POLYMER CHEMISTRY

Chris Schaller
College of Saint Benedict/Saint John's
University

LibreTexts™

College of Saint Benedict/Saint John's University

Polymer Chemistry

Chris Schaller

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the hundreds of other texts available within this powerful platform, it is freely available for reading, printing and "consuming." Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects.

Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts’ web based origins allow powerful integration of advanced features and new technologies to support learning.

The LibreTexts mission is to unite students, faculty and scholars in a cooperative effort to develop an easy-to-use online platform for the construction, customization, and dissemination of OER content to reduce the burdens of unreasonable textbook costs to our students and society. The LibreTexts project is a multi-institutional collaborative venture to develop the next generation of open-access texts to improve postsecondary education at all levels of higher learning by developing an Open Access Resource environment. The project currently consists of 14 independently operating and interconnected libraries that are constantly being optimized by students, faculty, and outside experts to supplant conventional paper-based books. These free textbook alternatives are organized within a central environment that is both vertically (from advance to basic level) and horizontally (across different fields) integrated.

The LibreTexts libraries are Powered by NICE CXOne and are supported by the Department of Education Open Textbook Pilot Project, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org. More information on our activities can be found via Facebook (https://facebook.com/Libretexts), Twitter (https://twitter.com/libretexts), or our blog (http://Blog.Libretexts.org).

This text was compiled on 03/10/2025

TABLE OF CONTENTS

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

CHAPTER OVERVIEW

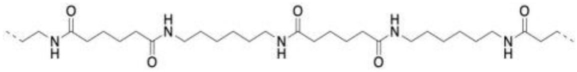
1: Monomers and Polymers

Template:HideTOC

Thumbnail: Space-filling model of a section of the polyethylene terephthalate polymer, also known as PET and PETE, a polyester used in most plastic bottles. Color code: Carbon, C (black), Hydrogen, H (white), and Oxygen, O (red). (Public Domain; Jynto).

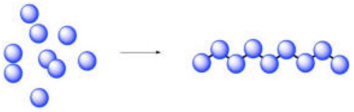
1.1: Difunctional Carboxyloids

The first synthetic polymer to really seize the public's consciousness -- the first one to change the course of world events -- was nylon. Not long after its discovery in the 1930s, it had supplanted silk as the material of choice for stockings, having transformed a luxury item into a widely available commodity. Nylon came just in time for the Second World War. Soon, parachutes, too, went from being made of silk to being fabricated from nylon.

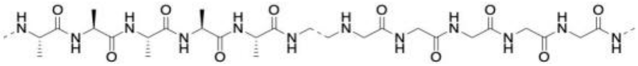


The development of nylon took place at Du Pont's Experimental Research Station in Delaware. For much of the twentieth century, Du Pont and other large companies relied on the pursuit of basic science as an engine of future development. Knowledge was the infrastructure that made future products possible, and so scientists were asked to explore the unknown; the applications of this work would follow naturally.

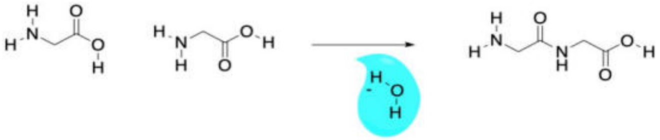
When Wallace Carrothers of Du Pont developed nylon, he had been trying to explore some ideas proposed by Hermann Staudinger at ETH Zurich. These ideas, initially controversial, held that many materials around us, including things like cotton and spider silk, are made of small molecular units covalently bonded to each other. These little molecules, *monomers*, bind together to form immensely long chains. In so doing, the monomers lose their individual identities and simply become repeating units in a long chain. They come together to form *polymers*.



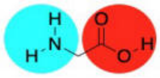
Nylon, in particular, is an example of a *polyamide*. It is composed of very long chains that contain regularly repeating amide bonds, N-C=O. That's the same motif found in proteins in biology, and it's the same pattern found in spider's silk, which is composed of protein.



