

POGIL Polymers

*Guided-Inquiry Activities
for Polymer Chemistry and Polymer Physics*

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The current source for these materials is accessible on Github:
<https://github.com/jlaaser/pogil-polymers>

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Part I

Introduction to Polymers

Chapter 1

From Molecules to Polymers

Part II

Polymer Chemistry

Chapter 2

Fundamentals of Polymer Chemistry

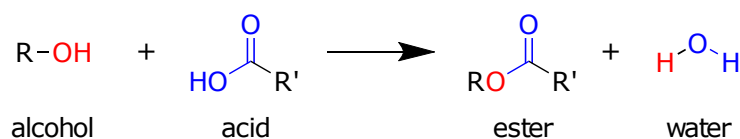
Chapter 3

Step-Growth Polymerizations

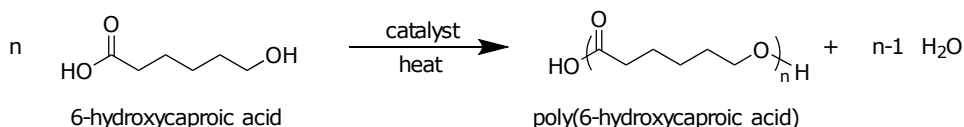
Activity 1: Chemistries of Step-Growth Polymerizations

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:

- Consider the 6-hydroxycaproic acid monomer shown in Model 1:
 - As drawn, what type of functional group is on the *left* side of the monomer?
 - As drawn, what type of functional group is on the *right* side of the monomer?

Information:

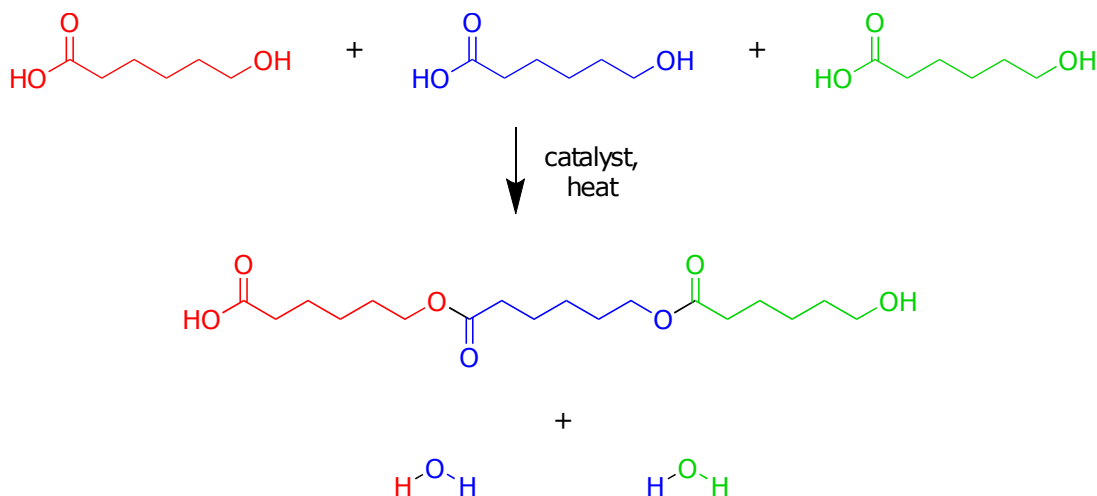
When a monomer used in a step-growth polymerization has different reactive functional groups on each end, it is called an “AB-type” monomer.

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:

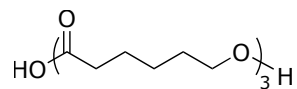


The molecules are color-coded so that you can see which atoms in the oligomer came from which monomer.

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

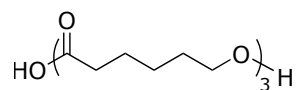
b) Explain, in one or two complete sentences, why you think we classify this polymer as a “polyester”:

c) When we write the structure of this oligomer as

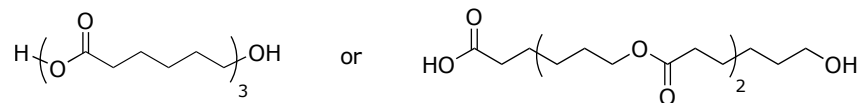


how many monomers make up each repeat unit in the polymer chain?

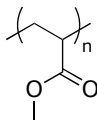
d) Explain, in one or two complete sentences, why we generally abbreviate the product of this reaction as



rather than as



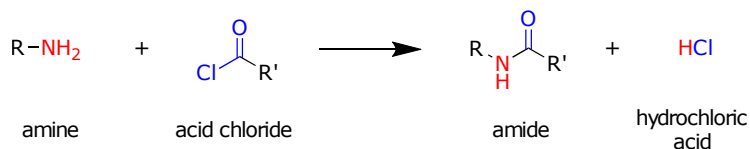
4. Consider the following polymer:



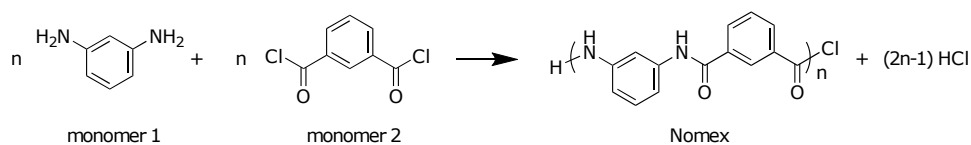
- a) Does this polymer have ester bonds in the polymer backbone?
- b) Would you be able to produce this polymer by esterification reactions of small molecules? Why or why not?
- c) Based on your answers to the previous two questions, would you classify this polymer as a polyester? Why or why not?

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:

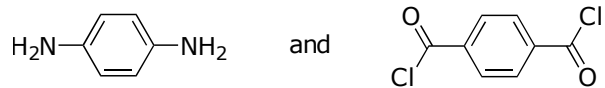
**Critical Thinking Questions:**

- Why is this polymer classified as a polyamide?
- What functional groups does monomer 1 have? Would you classify this monomer as an AA-type monomer or an AB-type monomer?
- 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:

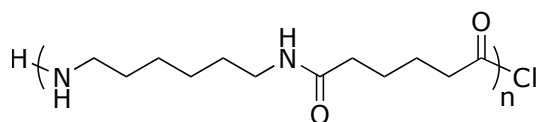
9. How many monomers make up each repeat unit?

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.

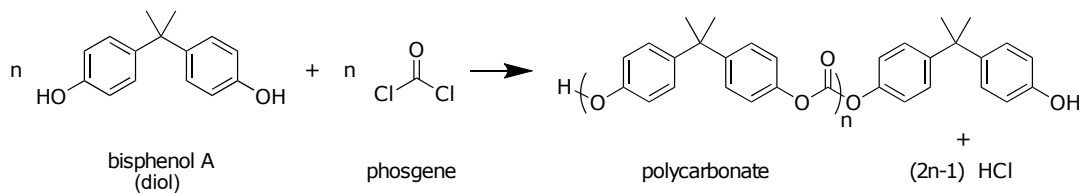
Critical Thinking Questions:

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?

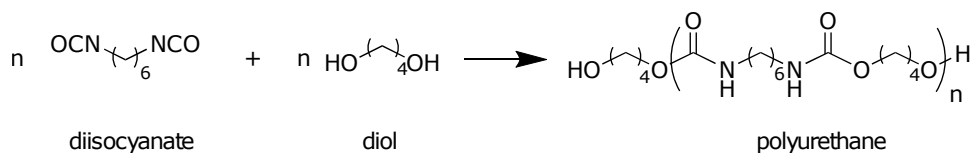
Model 3: Other Chemistries used for Step-Growth Polymerization

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

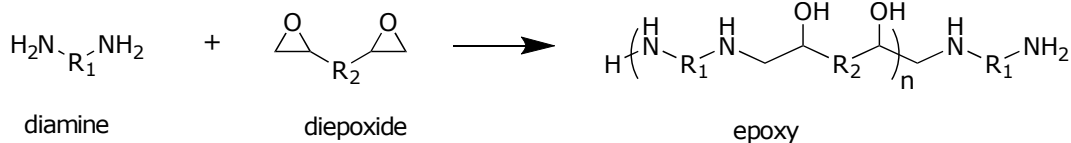
a) polycarbonate (high transparency and impact resistance; used in DVDs, glasses, etc.)



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



c) epoxies (adhesives; coatings)

**Critical Thinking Questions:**

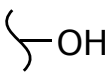
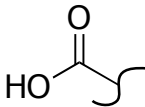
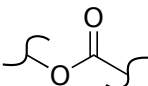
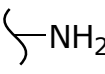
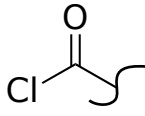
14. Classify each of the reactions in the above Model as either an “AB-type” or “AA+BB-type” polymerization:

a)

b)

c)

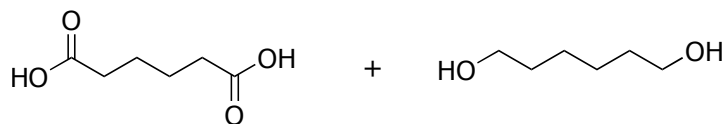
15. Complete the following table for the polymerizations depicted in Models 1-3:

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

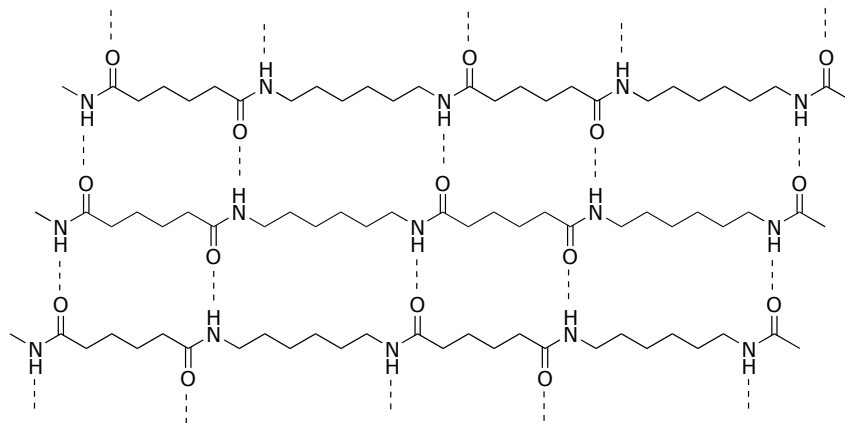
16. Which of the above polymerization reactions would you classify as condensation polymerizations? Briefly explain your answer in 1-2 complete sentences.

