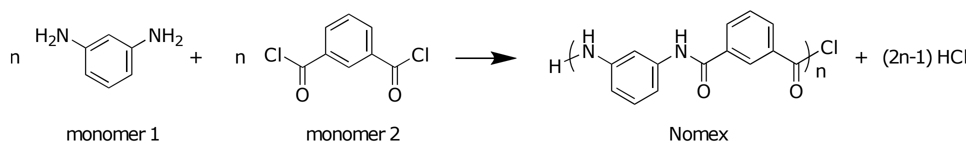
b) Based on your answer to the previous question, would you classify this polymer as a polyester? Why or why not?

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?

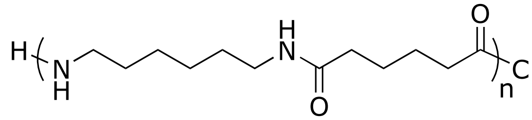
8. Explain, in one or two complete sentences, why we might describe this reaction as an “AA+BB”-type polymerization:

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,

what do you predict the structure of the polymer should look like?

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:

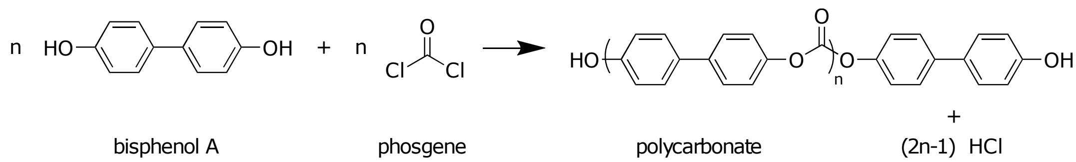
12. Is the esterification reaction in Model 1 a condensation polymerization? If so, what is the small-molecule byproduct that is produced?

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

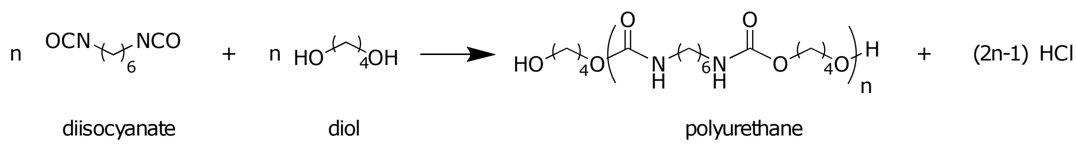
Model 3: Other Chemistries used for Step-Growth Polymerization

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

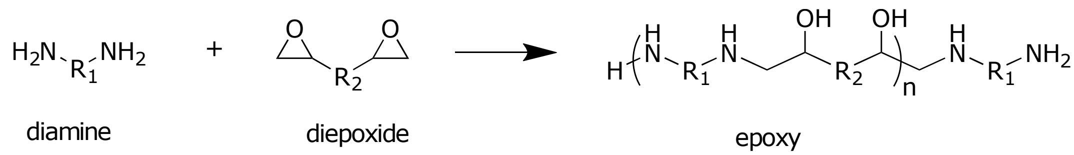
a) polycarbonate (high transparency and impact resistance; used in DVDs, glasses, etc.)



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



c) epoxies (adhesives; coatings)



Critical Thinking Questions:

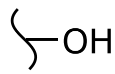
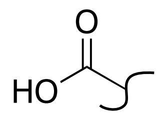
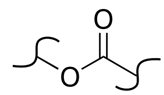
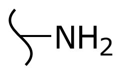
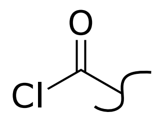
14. Classify each of the reactions in the above Model as either an "AB-type" or "AA+BB-type" polymerization:

    a)

    b)

    c)

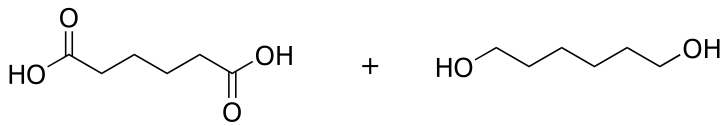
15. Complete the following table for the polymerizations depicted in Models 1-3:

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:

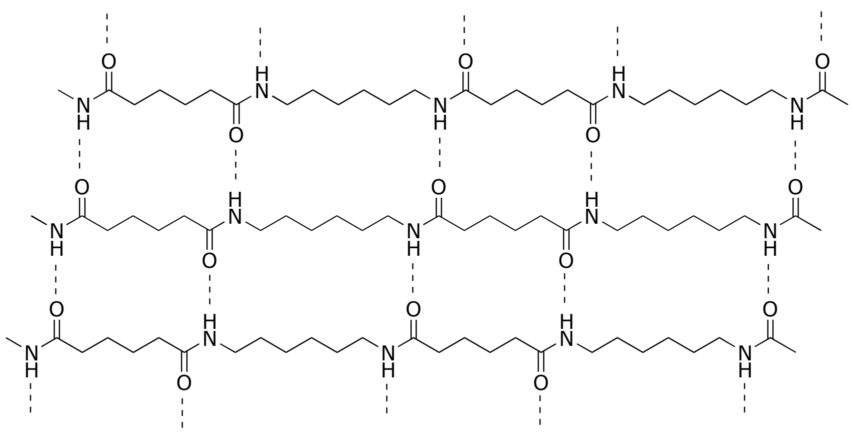
1. Although the polymers formed by AB-type and AA+BB-type step-growth polymerizations are similar, there are some subtle but important differences. Consider the synthesis of a polyester from the following two monomers:



   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?

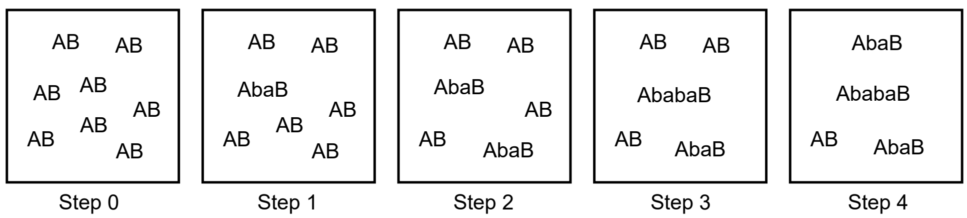
Activity 2: Degree of Polymerization in Step-Growth Polymerizations

Model 1: Polymerization of "AB"-Type Monomers

The simplest type of step-growth polymerization is one in which each monomer has one "A"-type reactive group and one "B"-type reactive group. These types of monomers are referred to as "AB"-type monomers.

In each step of the polymerization, an "A" group on one molecule reacts with a "B" group on another molecule to form an "ab" bond, as shown below:

For example, for a simple reaction mixture containing 8 "AB"-type monomers, the evolution of the reaction mixture might look something like this:



Critical Thinking Questions:

1. For the reaction mixture shown in Model 1, fill out the following table. When counting the number of molecules, make sure to count *both* the unreacted monomers and the growing oligomer/polymer chains (that is, you should count each 'AB', 'AbaB', 'AbabaB', etc. as one molecule).

Step	Number of unreacted "A" groups	Number of molecules
0		
1		
2		
3		
4		

2. Explain, in a complete sentence, how the number of molecules in the mixture is related to the number of unreacted "A" groups.

Information:

At any given time, the number-average degree of polymerization, N_n, is the total *initial* number of monomers divided by the total number of molecules *currently* present. That is,

$$N_n = \frac{\text{initial number of monomers}}{\text{current number of molecules}}$$

Critical Thinking Questions:

3. In Model 1, there were 8 monomers in the initial reaction mixture. Using this information, calculate the number-average degree of polymerization for each step shown in Model 1.

Step	**0**	**1**	**2**	**3**	**4**
$\mathbf{N_n}$					

4. Suppose that you had initially started with 100 monomers. Then, suppose that at some time later, you had only 8 unreacted "A" groups left.

   a) How many molecules would there be in the reaction mixture at this point?

   b) What would the number-average degree of polymerization be at this point?

5. More generally, suppose you started with v_A^0 monomers, and at some time later, you had only v_A unreacted "A" groups left. What would the number average-degree of polymerization be at this point, in terms of v_A^0 and v_A?

Information:

Usually, we find it more useful to work in terms of the *fraction* of all "A" groups that have reacted, rather than the total *number* of "A" groups that have reacted.

In step-growth polymerizations, we refer to the fraction of "A" groups that have *reacted* as the "extent of reaction", p. When the fraction of "A" groups that *have* reacted is p, the fraction of "A" groups that have *not* reacted is $1 - p$.