Conceptually, we are taught in biology class that proteins are made of amino acids. An amide bond (or peptide bond) occurs when the nitrogen of an amine is brought together with the carbon of a carboxylic acid. A molecule of water is lost, and the nitrogen takes the place of the oxygen on the carboxylic acid, forming an amide, instead. The loss of water leads to the term "condensation reaction" because early studies of these reactions led to water forming droplets on laboratory glassware as it bubbled out of the reaction. In practice, industrial nylon production is really no more complicated than that.

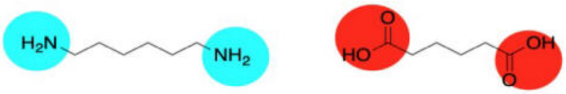


Of course, not just any old amide can become a protein. What makes amino acids special is the fact that they are *difunctional*. They contain not just one functional group (an amine, say, or a carboxylic acid), but two. So, when the amine group of an amino acid bonds with the carbonyl of a neighbour, the carboxyl group can bond to the amine of a different neighbour. It's like it has two hands; it can hold onto a friend with each hand, and each of those friends can hold onto another, and so on, forming a chain.

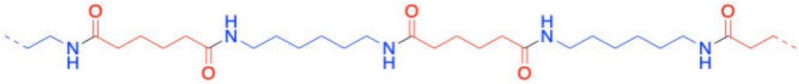


This *functionality* is a key part of how polymers can form. Because difunctional molecules can form bonds in two directions, a simple coupling reaction (an amine plus a carboxylic acid making an amide, two small molecules making another small molecule) becomes a polymerization (many small molecules forming an enormous molecule).

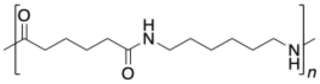
Well, nylon isn't made from an amino acid, although the coupling reaction is similar. Instead, it is made from two different molecules, both of which are difunctional: a diamine and a dicarboxylic acid. The diamine bonds to a neighbouring carbonyl through each end and the dicarboxylic acid bonds to a neighbouring amine through each end. For the most common material, each of the two reactants is six carbons long, giving rise to the term "nylon 66".



Nylon 66 is an example of something called an *alternating co-polymer*. It isn't just one unit repeating over and over along a chain, but two. The two monomers make the polymer together. We sometimes say that the monomers are *enchained* when they become part of a polymer. And of course, they have to alternate along the chain, so that one can bind to the complementary other.



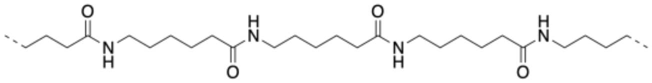
In the drawings above, the dashed lines are meant to suggest continuity: the pattern shown in the drawing keeps repeating to the right and to the left. More commonly, polymers are drawn using parenthetical notation. Below, the part shown in the parentheses is what keeps repeating. If we could make a stamp of that picture, we could construct the polymer chain by simply stamping that image over and over across a sheet of paper.



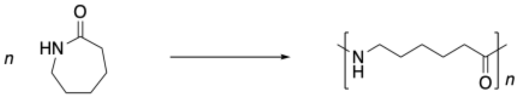
This page titled 1.1: Difunctional Carboxyloids is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller via source content that was edited to the style and standards of the LibreTexts platform.

1.2: Cyclic Carboxyloids

Carothers' development of nylon at Du Pont led indirectly to a very similar polymer that was made in a very different way. Across the Atlantic Ocean, Paul Schlack at IG Farben in Germany was looking for a way to make a similar material that would not be subject to Du Pont's patent. His efforts led to a material called perlon, sometimes referred to as nylon 6.



Nylon 6 is not an alternating co-polymer like nylon 66. It's just a polymer. And it isn't made from a difunctional monomer like nylon 66 or proteins. Instead, it's made from a cyclic amide, sometimes called a lactam. To polymerize, the lactam has to break open into a linear form, and the lactam monomers end up enchained head-to-tail. This process is called *ring-opening polymerization*.

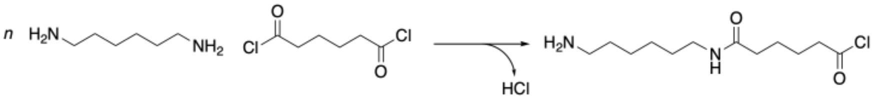


There are a number of things that are different about these two ways of making nylon. One of them turns on the whole concept of synthesis. Synthesis is the act of making things. It's a little like cooking. You gather the ingredients. You take the right amount of this and the right amount of that. You mix them together and you get something wonderful. But that's the difference here: in making nylon 66, Carrothers mixed two different compounds together. He poured one compound out of one bottle and another compound out of another bottle. He mixed them together and he got a polymer.