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.

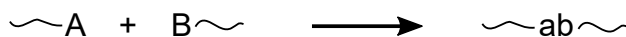
3. The epoxidation reaction shown in Model 3 formed a linear polymer with secondary amines. However, secondary amines can also attack epoxides. Draw out the polymer structure that you would expect to generate if this occurs. How would you describe this polymer architecture?

Activity 2: Degree of Polymerization in Step-Growth Polymerizations

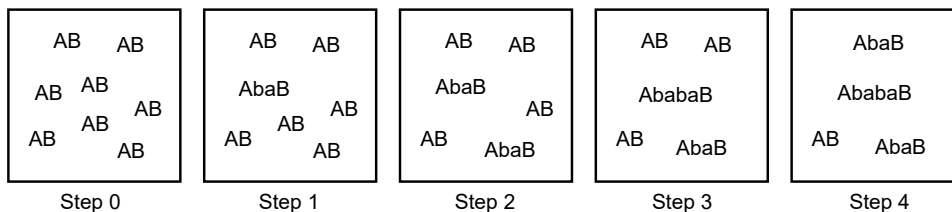
Model 1: Polymerization of “AB”-Type Monomers

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:



In this diagram, each string of letters represents one molecule; each molecule may be either an unreacted monomer (“AB”) or a growing polymer chain (e.g. “AbaB”, “AbabaB”, etc.).

Critical Thinking Questions:

- Fill out the following table for the reaction mixture shown in Model 1:

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
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 $1 - p$.

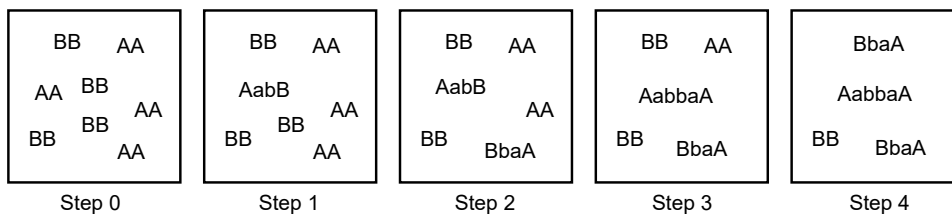
Critical Thinking Questions:

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 8 monomers, 4 of which are “AA”-type monomers and 4 of which are “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.

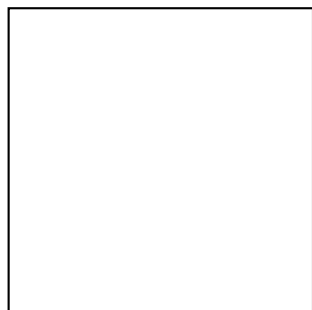
Information:

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

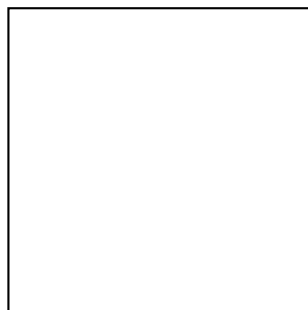
Critical Thinking Questions:

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



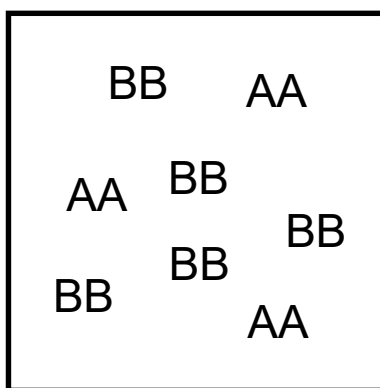
Model 2

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.

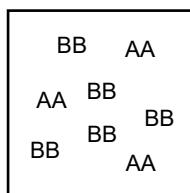
In this model, consider a reaction mixture that starts with 3 AA-type monomers and 5 BB-type monomers:



Step 0

Critical Thinking Questions:

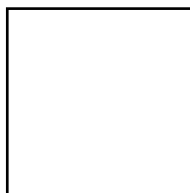
14. Fill in the blank spaces in the figure below with reasonable predictions for what the reaction mixture might look like in each successive step.



Step 0



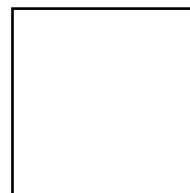
Step 1



Step 2



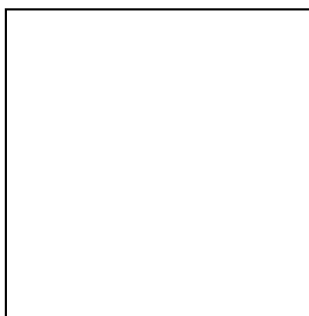
Step 3



Step 4

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. Often, when calculating extents of reaction and degrees of polymerization, our usual rules regarding significant figures don't work well. To see why, do the following:
- a) Rearranging our equation for N_n for a stoichiometrically-balanced reaction and solving for p , we find that $p = \frac{N_n - 1}{N_n} = 1 - \frac{1}{N_n}$.
Using this equation, calculate the extent of reaction necessary to reach each of the following degrees of polymerization. Write out as many digits as your calculator gives you.

N_n	p
10	
100	
300	
320	
1000	
10000	

- b) How many significant figures are given in each of the N_n values in the preceding problem? What value(s) would you get for p if you round your answer following the usual sig fig rules?
- c) In the context of your results, does the “usual” rule for sig figs make sense when calculating extents of reactions? Explain your reasoning in 1-2 complete sentences.
- d) Propose an alternate sig fig rule that would make more sense for calculating extents of reaction.
2. 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?
3. 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?*
4. 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?

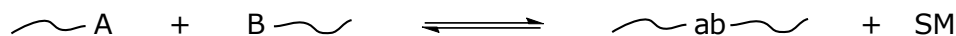
- b) Monofunctional reagents are a common impurity in supplies of difunctional monomers. Briefly explain why this means it is necessary to rigorously purify the starting materials used in step-growth polymerizations.

Activity 3: 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 (\rightleftharpoons) 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 1 to find an expression for K_{eq} in terms of v_A^0 and x .

Note: your expression from question 1 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 1 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 the next question easier, leave the denominator in the form $(1-p)^2$ instead of multiplying it out.

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

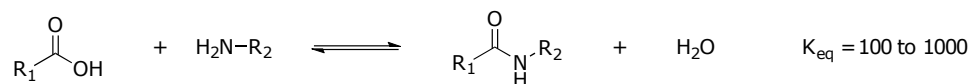
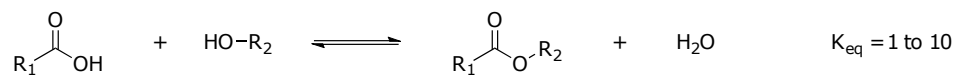
Hint: start by taking the square root of both sides of the equation.

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:**

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

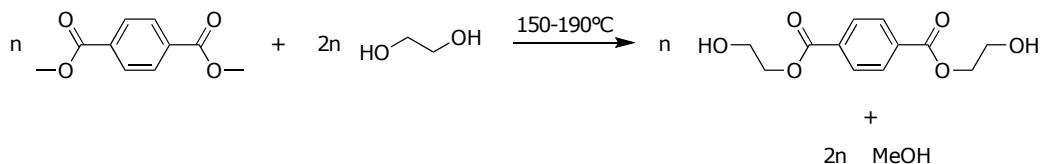
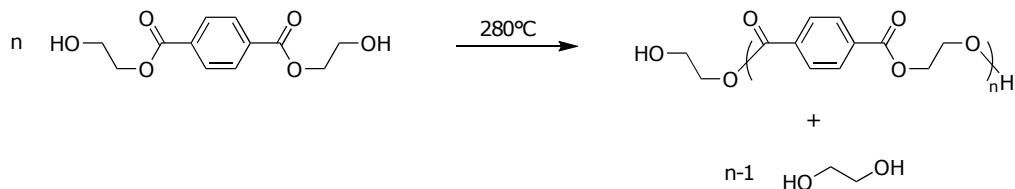
10. Propose at least one way that you could increase the degree of polymerization for polymers produced using the reactions shown in Model 2. Explain your proposed solution in 2-3 complete sentences.

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:

Step 1**Step 2****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:

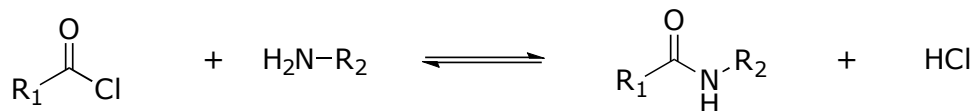
The boiling point of methanol is 64.7°C.

The boiling point of ethylene glycol (HOCH₂CH₂OH) is 196°C.

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?

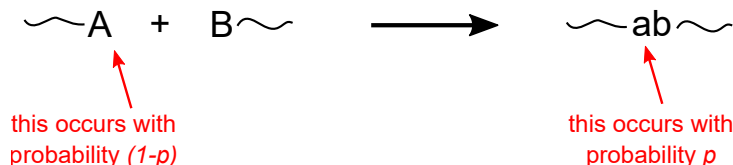
3. Why does the first reaction in Model 3 (i.e. “Step 1”) produce only a small oligomer rather than a large polymer chain? Explain your answer in terms of the reaction stoichiometry.
4. The reactions in Model 3 produce PET by transesterification of AA and BB-type monomers. Propose alternate monomers 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.

Activity 4: Molecular Weight Distributions in Step-Growth Polymerizations

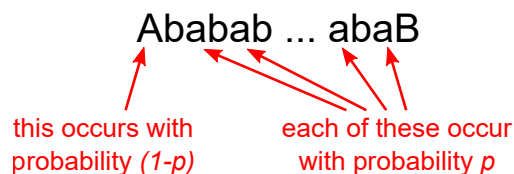
Model 1: Probabilities of Forming Different Chain Lengths

Recall that in a step-growth polymerization of AB-type monomers, the extent of reaction p gives the fraction of 'A' groups that have reacted.