Critical Thinking Questions:

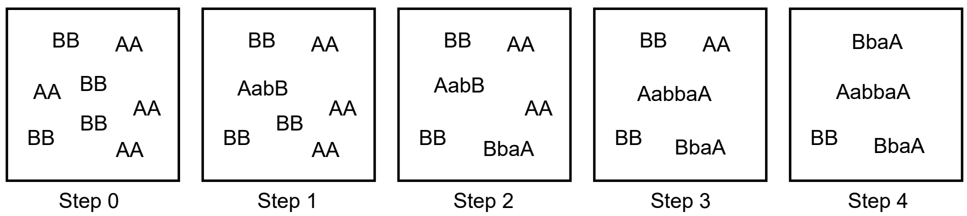
6. If we start with v_A^0 "A" groups, what is v_A (that is, how many "A" groups are still unreacted) when the extent of reaction is equal to p?

7. Using your answers to critical thinking questions 5 and 6, derive an expression for N_n in terms of p.

Model 2: Polymerization of "AA" and "BB"-Type Monomers

Now, let's consider a slightly more complicated reaction, with two different types of monomers that each have *either* two "A" reactive groups *or* two "B" type reactive groups. We call monomers with two "A" groups "AA"-type monomers, and we call monomers with two "B" groups "BB"-type monomers.

Suppose we start with 4 "AA"-type monomers and 4 "BB"-type monomers. In this case, the evolution of the reaction mixture might look something like this:



Critical Thinking Questions:

8. For the reaction mixture shown in Model 2, fill out the following table:

Step	Number of unreacted "A" groups	Number of molecules	N_n
0			
1			
2			
3			
4			

9. Compare your answers in question 8 with those from question 1. What similarities and/or differences do you notice?

10. Consider the following statement:

    "In polymerizations of AA- and BB-type monomers, we should be able to use the same expressions to calculate N_n as we did for polymerizations of AB-type monomers."

    In two or three complete sentences, briefly critique or defend this statement, making sure to explain your reasoning.

Information:

> A reaction is *stoichiometrically balanced* if the initial reaction mixture contains exactly the same number of "A" and "B" reactive groups.

Critical Thinking Questions:

11. Are the reactions in Models 1 and 2 stoichiometrically balanced? Briefly explain your answer in one or two complete sentences.

12. Predict what the reaction mixtures in Models 1 and 2 might look like if you let them react until no more reactions could take place:

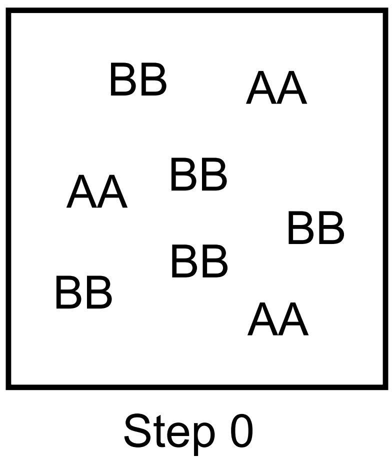
Model 1   Model 2

13. Calculate the number-average degree of polymerization for both of the “final” states you drew in response to the previous question:

Model 3: A Stoichiometrically-Imbalanced Reaction Mixture

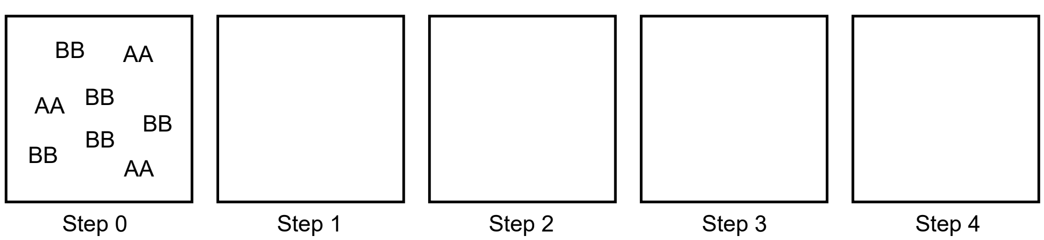
Practically speaking, it is often very difficult to ensure that a reaction mixture is perfectly stoichiometrically-balanced, and there is often a small excess of one type of monomer or the other.

In this model, consider a reaction mixture that starts with 3 AA-type monomers and 5 BB-type monomers:



Critical Thinking Questions:

14. Fill in the blank spaces in the figure below with reasonable predictions for what the reaction mixture might look like in each successive step.