In contrast, Schlack didn't mix anything together, at least as far as we have seen so far. It all came out of one bottle. So why wasn't it already nylon 6 in the bottle? If the monomers just react with themselves, couldn't they have just gone ahead and done that in the bottle?

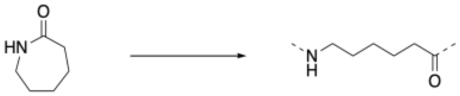
Ring-opening polymerization, at least in this context, is an example of a chain reaction. Chain reactions don't just happen by themselves; they need a jump start.

To understand why, you have to appreciate that these two materials come about through two very different classes of polymerization reactions. Nylon 66 is the product of a condensation reaction. An amine is mixed with a carboxylic acid, water is released, and an amide bond is formed. Even if the pair of reactants is chosen to be more synthetically efficient -- say, an amine and an acid chloride instead of a carboxylic acid -- a condensation reaction still results, in this case releasing hydrogen chloride.

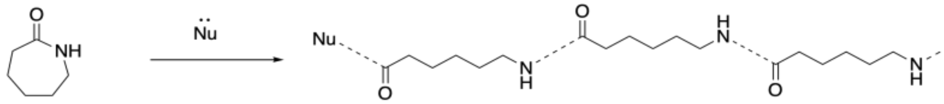


Nylon 6, on the other hand, is not the product of a condensation reaction -- at least at first glance. Look carefully at the monomer and the polymer. Count the atoms. There's nothing missing. No molecule of water or hydrogen chloride or anything else was released. The nitrogen at one end of the chain simply attaches to the carbonyl of the next.

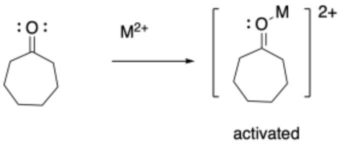
But if you walk down to the end of that chain, until you reach the very last carbonyl, what do you find there? There's no nitrogen attached. That nitrogen was the nucleophile that bound to the carbonyl in the next monomer. There has to be something, though, because the carbon cannot be sitting there with only three bonds. So there must have been some nucleophile that added to that carbonyl, springing loose the amine that added to the next carbonyl, springing the next amine, and so on. There had to be an original nucleophile.



This is the jump start that the chain reaction needed. A nucleophile had to be added to get things going. Once it reacted with the first monomer, the amine became the nucleophile for the next monomer, and that ring-opening produced another amine nucleophile, and so on. Because there is always a new nucleophile produced when the next ring opens, the reaction just keeps going. That first nucleophile, the one that got everything started, is called an *initiator*. The need for an initiator is a hallmark of chain reactions.



In addition to the initiator, ring-opening polymerizations frequently employ catalysts to accelerate the reaction, just as in some condensation polymerizations. The catalyst may be a Lewis acid that activates the carbonyl or an "organocatalyst" that does the same thing via hydrogen bonding. Both catalytic approaches can also make use of nucleophilic catalysis. In that case, the nucleophilic of the nucleophile may be enhanced, or else a temporary nucleophile may add to the carbonyl until it is replaced by the nucleophilic group resulting in enchainment.



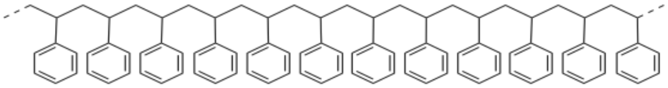
Other polyamides can also be made by ring-opening cyclic amides. The same approach is also used to prepare polyesters from cyclic esters, also called lactones. In that case, the reaction is sometimes called *ring-opening trans-esterification polymerization*, or *ROTEP* for short.

1.3: Olefins

Polyolefins are made from "olefins", which you may know as alkenes. Olefin is an older term for an alkene that is still commonly used in the industry.

These compounds make up a significant fraction of commercially-used polymers today. If you think of the common recyclable plastics, polyethylene (#2 and #4, depending on how the material is made), poly(vinyl chloride) (#3), polypropylene (#5) and polystyrene (#6) are all examples of polyolefins.