In terms of probabilities, the *probability* that a particular 'A' group reacts (turns into an 'a' group) is p , while the probability that it *does not* react (remains an 'A' group) is $1 - p$:



Each molecule has some combination of unreacted 'A' groups and reacted 'a' groups, each of which occurs with probability p or $(1 - p)$ as appropriate:



The *total* probability of forming this molecule is just the product of the probabilities for each group:

$$P(\text{molecule}) = \underbrace{(p \times p \times p \times \dots)}_{\text{one factor of } p \text{ for each reacted 'a' group}} \times \underbrace{((1-p) \times (1-p) \times \dots)}_{\text{one factor of } (1-p) \text{ for each unreacted 'A' group}}$$

or, more concisely,

$$P(\text{molecule}) = p^{(\text{number of reacted 'a' groups})} \times (1-p)^{(\text{number of unreacted 'A' groups})}$$

Critical Thinking Questions:

1. Consider an AbabaB trimer:

a) How many monomers came together to form this molecule (that is, what is its degree of polymerization)?

b) How many *unreacted* 'A' groups are in this molecule?

- c) How many *reacted* 'a' groups are in this molecule?
 - d) What is the probability of forming an AbabaB trimer?
2. More generally, consider a molecule with degree of polymerization i (that is, a molecule that was made by linking together i AB-type monomers).
- a) How many *unreacted* 'A' groups are in this molecule?
 - b) How many *reacted* 'a' groups are in this molecule?
 - c) What is the probability of forming a molecule with degree of polymerization i ?

Information:

The *probability* that a molecule has degree of polymerization i is the same as the *fraction of molecules* that have degree of polymerization i .

Critical Thinking Questions:

3. Complete the following statement:
- "The fraction of molecules, x_i , that have degree of polymerization i is _____."

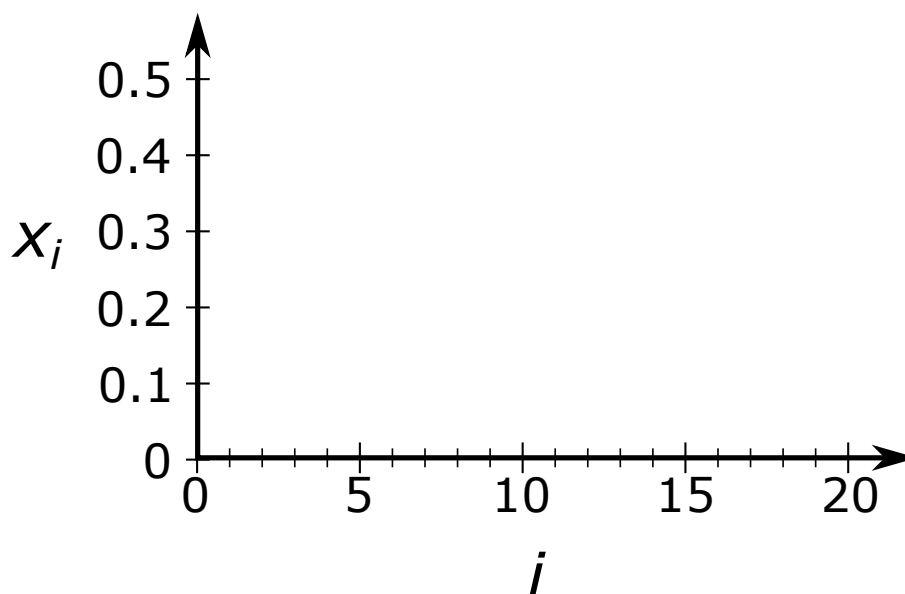
Model 2: Chain Length Distributions

The following table gives selected values of x_i calculated at two different extents of reaction, p , using the expression you derived in Model 1:

i	x_i when $p = 0.5$	x_i when $p = 0.9$
1	0.5	0.1
2	0.25	0.09
3	0.125	0.08
5	0.0313	0.065
10	9.7×10^{-4}	0.0387
15	3.1×10^{-5}	0.0229
20	9.5×10^{-7}	0.0135

Critical Thinking Questions:

4. Plot the data given in Model 2 on the following axes. Make sure to use a different symbol for points corresponding to $p = 0.5$ than for the points corresponding to $p = 0.9$.



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- 42

Model 3: M_n and M_w for Step-Growth Polymerizations

To calculate M_n and M_w , we need to know n_i , or the total number of chains with i monomers.

If we started with v_A^0 monomers, then when the extent of reaction is equal to p , there will be $(1-p)v_A^0$ unreacted A groups left. Recalling that the number of unreacted A groups is equal to the number of molecules in the reaction mixture, this lets us write

$$\begin{aligned} n_i &= (\text{fraction of molecules that have length } i) \times (\text{number of molecules in reaction mixture}) \\ &= (p^{i-1}(1-p)) ((1-p)v_A^0) \\ &= p^{i-1}(1-p)^2 v_A^0 \end{aligned}$$

If we plug this expression into our equation for M_n , we get

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = M_0 \frac{\sum_i p^{i-1}(1-p)^2 i}{\sum_i p^{i-1}(1-p)^2}$$

where M_0 is the molecular weight of the monomer ($M_i = M_0 i$).

Evaluating these sums (see Exercise 2), we obtain

$$M_n = \frac{M_0}{1-p} \quad \text{or} \quad N_n = \frac{M_n}{M_0} = \frac{1}{1-p}$$

which is exactly what we came up with in our previous activity on degree of polymerization.

Similarly, plugging the above expression for n_i into our expression for M_w and evaluating the sums, we obtain

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = M_0 \frac{1+p}{1-p} \quad \text{or} \quad N_w = \frac{M_w}{M_0} = \frac{1+p}{1-p}$$

Critical Thinking Questions:

- Calculate the dispersity for a step-growth reaction with extent of reaction p .

9. What is the value of the dispersity when $p = 0$? Briefly comment on whether or not this answer makes sense.
10. What is the value of the dispersity when $p = 1$?
11. Can the dispersity of a polymer produced by a step-growth polymerization ever be greater than 2? Briefly defend your answer in 1-2 complete sentences.

Exercises:

1. Suppose you synthesized a polymer by step-growth polymerization and found that it had a dispersity of 1.86.
- a) What must the extent of reaction have been in this polymerization?
 - b) What would you expect the number-average degree of polymerization of this polymer to be?
2. Show that the summation expression for M_n given in Model 3 simplifies to the expected result by doing the following:
- a) First, show that the summation expression for M_n given in Model 3 can be rewritten

$$M_n = M_0 \frac{\sum_i i p^{i-1}}{\frac{1}{p} \sum_i p^i}$$

- b) The denominator of this expression is just a geometric series. Recall that if $p < 1$, then

$$\sum_{i=1}^{\infty} p^i = \frac{p}{1-p}$$

Substitute this expression into your equation for M_n and simplify.

- c) The remaining sum can be calculated by differentiating both sides of the equation for $\sum_i p^i$. Carry out this differentiation to show that

$$\sum_{i=1}^{\infty} i p^{i-1} = \frac{1}{(1-p)^2}$$

- d) Finally, substitute this expression into M_n and show that you obtain the expected solution.

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

Activity 5: Viscoelasticity of Polymeric Materials

Model 1: Properties of Silicone Putty

Obtain a small sample of silicone putty from your instructor.

Do the following experiments, and note your observations about how the material responds:

1. Place a small ball of putty on a table, and hit it quickly with your hand.
 - Observations:

2. Hold a small ball of putty approximately 6 inches above your desk and drop it.
 - Observations:

3. Place a small ball of putty on your desk, and let it sit without touching it for 1-2 minutes.
 - Observations:

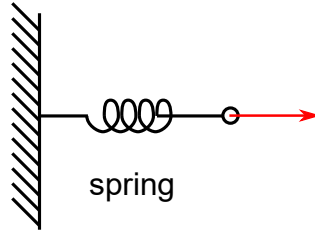
4. Take a small piece of putty and stretch it between your hands. Vary the rate at which you stretch it (quickly vs. slowly).
 - Observations:

Critical Thinking Questions:

1. In which of your experiments would you say the putty behaved more like an *elastic solid*? Briefly explain your reasoning.
2. In which of your experiments would you say the putty behaved more like a *viscous liquid*? Briefly explain your reasoning.
3. How did your observation of solid-like or liquid-like properties depend on the timescale on which you observed it?
4. Explain, in one or two complete sentences, why you think we might describe this putty as a “viscoelastic” material.

Model 2: The Stress Response of Solids

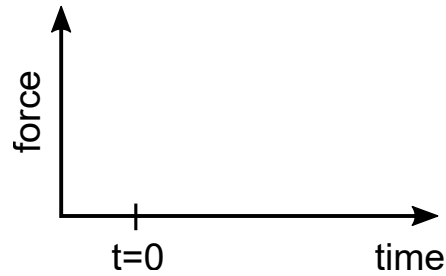
When analyzing the response of elastic solids, we usually represent them as a spring:



An example of an elastic solid that you may be familiar with is a *rubber band*.

Critical Thinking Questions:

5. Suppose you take a rubber band and, at time $t = 0$, you rapidly pull it to twice its original length. You then hold it at its new length.
 - a) On the following axes, sketch the force that you would expect to feel as a function of time:



- b) Qualitatively, how is the force related to the amount of deformation?

- c) Does stretching the rubber band release energy, or require you to put energy in?

6. Suppose that after holding the rubber band at double its initial length for some amount of time, you then let go of the end that you pulled.

a) What do you expect to happen to the rubber band?

b) Does this process release energy, or require you to put energy in?

c) Why might we say that an elastic solid (such as the rubber band) *stores* energy? Briefly explain your answer in 1-2 complete sentences.