15. Which type of reactive group is the "limiting reagent" in this reaction? Briefly explain your reasoning.

16. Predict what the reaction mixture in Model 3 might look like if you let it react until no more reactions could take place:

Model 3

17. Calculate the number-average degree of polymerization for the "final" state you drew in response to the previous question:

18. Is the final degree of polymerization for this stoichiometrically-unbalanced reaction smaller than, equal to, or larger than the final degree of polymerization you calculated for the stoichiometrically-balanced reactions in Models 1 and 2?

19. Which type of reactive group is on the ends of all of the chains you drew in question 16?

20. Briefly critique or defend the following statement:

    "When drawing the structure of a polymer produced by a step-growth polymerization, we should always make sure that we draw end groups consistent with whichever reactive species was present in excess."

Information:

In stoichiometrically-imbalanced step-growth polymerizations with an excess of B groups, we define a parameter r that reflects the ratio of A groups to B groups. If the initial number of A groups is v_A^0 and the initial number of B groups is v_b^0, then

$$r = \frac{v_A^0}{v_B^0}$$

For a reaction mixture with stoichiometric imbalance r at extent of reaction p, the number-average degree of polymerization is given by

$$N_n = \frac{1+r}{1+r-2pr}$$

Critical Thinking Questions:

21. Using this expression, fill in the following table with the expected number-average degree of polymerization for different combinations of r and p values:

	$p = 0.9$	$p = 0.99$	$p = 0.999$
$r = 0.9$			
$r = 0.99$			
$r = 0.999$			

22. On the basis of your answers to the previous question, briefly critique or defend the following statement:

    "Achieving high molecular weights in step-growth polymerizations requires both very precise measurement of the reagents, and reaction conditions which strongly favor the bond-forming reaction."

Exercises:

1. In the stoichiometrically-balanced reactions in models 1 and 2, the number of molecules was equal to the number of unreacted 'A' groups in each step. Is the same thing true for the stoichiometrically-imbalanced reaction in Model 3? Why or why not?

2. In this activity, we only calculated the number-average *degree of polymerization* of the polymers produced in step-growth polymerizations. However, usually, we want to be able to calculate the *molecular weight* of the polymers as well.

    a) In Model 1, we considered a reaction of AB-type monomers. If each monomer had mass m_{AB}, how would you calculate the number-average molecular weight, M_n, of the polymer produced when the extent of reaction is equal to p?

    b) In Model 2, we considered a stoichiometrically-balanced reaction of AA- and BB-type monomers. If the AA-type monomers each had mass m_{AA} and the BB-type monomers each had mass m_{BB}, how would you calculate the number-average molecular weight of the polymer produced when the extent of reaction is equal to p?

       Note: this question is a little tricky - remember that N_n counts monomers*, but in this reaction, not all of the monomers have the same molecular weight. How might you be able to correct for this?*

3. In Model 3, we considered a stoichiometrically-imbalanced reaction of AA- and BB-type monomers. However, another important limit occurs when we have equal numbers of AA- and BB-type monomers, but add in an extra monofunctional reagent "Bx" that can only react on one side.

    In this exercise, suppose that we have v_A^0 'A' groups from AA-type monomers, v_B^0 'B' groups from BB-type monomers, and $v_{B'}^0$ 'B' groups from Bx-type molecules.

    a) Consider the following statements from two students:

        - **Student 1:** *"The total number of 'B' groups is just $v_B^0 + v_{B'}^0$, so we can account for the presence of monofunctional Bx molecules by replacing $r = \frac{v_A^0}{v_B^0}$ with $r' = \frac{v_A^0}{v_B^0 + v_{B'}^0}$."*

- **Student 2:** *"One Bx molecule has the same effect on the degree of polymerization as one BB-type molecule. Since Bx-type molecules have the same effect with half as many 'B' groups, that means that a 'B' group from a Bx molecule is twice as effective at stopping chain growth as a 'B' group from a BB molecule, so we should replace r with $r' = \frac{v_A^0}{v_B^0 + 2v_{B'}^0}$."*

Which student do you agree with, and why?

b) Monofunctional reagents are a common impurity in supplies of difunctional monomers. Briefly explain why this means it is necessary to rigorously purify the starting materials used in step-growth polymerizations.

Chapter 4

Free-Radical Polymerization

Chapter 5

Controlled Polymerizations

Chapter 6

Copolymers

Part III

Polymer Physics

Chapter 7

Conformations of Polymer Chains

Chapter 8

Mechanical Properties of Polymers

Chapter 9

Phase Behavior of Polymers & Their Solutions

Chapter 10

Thermal Properties of Polymers