Polyolefins have been known for some time, although it took about a century from the time that they were first documented until they were recognized as polymers. German chemists in the mid-1800s were aware that certain tree resins gave rise to hard materials over time, and these materials included polystyrene.



If you compare the repeating structure of polystyrene to the structure of styrene, you can imagine that polystyrene is made from a series of styrene molecules that have been strung together. Essentially, the double bond of styrene has moved to attach to the next molecule, and the double bond there has done the same thing, and so on.

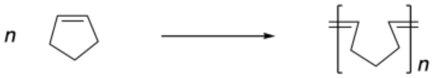
Polyolefins are formed in the same way from a wide variety of alkenes, leading to an array of different materials with properties that are suited to unique applications.

Note that, like ring-opening polymerization, olefin polymerization depends on molecules reacting with other molecules that are just like them. That isn't likely to happen; they will need something to come along and induce reaction between them. Olefin polymerization is thus another case in which monomers are tied together through a chain reaction. The reaction will require an initiator to get things started. That initiator is likely to become an end group, hanging from one end of the polymer chain or the other.

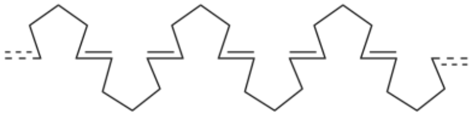
1.4: Cyclic Olefins

Polyolefins are usually made from olefins by tethering one alkene unit to the next, trading in a pi bond within a monomer for a single bond between two repeat units. However, there is another approach that converts cyclic alkenes into polymers. This approach is reminiscent of the ring-opening of cyclic esters and amides.

For example, imagine a cyclopentene ring opening up at the double bond and reaching out to join with other rings on either side of it.



A series of cyclopentene rings that joined together in a row would look something like this:



We would probably draw it in the usual zig-zag conformation.

This act of taking a cyclic alkene, splitting open its double bond, and knitting it together with other such alkenes in a long chain is called *ring-opening metathesis polymerization*. Sometimes it is called *ROMP* for short. It has some things in common with other ring-opening polymerizations, such as ROTEP. In both ROTEP and ROMP, like molecules react together to form a polymer. In ROTEP, it would be two cyclic esters. In ROMP, it would be two cyclic alkenes. That was different from condensation polymerization, which required two complementary molecules, such as a difunctional amine and a difunctional acid chloride.

Partly as a consequence of like molecules reacting together, ROTEP and ROMP are both chain reactions. In order to get the molecules to react with themselves, they need an initiator. The initiator jump-starts the reaction.

Other olefin polymerizations followed this pattern as well. Alkenes don't normally react together (there are some circumstances when they will, but we needn't get into that now, as those events don't usually have anything to do with polymerization). Olefin polymerizations, in general, go through chain reactions that require an initiator to get started.

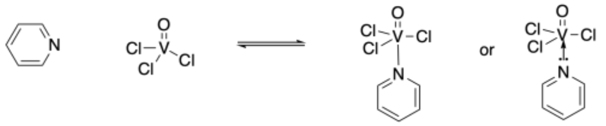
Despite these similarities, ROTEP and ROMP reactions are actually quite different in how they occur, as are regular olefin polymerizations, and the conditions required to initiate polymerization are unique to each case. ROMP requires something called an olefin metathesis catalyst. An olefin metathesis catalyst is a transition metal compound that is capable of splitting the double bond of an alkene in half and putting the two pieces together with other alkenes. The key part of an olefin metathesis catalyst is a metal-carbon double bond. That is the group that is capable of switching the ends of alkenes around with different partners.

1.5: Coordination Polymers

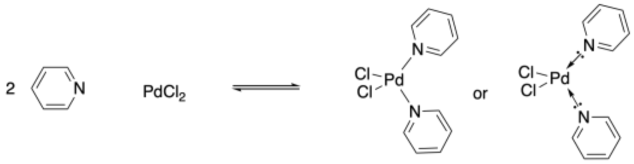
Polymers are long-chain molecules formed from individual molecular building blocks. Typically, the building blocks are organic molecules held together via covalent bonds. What other kinds of building blocks are available?