Information:

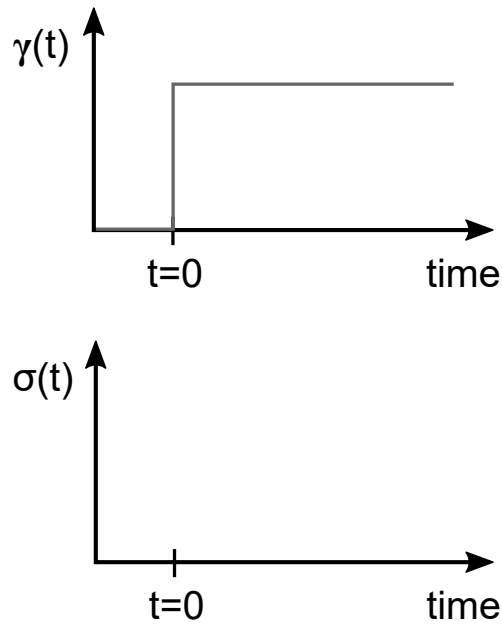
Solid-like materials are typically described in terms of their *modulus*, E (for extensional strain) or G (for shear strain). For an elastic solid subjected to a strain of size ϵ (for extensional strain) or γ (for shear strain), the resulting stress, σ , is directly proportional to the strain:

$$\begin{aligned}\sigma &= E\epsilon \quad (\text{extensional strain}) \\ \text{or } \sigma &= G\gamma \quad (\text{shear strain})\end{aligned}$$

Critical Thinking Questions:

7. The experiment described in question 5 is a *step strain* experiment.

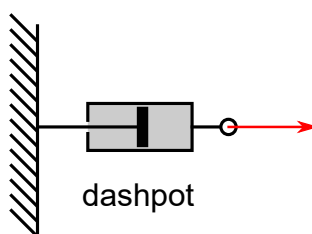
- a) A step-strain profile is shown below. Based on the equations given above, sketch the resulting stress that you expect to measure from an elastic solid undergoing this strain:



- b) Briefly comment on whether or not your sketch from the previous question agrees with what you drew in question 5.

Model 3: The Stress Response of Liquids

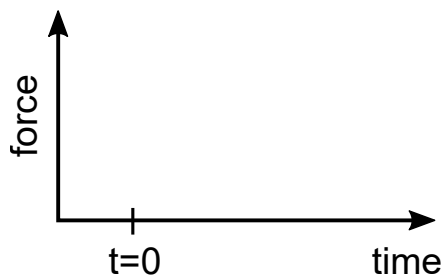
When analyzing the response of viscous liquids, we usually represent them as a “dashpot”:



A dashpot is just a device that contains a piece of material moving through a viscous liquid. An physical analogy for the behavior of a dashpot is moving your hand through a pool of water.

Critical Thinking Questions:

8. Suppose you put your hand in a pool of water. At time $t = 0$, you move it rapidly one foot to the right, and then hold your hand in its new position.
- a) On the following axes, sketch the force that you would expect to feel as a function of time:



- b) Qualitatively, is the force more closely related to the *amount* of displacement, or the *rate* of displacement?
- c) Does moving your hand through the water release energy, or require you to put energy in?

- d) As you hold your hand in its new position, what happens to the force you feel?
9. Suppose that after holding your hand in its new position for some amount of time, you then rapidly move it back to its original position.
- a) Does this process release energy, or require you to put energy in?
- b) Why might we say that a viscous liquid (such as the water in the pool) *dissipates* energy? Briefly explain your answer in 1-2 complete sentences.

Information:

Liquid-like materials are typically described in terms of their *viscosity*, η . For a liquid, the stress is proportional to the strain *rate*:

$$\sigma = \eta \frac{d\epsilon}{dt} = \eta \dot{\epsilon} \quad (\text{extensional strain})$$

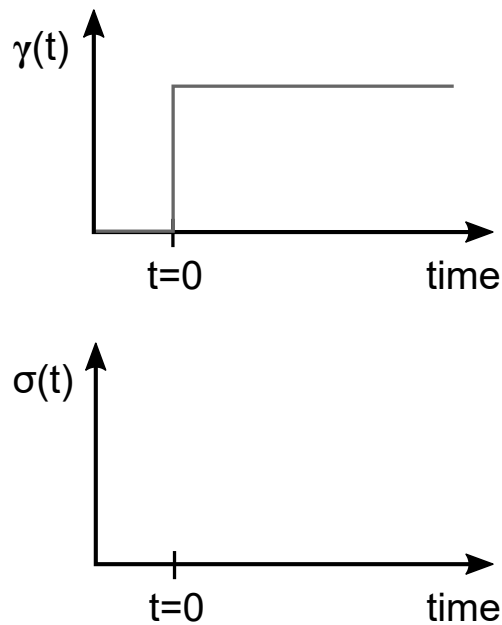
or

$$\sigma = \eta \frac{d\gamma}{dt} = \eta \dot{\gamma} \quad (\text{shear strain})$$

Critical Thinking Questions:

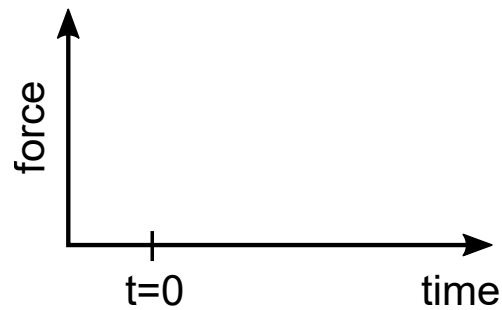
10. The experiment described in question 8 is again a step strain experiment.

- a) Based on the equations given above, sketch the stress you expect to measure from a viscous liquid undergoing a step strain (the strain profile is reproduced below for reference):



- b) Briefly comment on whether or not your sketch from the previous question agrees with what you drew in question 8.

c) Sketch the force that you would expect to feel as a function of time:



Information:

As shown in Exercise 2, the time-dependent stress for a step-strain experiment on a Maxwell element works out to be:

$$\sigma(t) = \sigma_0 e^{-tG_0/\eta_0} \quad \text{or} \quad \sigma(t) = \sigma_0 e^{-t/\tau}$$

where $\tau = \eta_0/G_0$.

Critical Thinking Questions:

12. Is this equation consistent with your prediction from question 11c? Why or why not?

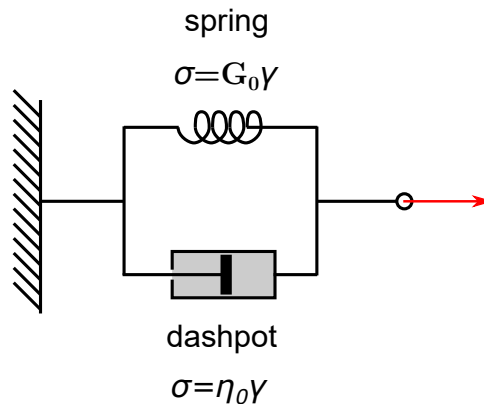
13. At what time t will $\sigma(t)$ drop to $1/e$ of its initial value?

14. Why might we refer to τ as the “characteristic relaxation timescale”? Explain your reasoning in 1-2 complete sentences.
15. The silicone putty that you investigated at the beginning of this activity has a characteristic relaxation timescale of approximately 10 minutes.
- a) On timescales *shorter* than this characteristic relaxation time, did the putty appear to be more liquid-like or more solid-like?
 - b) On timescales *longer* than this characteristic relaxation time, did the putty appear to be more liquid-like or more solid-like?
 - c) In 2-3 complete sentences, briefly summarize the relationship between the characteristic relaxation time, the timescale of your observation, and the perceived liquid-like or solid-like properties of the material.

Exercises:

1. Viscoelastic properties can arise from a number of molecular-scale interactions. Which of the following do you think would give rise to viscoelastic properties in a polymeric material? For each interaction that you think would cause a viscoelastic response, identify the physical process that you think would be most closely associated with the relaxation time of the material.
 - a) Covalent crosslinking of the polymer chains
 - b) Hydrogen bonds (or other “sticky” noncovalent interactions) between polymer chains
 - c) “Tangling” of long polymer chains around each other
2. Derive the step-strain response of the Maxwell element by doing the following:
 - a) Because the spring and dashpot are connected in series, the total strain (γ_{tot}) is the *sum* of the strain in the spring (γ_{spring}) and the strain in the dashpot ($\gamma_{dashpot}$). Write an equation reflecting this relationship.
 - b) Differentiate both sides of this equation with respect to time. Because the strain γ_{tot} is constant at times $t > 0$, what happens to the left-hand side of the equation?
 - c) Using the appropriate relationships for a spring with modulus G_0 and a dashpot with viscosity η_0 , rewrite this equation in terms of the *stresses* in the spring and the dashpot, σ_{spring} and $\sigma_{dashpot}$.
Hint: you will probably find it useful to differentiate the equation for the spring to yield an expression in terms of $\dot{\sigma}$ and $\dot{\gamma}$.
 - d) Because the spring and dashpot are connected in series, they each feel the same stress, σ_{tot} . Rewrite your expression from the previous equation, replacing both σ_{spring} and $\sigma_{dashpot}$ with σ_{tot} .
 - e) The equation you derived in the previous step is a first-order differential equation, whose solution has the form $\sigma(t) = Ae^{Bt}$. Plug this form into the differential equation and find the value of the coefficient B in terms of G_0 and η_0 .
 - f) If, at $t = 0$, the stress is σ_0 , what is the value of the coefficient A ?
 - g) Combine your answers to the previous two questions to obtain an expression for $\sigma(t)$ in terms of σ_0 , G_0 , and η_0 , and verify that it matches the information given in the activity.
3. The Maxwell element is a simple model for viscoelastic liquids, which dissipate all of their stored energy on long timescales. However, it is also possible for materials to be viscoelastic *solids*, which store some energy on long timescales.

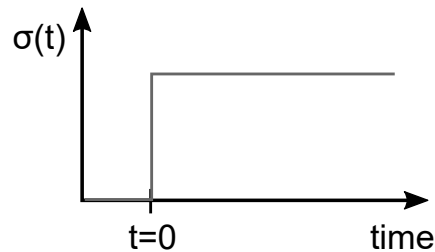
A simple model for the behavior of viscoelastic solids is the Voigt element, in which the spring and dashpot are connected in parallel rather than in series:



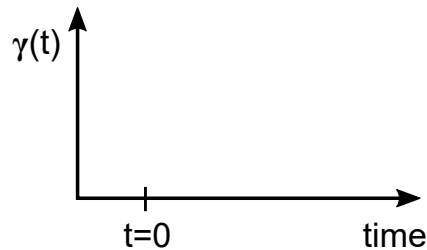
In this case, the total *stress* is the sum of the stresses across the two components, while the total *strain* is identical for each component.

- a) Express the above statement using appropriate mathematical equations.
- b) When considering the Voigt model, we usually consider its response to an increase in stress rather than an increase in strain.

A step-strain strain profile is shown below:



- i. What do you expect to happen in the instant immediately after the stress (force) is applied?
- ii. What do you expect to happen as you continue to apply the force?
- iii. Sketch the strain that you would expect to measure as a function of time:

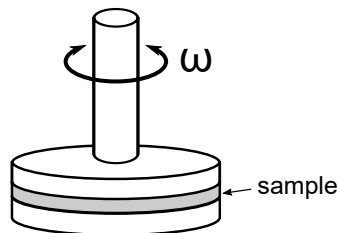


Activity 6: Small-Amplitude Oscillatory Shear Rheology

Model 1: Small-Amplitude Oscillatory Shear Rheology

One of the most common experimental techniques used to characterize the viscoelasticity of polymeric materials is small-amplitude oscillatory shear rheology (SAOS).

In a SAOS measurement, the sample is sandwiched between two surfaces that rotate back and forth at frequency ω , resulting in a sinusoidally-varying strain:



$$\gamma(t) = \gamma_0 \sin(\omega t)$$

The instrument (a rheometer) then measures the resulting force as a function of time, $\sigma(t)$, and breaks it down into two components: one that is proportional to $\sin(\omega t)$ and one that is proportional to $\cos(\omega t)$. The response of the material can thus be expressed as follows:

$$\frac{\sigma(t)}{\gamma_0} = G' \sin(\omega t) + G'' \cos(\omega t)$$

where we have normalized the stress, $\sigma(t)$, by the magnitude of the strain, γ_0 .

Critical Thinking Questions:

1. In this experiment, the strain is proportional to $\sin(\omega t)$.
 - a) Which coefficient, G' or G'' , tells you how much of the response is directly proportional to the applied strain?
 - b) Does this coefficient tell you about the elastic response of the material, or the viscous response of the material?

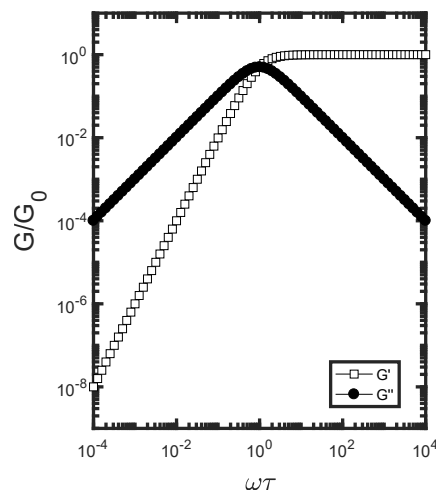
2. Since $\frac{d}{dt} \sin(\omega t) \sim \cos(\omega t)$, the strain *rate* in this experiment is proportional to $\cos(\omega t)$.
- a) Which coefficient, G' or G'' , tells you how much of the response is proportional to the strain rate?
- b) Does this coefficient tell you about the elastic response of the material, or the viscous response of the material?
3. Remembering that elastic responses store energy, and viscous responses dissipate energy, explain why we call G' the “storage modulus” and G'' the “loss modulus” of the material.

Model 2: Dynamic Moduli of the Maxwell Model

As shown in Exercise 2, the storage and loss moduli for the Maxwell Model are given by:

$$G' = G_0 \frac{\omega^2 \tau^2}{\omega^2 \tau^2 + 1} \quad \text{and} \quad G'' = G_0 \frac{\omega \tau}{\omega^2 \tau^2 + 1}$$

A plot of these moduli as a function of frequency is given below:



Note that both axes of this graph are plotted on a log scale; the x axis has been scaled by the characteristic relaxation time, τ , and the y axis has been scaled by the modulus, G_0 .

Critical Thinking Questions:

4. First, consider the low-frequency portion of the response:

a) At low frequencies, which is larger, the storage modulus or the loss modulus?

b) Do low frequency measurements correspond to fast (short) timescales, or long (slow) timescales?

- c) Are your answers to the preceding two questions consistent with your understanding of the relationships between the characteristic relaxation time, the timescale of observation, and the type of properties you should observe? Explain your reasoning in 1-2 complete sentences.

5. Now, consider the high-frequency portion of the response:

- a) At high frequencies, which is larger, the storage modulus or the loss modulus?
- b) Do high frequency measurements correspond to fast (short) timescales, or long (slow) timescales?
- c) Are your answers to the preceding two questions consistent with your understanding of the relationships between the characteristic relaxation time, the timescale of observation, and the type of properties you should observe? Explain your reasoning in 1-2 complete sentences.

6. At what frequency is the storage modulus exactly equal to the loss modulus? Give your answer in terms of the characteristic relaxation time, τ .

Note: you can answer this question using either the graph or the equations, but you will probably find it easier to work from the equations.

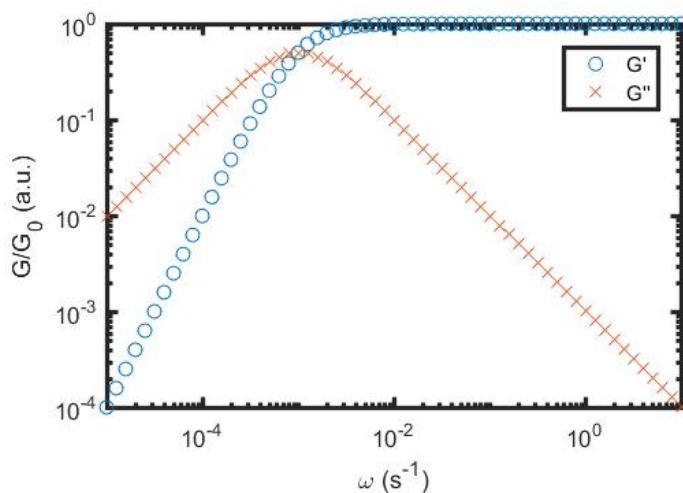
7. The frequency identified in the previous question is called the “crossover frequency”, because it is where the plots for G' and G'' cross each other.

a) Rearrange your answer to the previous question to find an expression for the characteristic relaxation time in terms of the crossover frequency.

b) Propose a method you could use to identify the characteristic relaxation time of a material from an SAOS measurement. Describe your proposed method in 2-3 complete sentences.

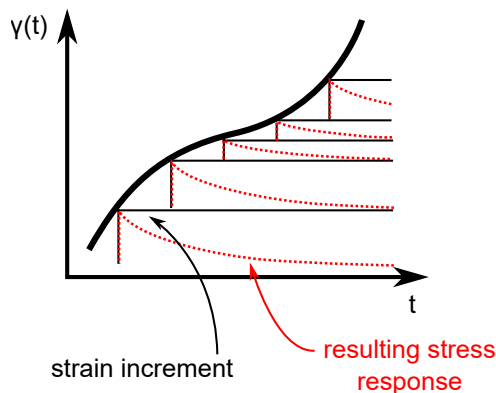
Exercises:

1. Consider the polymer characterized in the following plot:



- a) Find the characteristic relaxation time of this polymer.
- b) If you were to pick up a sample of this polymer, would you expect it to feel more like a liquid or more like a solid? Briefly justify your answer.
Hint: think about how the timescale on which you are observing/interacting with the polymer compares to the relaxation time!
2. In the previous activity we considered step-strain experiments, while in this activity, we considered oscillatory strain experiments. As it turns out, we can *use* the step-strain result to *derive* the oscillatory strain result via the *Boltzmann superposition principle*.

The Boltzmann superposition principle says that we can effectively break down the time-dependent strain into a series of step strains, each of which has their own stress response:



The total stress response of the material is then the sum of each of these individual responses.

Mathematically, we find that for a material whose response to a step strain of size γ_0 is given by $\sigma(t) = G(t)\gamma_0$, the response to an arbitrary strain $\gamma(t)$ is given by

$$\sigma(t) = \int_0^\infty G(t')\dot{\gamma}(t-t')dt'$$

- a) Use this equation to find an expression for $\sigma(t)$ for a material with an arbitrary stress relaxation modulus $G(t)$ undergoing oscillatory strain of the form $\gamma(t) = \gamma_0 \sin(\omega t)$.
Hint: to make the next step easier, you will want to rewrite the cos term in the integral using the angle addition formula $\cos(a+b) = \cos(a)\cos(b) + \sin(a)\sin(b)$.
- b) Use your result to find expressions for the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, of the material.
- c) What is $G(t)$ for the Maxwell model? (*Recall that for the Maxwell model, the initial stress, σ_0 , is equal to $G_0\gamma_0$.*)
- d) Use your answers to the preceding two questions to calculate $G'(\omega)$ and $G''(\omega)$ for the Maxwell model, and verify that your answer are consistent with the results given in Model [2](#).

Chapter 9

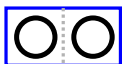
Phase Behavior of Polymers & Their Solutions

Activity 7: Regular Solutions & Flory-Huggins Theory

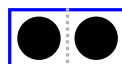
Model 1: Ideal Mixtures: A Toy Model

A simple model for mixing of two small-molecule liquids is shown below. In this model, each molecule is shown as a circle, and we place them in a grid where each molecule takes up exactly one “space” in the grid.

Initially, the molecules of each type are isolated in their own containers:

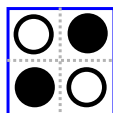


2 molecules of type 1
in 2 spaces



2 molecules of type 2
in 2 spaces

After combining the two containers, the molecules mix together:



2 molecules of type 1
and 2 molecules of type 2
in 4 spaces

The critical elements of this model are that

1. the number of molecules of each type does not change,
2. the molecules each take up exactly the same volume (here, one square on the grid),
3. the total volume after mixing is the sum of the two initial volumes, and
4. the mixing is entirely random.

Critical Thinking Questions:

1. Consider the simple system shown in Model 1, which contains two molecules of type 1 molecules and two molecules of type 2:
 - a) How many different ways can you distribute the two molecules of type 1 in their initial box, assuming the molecules are indistinguishable (you can't tell them apart)? Sketch the possible configurations below. Note that you may not need to use all of the boxes; cross off any you don't need.