The formation of coordination compounds is one of many important aspects of inorganic chemistry. In a coordination compound, an electron pair donor, called a ligand, shares its electron pair with a metal atom. Frequently, the metal atom is a transition metal, and very commonly it is a transition metal ion, but there are other examples as well.

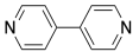
For example, the nitrogen in a pyridine ring has a lone pair. Pyridine can act as a ligand if its lone pair is shared with a metal center, such as the vanadium in trichloro(oxo)vanadium. The lone pair becomes a nitrogen-vanadium bond. Sometimes, this bond is drawn as a short arrow from the lone pair to the vanadium, emphasizing its origin, but more often it is simply drawn as a line, like any other bond.



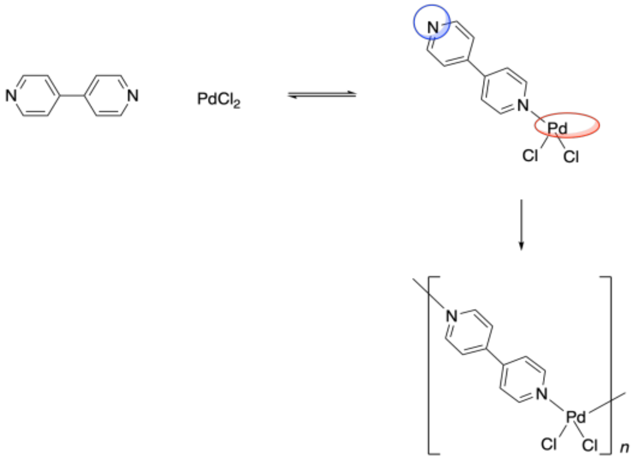
One of the interesting things about metal atoms is their capacity to form variable numbers of bonds. Although palladium dichloride could form a coordination complex by binding with one pyridine ligand, it can also do so with two pyridines. In the former case, it would form a three-coordinate complex, but the latter case would lead to a four-coordinate palladium compound.



Remember, the ability to bond with two neighbouring groups, rather than just one, is an important feature that can allow a small molecule to become enchained in a polymer. The palladium here is a link in a chain that is three units long. What if the ligand also had this capacity to bind to two things? What if, instead of pyridine, the ligand were 4,4'-bipyridine?

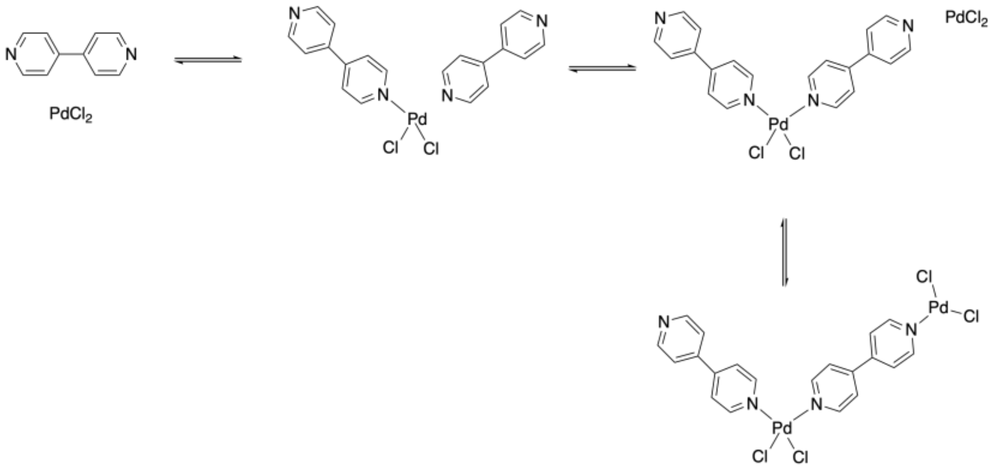


That molecule could bind a palladium atom on either end. Once a bpy (that's an abbreviation for bipyridine, pronounced "bippy") bound to a palladium atom, it would still have a second nitrogen lone pair that it could use to bind another. The palladium, too, would be free to bind a second bpy. As a result, these two monomeric units are able to form an alternating chain.



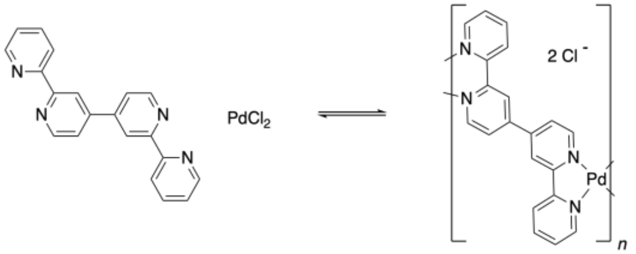
Why would people want to do that? The general idea is to exploit the properties of these metal atoms in new ways. What are metals good at? They are good at conducting electricity, and sometimes they hold useful magnetic properties. If these properties can be incorporated into a material that is more like organic polymers, which tend to be inexpensive and very lightweight, then maybe they can be used to make materials that will have all sorts of applications in everyday life. Metals are also very good catalysts for a wide range of reactions. A coordination polymer serves to space metal atoms out evenly within a structure that has a lot of surface area, which could promote catalytic efficiency. All of these potential uses have driven a great deal of research into coordination polymers in recent years (as well as related "metal-organic frameworks").

Now, can all of the bonds along this metal-ligand chain really hold together to form a polymer? One key difference between the covalent bonds you have seen in organic polymers and the dative bonds here is that dative bonds are reversible. There is always an equilibrium between the metal-ligand complex and the free metal and ligand. Of course, this bond might be very strong, in which case the equilibrium lies toward the metal-ligand complex. In other words, a large fraction of the material would form the metal-ligand complex. How large a fraction? The real value isn't that important at the moment. For our purposes, let's just say we put a metal and a ligand together and 90% of the molecules form a complex. And suppose that's also true in the next step, bringing another ligand into the picture to bind to the metal, and in the step after that, bringing another metal in to bind to the other end of one of the ligands, and so on. So, suppose each of these events leads to 90% product formation.



Just getting to that four-unit chain relies on three different equilibria. If, as we say, each step proceeds about 90% of the way (which sounds pretty good; you would be happy with a 90% yield on a reaction in the lab), then the entire three-step process would yield 0.90 x 0.90 x 0.90 = 0.73, or 73% product. Not bad. But useful polymer chains might be a thousand units long or more, in which case the amount of polymer actually formed of the proper chain length would be about $(0.90)^{999} = 1.94 \times 10^{-46}$ or 1.94×10^{-44} %, and that's a ridiculously small amount.

Now, a real calculation of the equilibrium concentration is of course more sophisticated than that, but this quick exercise underscores an important point: in order to form a stable coordination polymer of an appreciable length, the metal must bind the ligand very tightly. For that reason, many approaches to coordination polymers have employed multidentate ligands, which of course bind more tightly than monodentate ligands. For example, the polymer formed using the bidentate binding shown below would be much more stable with respect to depolymerization (i.e. falling apart into monomers again) than the monodentate example shown earlier.

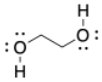


This page titled 1.5: Coordination Polymers is shared under a CC BY-NC 3.0 license and was authored, remixed, and/or curated by Chris Schaller via source content that was edited to the style and standards of the LibreTexts platform.

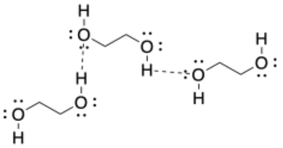
1.6: Supramolecular Assemblies

So far, we have seen how covalent bonds can be used to bind monomers together into longer chains, forming polymers. There has also been a great deal of interest recently in using intermolecular attractions to make similar structures. Of course, intermolecular attractions are very important in forming large, organized structures in biology. Think about the twin helices held together in DNA, or the secondary and higher-order structures in proteins. Clearly, intermolecular attractions can be used to form large, stable structures.