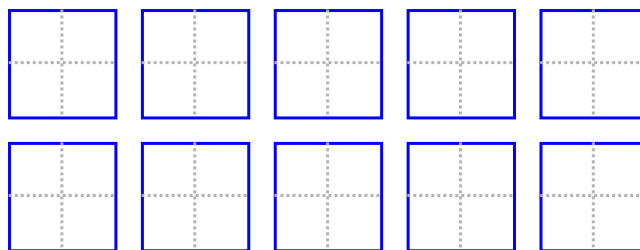
Number of configurations (Ω_1) = _____

- b) How many different ways can you distribute the two molecules of type 2 in their initial box, assuming the molecules are indistinguishable (you can't tell them apart)? Sketch the possible configurations below. Again, you may not need to use all of the boxes.



Number of configurations (Ω_2) = _____

- c) How many different ways can you distribute the four molecules in the final mixture, assuming that you can't distinguish molecules of the same type from each other? Sketch them below. Again, you may not need to use all of the boxes.



Number of configurations (Ω_{mixed}) = _____

2. Recall that if Ω is the number of ways that the molecules in the system can be arranged, then the entropy of that system is given by

$$S = k \ln \Omega$$

where k is the Boltzmann constant. Using this relationship, and your answers from question 1, calculate

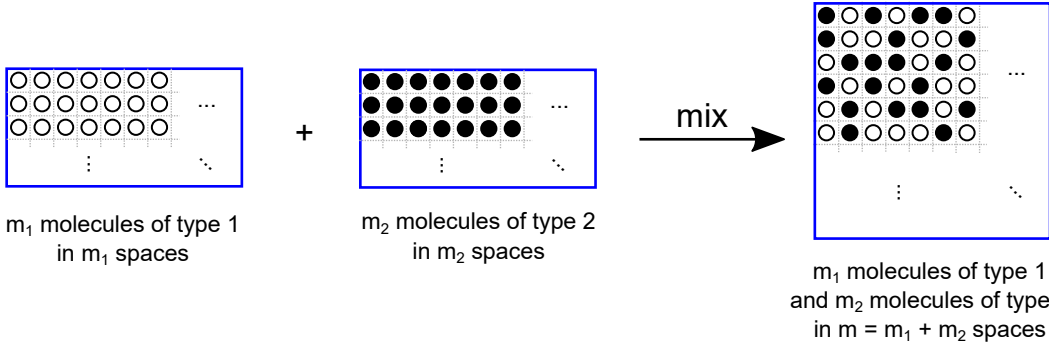
- a) the entropy of the initial state ($S_{initial} = S_1 + S_2$, where $S_1 = k \ln \Omega_1$ and $S_2 = k \ln \Omega_2$):

- b) the entropy of the final (mixed) state, S_{mixed} :

- c) the change in entropy upon mixing ($\Delta S_{mix} = S_{mixed} - S_{initial}$):

Model 2: Ideal Mixtures: The General Case

A more general case of the mixing process described in Model 1 is shown below:



m_1 molecules of type 1
in m_1 spaces

m_2 molecules of type 2
in m_2 spaces

m_1 molecules of type 1
and m_2 molecules of type 2
in $m = m_1 + m_2$ spaces

As you analyze this general case, you will find it helpful to know that mathematically, the number of ways to fill N boxes with n items of one type and $N - n$ items of a second type is

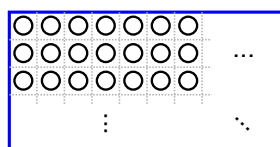
$$\Omega = \binom{N}{n} = \frac{N!}{n!(N - n)!}$$

where $n! = n \cdot (n - 1) \cdot (n - 2) \cdot \dots \cdot 2 \cdot 1$.

Note that by definition, $0! = 1$.

Critical Thinking Questions:

3. Considering *only* the type-1 molecules in the initial state, shown below,



m_1 molecules of type 1
in m_1 spaces

- a) What is N , the number of boxes? (*Note: Do not count the boxes - give your answer in terms of the variables m_1 and m_2 .*)
- b) What is n , the number of type-1 molecules? Give your answer in terms of m_1 and m_2 .

- c) What is $N - n$, the number of type-2 molecules? Give your answer in terms of m_1 and m_2 .

- d) Using the mathematical expression given above, calculate Ω_1 , the number of configurations accessible to the type-1 molecules in the initial state.

- e) Similarly, what is Ω_2 , the number of configurations accessible to the type-2 molecules in the initial state?

- f) What is the total entropy of the initial state?

- 4. For the *final* (mixed) state of the system shown in Model 2,
 - a) What is N , the number of boxes? Give your answer in terms of m_1 and m_2 .

 - b) What is n , the number of type-1 molecules? Give your answer in terms of m_1 and m_2 .

 - c) What is $N - n$, the number of type-2 molecules? Give your answer in terms of m_1 and m_2 .

d) Using your answers to the preceding three questions, calculate Ω_{mixed} , the number of configurations possible for the final (mixed) state.

e) What is the entropy of the final (mixed) state?

5. What is the entropy of mixing, $\Delta S_{mix} = S_{mixed} - S_{initial}$, for the system shown in Model 1?

Information:

Logarithms of factorials can be approximated using Stirling's approximation,

$$\ln N! \approx N \ln N - N$$

Using this approximation, it is possible (after some algebra) to rewrite your expression for ΔS_{mix} as

$$\Delta S_{mix} = -k \left(m_1 \ln \left(\frac{m_1}{m} \right) + m_2 \ln \left(\frac{m_2}{m} \right) \right)$$

Critical Thinking Questions:

6. If you were to double both m_1 and m_2 (thus doubling the total number of molecules, m , while keeping the ratio of type-1 and type-2 molecules the same), what would happen to the value of ΔS_{mix} ?

7. Recall that *extensive* properties are properties that depend on the total number of molecules in the system, while *intensive* properties do not depend on the total number of molecules present.

Based on your answer to the previous question, is ΔS_{mix} an intensive or extensive property?

8. Usually, it is most convenient to divide by the total number of molecules, which leaves us with an intensive expression for the entropy,

$$\Delta S_{mix}^{(int)} = \frac{1}{m} \Delta S_{mix}$$

Write an expression for $\Delta S_{mix}^{(int)}$ in terms of m_1 , m_2 , and m .

9. We also often prefer to work in terms of *mole fractions* rather than numbers of molecules.

Rewrite your expression for $\Delta S_{mix}^{(int)}$ in terms of the mole fractions

$$x_1 = \frac{m_1}{m_1 + m_2} = \frac{m_1}{m} \quad \text{and} \quad x_2 = \frac{m_2}{m_1 + m_2} = \frac{m_2}{m}$$

10. The mole fractions, x_1 and x_2 , must both be between 0 and 1. In this case,

a) Will $\ln x_1$ (and $\ln x_2$) be positive or negative?

b) Will $\Delta S_{mix}^{(int)}$ be positive or negative?

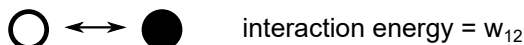
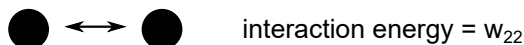
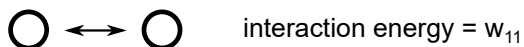
11. Explain, in 1-2 complete sentences, why we say that ideal mixing is an *entropy-driven* process.

Model 3: Real Mixtures: Enthalpy of Mixing

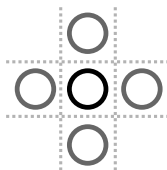
In *ideal* mixtures, such as those described in Models 1 and 2, the molecules do not interact with each other, and entropy is the only thermodynamic consideration that affects mixing. In *real* mixtures, however, molecules do interact with each other, and we must take those interactions into account when determining whether mixing is favorable or unfavorable.

To incorporate the energetics of intermolecular interactions into our model, we must make two key assumptions:

1. First, we assume that molecules interact only with their immediate neighbors, and that each interaction involves only two molecules. The interaction energies between different types of pairs are as follows:



2. Second, we assume that each molecule has some specific number of neighbors, z , which we refer to as the “coordination number”. For example, the central molecule shown below has 4 nearest neighbors, so its coordination number is 4:



Critical Thinking Questions:

12. In the initial state (before mixing),

- there are m_1 molecules of type 1 that each have z neighbors of type 1, for a total interaction energy of $H_1 = m_1 z w_{11}$
- there are also m_2 molecules of type 2 that each have z neighbors of type 2, for a total interaction energy of $H_2 = m_2 z w_{22}$.

a) Why is the total energy for all of the type-1 molecules interacting with their neighbors in the initial state $m_1 z w_{11}$? Explain your reasoning in 2-3 complete sentences.

b) What is the total energy (enthalpy) of the initial state, $H_{initial} = H_1 + H_2$?

13. In the final state (after mixing),

- Each of the m_1 type-1 molecules is surrounded by $x_1 z$ type-1 molecules and $x_2 z$ type-2 molecules
- Each of the m_2 type-2 molecules is surrounded by $x_2 z$ type-2 molecules and $x_1 z$ type-1 molecules.

a) What is the total energy of the interactions between type-1 molecules and their neighbors?

b) What is the total energy of the interactions between type-2 molecules and their neighbors?

c) What is the total energy (enthalpy) of the mixed state, H_{mixed} ?

14. How would you find the enthalpy of mixing, ΔH_{mix} ?

Note: you do not need to write out a full expression in terms of m_1 , m_2 , w_{11} , etc. - it is long! - but clearly specify how you would calculate it.

Information:

The procedure we have just followed led us to double-count most of the interactions, so we need to divide by 2 to correct for this. As with the entropy, it is also useful to divide by m to obtain an *intensive* expression for the enthalpy of mixing.

Doing so, and working through the algebra, we find

$$\Delta H_{mix}^{(int)} = x_1 x_2 z \Delta w$$

where x_1 and x_2 are the mole fractions of type-1 and type-2 molecules, respectively, and Δw is the exchange energy

$$\Delta w = w_{12} - \frac{w_{11}}{2} - \frac{w_{22}}{2}$$

Critical Thinking Questions:

15. From a molecular perspective, how would you interpret the exchange energy, Δw ? Explain your answer in 2-3 complete sentences.

Hint: when we mix the molecules, we break apart 1-1 interactions and 2-2 interactions, and form some number of new 1-2 interactions. How much does the total interaction energy change as this process occurs?