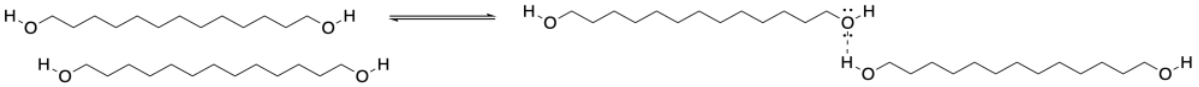
If the goal is to form a chain, analogous to the chains of monomers we have seen in other polymers, then it would be useful to have two sites within a monomer that can interact with other monomers. Such a molecule would be able to hold hands with two other partners, so to speak. If we take hydrogen bonding as an example of a strong intermolecular force, then we can look at a molecule such as ethylene glycol (also called 1,2-dihydroxyethane).



Ethylene glycol looks kind of like ethanol (CH_3CH_2OH) with an extra OH group. A physical sample of ethylene glycol is a colorless liquid, just like ethanol, but there are noticeable differences between the two. The boiling point of ethylene glycol is around 198°C, which is over a hundred degrees higher than that of ethanol. Furthermore, ethanol isn't very viscous; it pours quite easily, but if you tried to stir or pour ethylene glycol you would notice that it seems much thicker. Something is holding those ethylene glycol molecules very tightly together. It isn't hard to imagine the formation of chain structures involving groups of these molecules.

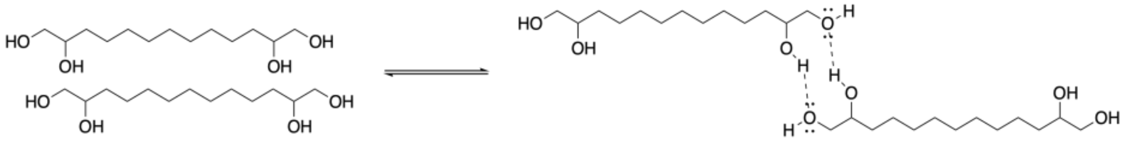


If we look at diols containing longer carbon chains, it's even easier to imagine something that looks kind of like a polymer, with monomers enchained together via hydrogen bonding interactions.



Hydrogen bonds are strong, but they are still just intermolecular attractions, rather than true covalent bonds. They are readily reversible, so any chains that formed via interaction between these diols could depolymerize very easily. Individual diols could readily fall of the end of the chain, and diol chains could just as easily break somewhere in the middle.

What about a tetraol? If there were two hydroxy groups at either end of the chain, then the chain would be much less likely to come apart. Even if one hydrogen bond broke at one of the linkages, there would still be a second one holding two neighbors together. A molecule like that could form a much more stable supramolecular assembly.



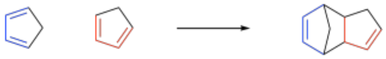
The dynamic nature of supramolecular assemblies is part of what makes them so interesting to researchers. Stable structures that can easily form under one set of circumstances, but gently come apart under another, could have lots of applications. For example, some researchers are interested in developing novel materials, such as liquid crystals, that might be converted from one form into another using different stimuli. Others are trying to develop materials that have useful medicinal and therapeutic applications.

1.7: Other Polymers

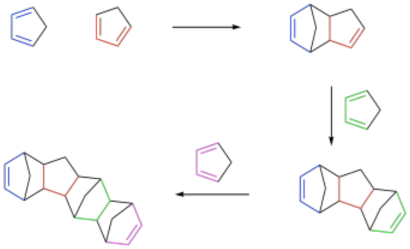
The principle of functionality means that almost any type of organic reaction could potentially be used to make polymers. For instance, if a compound has two functional groups of the same kind, it could undergo reaction at two different sites, forming new bonds with two neighbors. The compound thereby becomes enchained in a trio of formerly independent molecules. If the neighboring molecules are also difunctional, then this pattern can repeat, forming a polymer.

Take the Diels Alder reaction as an illustrative example. On paper, the reaction is fairly straightforward, even if it isn't all that common. A molecule with a pair of conjugated alkenes, the diene, cyclizes with another alkene, the dienophile, to form a new six-membered ring, a cyclohexene.

The diene needs two double bonds but the dienophile only needs one. Nevertheless, what happens if the dienophile has an extra double bond? The Diels Alder adduct that forms would end up with two double bonds: one formed from the original diene, as always, and the other leftover from the dienophile.



The resulting compound is a difunctional alkene. Each end of this molecule could potentially undergo another Diels Alder reaction with an additional diene. Each time that reaction occurs, a new alkene is left behind where the diene used to be, preserving that difunctionality for another step. That difunctionality forms the basis for potential polymer chemistry.