16. It is common to normalize the total energy of the interaction energy between a particle and its neighbors ($z\Delta w$) by the thermal energy, kT . This normalized quantity is defined as the *interaction parameter*, χ :

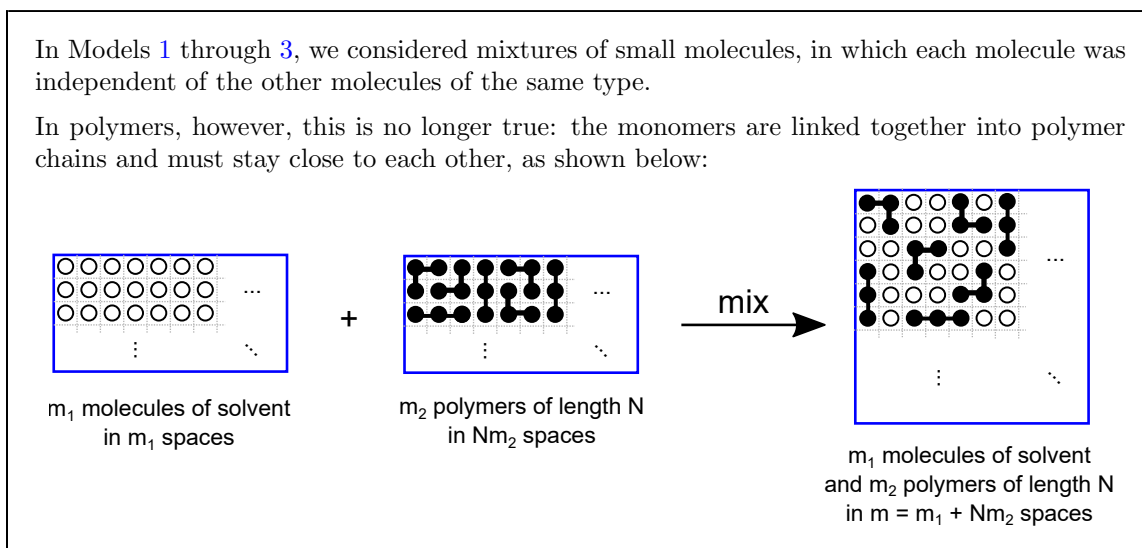
$$\chi = \frac{z\Delta w}{kT}$$

- a) Find an expression for $\Delta H_{mix}^{(int)}$ in terms of x_1 , x_2 , χ , k , and T .

- b) Recalling that $\Delta G = \Delta H - T\Delta S$, combine this expression with your answer from question 9 to find an expression for $\Delta G_{mix}^{(int)}$.

17. In question 10b, we noted that $\Delta S_{mix}^{(int)}$ is always positive, so the entropic term *always* favors mixing. Given that χ is *usually* (although not always) positive, does the enthalpic term usually favor mixing, or oppose it? Briefly explain your answer in 1-2 complete sentences.

Model 4: Polymer Solutions



Critical Thinking Questions:

18. *On average*, when the type-2 molecules are linked into chains...
- a) ... does it *significantly* change the number of ways that the type-1 solvent molecules can be distributed in the final mixture? Why or why not?

- b) ... does *significantly* change the number of ways that the type-2 monomers can be distributed in the final mixture? Why or why not?
- c) ... does it *significantly* change the total number of interactions between type-1 and type-2 molecules? Why or why not?

Information:

Flory-Huggins theory states that for a solution of m_1 solvent molecules (each of which takes up 1 space) and m_2 polymer molecules (each of which take up N spaces) the free-energy of mixing is given by

$$\frac{\Delta G_{mix}^{(int)}}{kT} = \underbrace{\phi_1 \phi_2 \chi}_{\text{enthalpic}} + \underbrace{\phi_1 \ln \phi_1 + \frac{\phi_2}{N} \ln \phi_2}_{\text{entropic}}$$

Note that this expression is given in terms of the *volume fractions* (ϕ_1 and ϕ_2) of each component. As in Models 1-3, ϕ_1 and ϕ_2 represent the *fraction of boxes* filled by each type of molecule; however, since each polymer chain (which we count as a single molecule) fills more than one box, the fraction of boxes is no longer the same as the mole fraction, so we use a different variable to denote it.

Critical Thinking Questions:

19. Based on your answers to questions 18a-18c, why is the entropic contribution from the polymer molecules reduced by a factor of $1/N$ relative to the small molecule case? Explain your answer in 1-2 complete sentences.

20. Qualitatively, do you expect this $1/N$ term to make mixing more or less favorable than in the small-molecule case? Explain your answer in 1-2 complete sentences.

Exercises:

1. Stirling's approximation (page 87) is very useful in polymer physics and statistical mechanics. Derive this formula by doing the following:
 - a) Rewrite $\ln N!$ as a summation of logarithms of individual numbers. Remember that $\ln(a \cdot b) = \ln a + \ln b$, and write your answer in the form $\ln N! = \sum_{i=1}^N \dots$
 - b) Use the trick $\sum_{i=1}^N f(i) \approx \int_1^N f(x) dx$ to rewrite your expression as an integral.
 - c) Evaluate the integral.
 - d) Your answer won't agree exactly with the form of Stirling's approximation given in the exercise. Why, in the limit that N is very large, doesn't the discrepancy matter?
2. Recall from Model 4 that the *volume fractions* ϕ_1 and ϕ_2 give the fraction of boxes filled by each type of molecule.
Write expressions for ϕ_1 and ϕ_2 in terms of m_1 (the number of solvent molecules), m_2 (the number of polymer molecules) and N (the number of monomers per polymer molecule).
3. In Model 4, we considered a polymer solution in which a polymer with degree of polymerization N is mixed with a small molecule solvent.
What expression do you expect you would obtain for $\Delta G_{mix}^{(int)}/kT$ if we instead considered mixing of two polymers, one with degree of polymerization N_1 and the other with degree of polymerization N_2 ?

Activity 8: Thermodynamics of Phase Separation

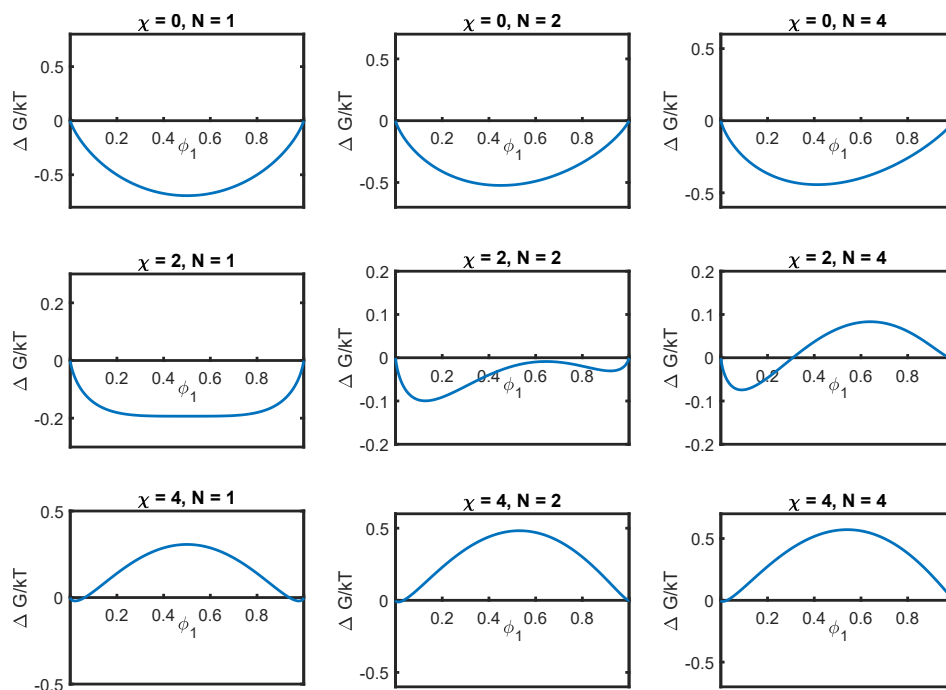
Model 1: Free-Energy Curves for Polymer Solutions

According to Flory-Huggins theory, the free energy of a polymer solution is

$$\frac{\Delta G_{mix}^{(int)}}{kT} = \phi_1 \phi_2 \chi + \phi_1 \ln \phi_1 + \frac{\phi_2}{N} \ln \phi_2$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, N is the degree of polymerization of the polymer, and χ is the interaction parameter.

This expression is plotted for several different χ and N values, below:



Critical Thinking Questions:

1. One of the plots shown in this model corresponds to mixing two identical small-molecule liquids. Which one is it? Briefly justify your reasoning.

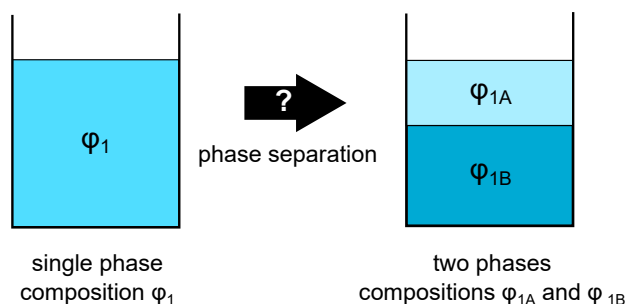
2. Qualitatively, how do the free energy curves change when you...

a) ... increase χ ?

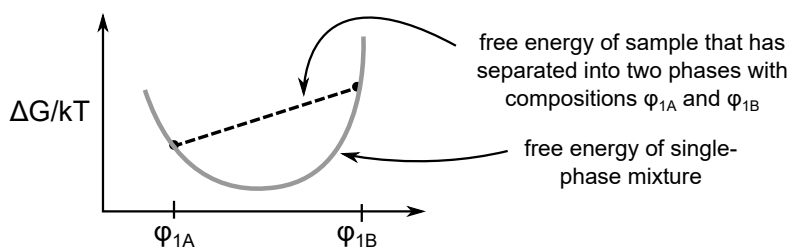
b) ... increase N ?

Model 2: Free Energy Changes on Phase Separation

When a polymer solution is prepared with a specific composition (that is, with a specific value of ϕ_1), it can either remain a homogeneous, single-phase mixture with composition ϕ_1 , or it can phase separate into two new phases with different compositions, ϕ_{1A} and ϕ_{1B} , as shown below:



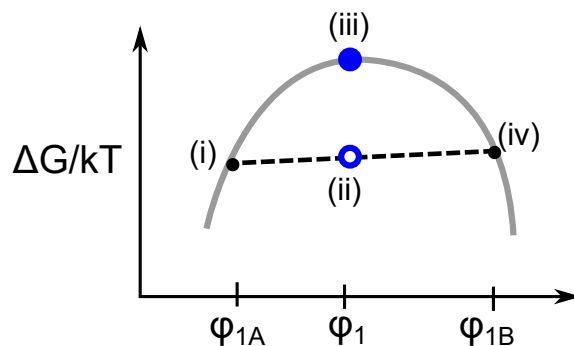
Working through the math, it turns out that the free energy of the phase-separated mixture falls on a line connecting the free energies of the two individual phases:



If the free energy of the phase-separated mixture is lower than that of the homogeneous solution, the mixture will phase separate; otherwise, it will remain a single, stable phase.

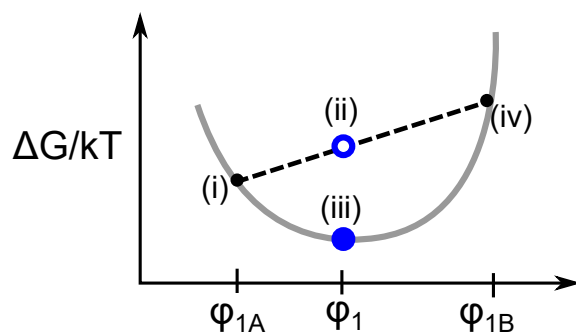
Critical Thinking Questions:

3. Consider a section of a free energy curve that is concave down, as shown below:



- Which point on this plot represents a *homogeneous solution* prepared at composition ϕ_1 ?
- Which point on this plot represents a mixture with total composition ϕ_1 that has phase-separated into two phases with compositions ϕ_{1A} and ϕ_{1B} , respectively?
- Which state has the lower free energy, the phase-separated state or the homogeneous mixed state?
- Will a sample prepared with overall composition ϕ_1 separate into two phases with compositions ϕ_{1A} and ϕ_{1B} ? Why or why not? Briefly explain your answer in 1-2 complete sentences.

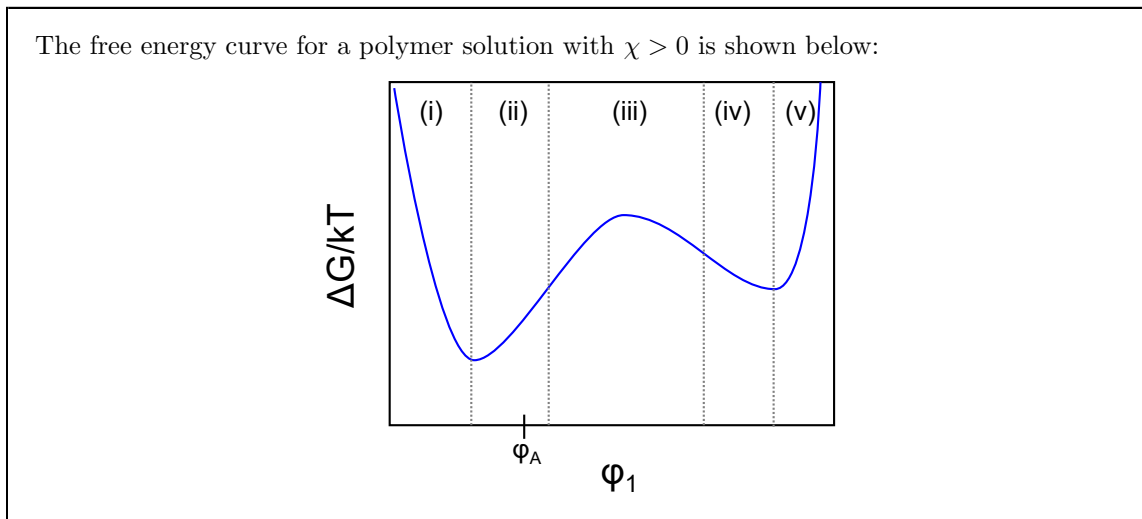
4. Next, consider a section of a free energy curve that is concave up, as shown below:



- a) Which point on this plot represents a *homogeneous solution* prepared at composition ϕ_1 ?
- b) Which point on this plot represents a mixture with total composition ϕ_1 that has phase-separated into two phases with compositions ϕ_{1A} and ϕ_{1B} , respectively?
- c) Which state has the lower free energy, the phase-separated state or the homogeneous mixed state?
- d) Will a sample prepared with overall composition ϕ_1 separate into two phases with compositions ϕ_{1A} and ϕ_{1B} ? Why or why not? Briefly explain your answer in 1-2 complete sentences.

5. We can describe these two cases mathematically by looking at the second derivative of ΔG with respect to ϕ_1 . What is the *sign* of $\frac{\partial^2 \Delta G}{\partial \phi_1^2}$ when...
- a) ... the free energy curve is concave down?

 - b) ... the free energy curve is concave up?
6. Describe, in 2-3 complete sentences, how you could use the second derivative of ΔG to determine whether or not a mixture prepared at a given composition will phase separate.

Model 3: Phase Boundaries for Polymer Solutions**Critical Thinking Questions:**

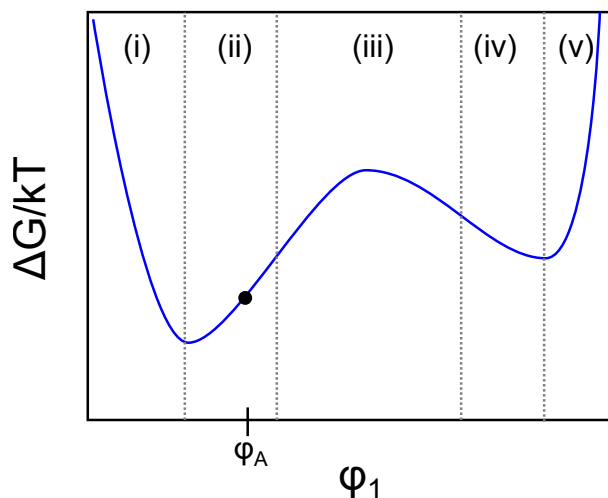
7. In what regions of this plot is the free energy curve...

a) ... concave up?

b) ... concave down?

8. Based *solely* on your answers to question 7, would you expect a mixture prepared with composition $\phi_1 = \phi_A$ to phase separate? Briefly explain your reasoning.

9. Can you draw a line connecting *any* two points on the free energy curve that would pass below the point on the curve at $\phi_1 = \phi_A$? If so, sketch it below:



10. Based *solely* on your answer to question 9, would you expect a mixture prepared with composition $\phi_1 = \phi_A$ to phase separate? Briefly explain your reasoning.
11. Do your answers to questions 8 and 10 agree? Why or why not?

8

Information:

In polymer solutions, there are two different ways we can think about phase separation. First, if there is *any* way to decrease the free energy by undergoing phase separation, then phase separation must be, overall, thermodynamically favorable.

But separating into two phases with very different compositions requires big changes in the local composition, which can be slow, or kinetically unfavorable.

To determine where the *kinetic* limits of phase separation are, we can look at the concavity of the free energy curve:

- If the free energy is concave down, then any small fluctuations in local composition will lower the free energy, promoting rapid phase separation.
- If the free energy curve is concave up, then any small fluctuations in the local composition will increase the free energy and are unfavorable, hindering phase separation.

Thus, even if it is *thermodynamically* favorable for phase separation to occur, it is possible for it to be *kinetically* unlikely. We refer to mixtures that are trapped in this sort of local minimum as *metastable*.

Critical Thinking Questions:

12. In which regions of the plot shown in Model 3 do you expect mixtures to...

a) ... always phase separate?

b) ... never phase separate?

c) ... be metastable?

13. In 2-3 complete sentences, briefly explain your reasoning for the previous question:

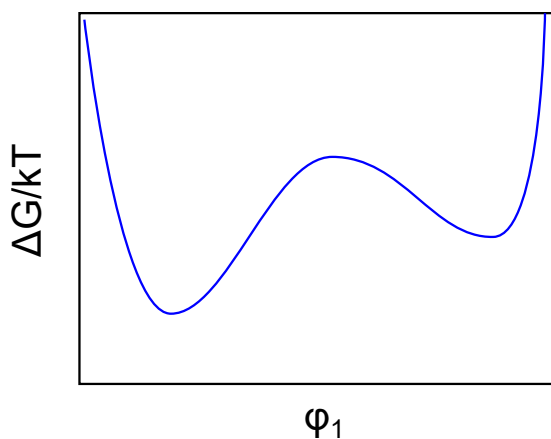
Information:

The points that define the boundaries of the regions that will always spontaneously phase separate are called *spinodal* points.

The points that define the boundaries of the region where phase separation is thermodynamically favorable, even if it might not happen spontaneously, are called *binodal* points.

Critical Thinking Questions:

14. Locate and label the spinodal points (with an “S”) and the binodal points (with a “B”) on the free energy curve shown below:



15. Propose a *mathematical* method that you could use to find the spinodal points of an arbitrary free energy curve. Describe your procedure in 2-3 complete sentences.

Hint: remember that in the concave-up regions, $\frac{\partial^2 \Delta G}{\partial \phi_1^2} > 0$ and in the concave-down regions, $\frac{\partial^2 \Delta G}{\partial \phi_1^2} < 0$. What must be true about this derivative at the points where the curve transitions between concave up and concave down?

16. Propose a *graphical* method that you could use to find the binodal points on the free energy curve. Describe your procedure using 2-3 complete sentences and any diagrams necessary to illustrate your approach.

Exercises:

1. Find the spinodal points for a polymer solution whose free energy is given by

$$\frac{\Delta G_{mix}^{(int)}}{kT} = \phi_1 \phi_2 \chi + \phi_1 \ln \phi_1 + \frac{\phi_2}{N} \ln \phi_2$$

You will find it helpful to remember that $\phi_2 = 1 - \phi_1$.

Chapter 10

Thermal Properties of Polymers