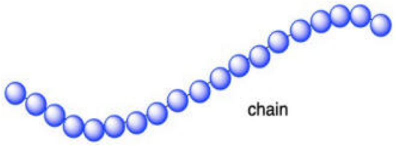


In fact, Diels Alder reactions have been exploited by researchers in a number of ways to make materials with useful properties. The fact that six-membered rings are introduced along the backbone, rather than a chain of single bonds, means that these materials display varying levels of conformational rigidity, resulting in some unique properties.

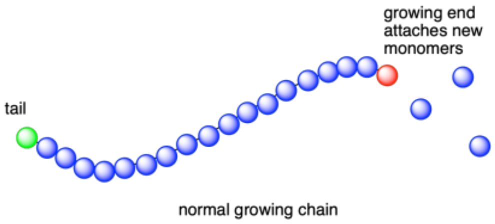
1.8: Polymer Topology

Polymers are very large molecules made from smaller ones. How those smaller units are arranged within the polymer is an issue we haven't addressed very closely yet. Topology is the study of three-dimensional shapes and relationships, or of how individual parts are arranged within a whole. Let's take a look at the topology of polymers.

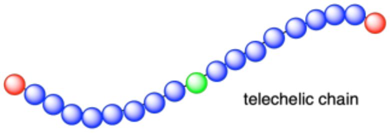
At the simplest level, we have been thinking of polymers as chains of monomers strung together like beads on a string. We even use the verb "enchain" to describe the act of taking a monomer and tying it into a larger polymer. The chain is the most basic of polymer structures. This topology is often referred to simply as a chain or, to underscore the structure, a linear polymer.



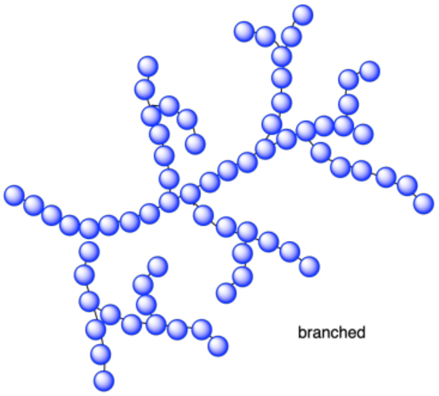
Even a simple chain, in this context, can have additional structural features worth considering. These features are connected to how a polymer chain grows up from individual monomers. If the polymer results from a chain reaction, typically used for the polymerization of alkenes, then the growing chain usually has two distinct ends. One end, sometimes called the tail, is the site of the first monomer to be incorporated into the polymer, as well as some remnant of the initiator to begin the polymerization process. The other end, sometimes called the head but more commonly just the growing end, is the active site, the place where new monomers are about to be enchained into the polymer.



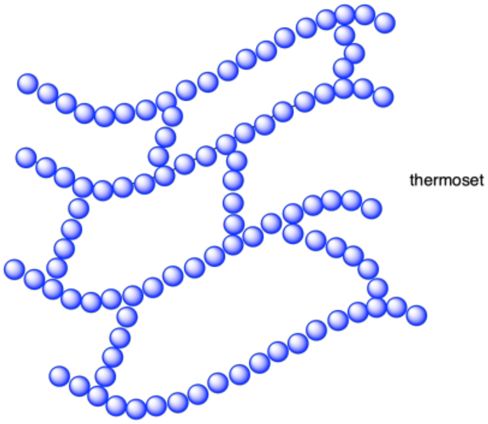
That's what happens in most cases when the initiator is capable of reacting with one monomer and starting the chain reaction. However, sometimes initiators are difunctional. Difunctional initiators are capable of getting two monomers to start growing a polymer chain: one in each direction. In that case, the initiator fragment is left behind in the middle of this new growing chain, which grows outward from the middles. Both ends of the chain are growing ends. In this type of growth, the chain is referred to as "telechelic".



Sometimes, polymer chains do not have simple, linear structures. Instead, their chains branch out here and there. This topology is called "branched". Instead of looking like a snake or a piece of spaghetti, this structure looks more like a length of seaweed. Branching is sometimes an artifact of how the polymer was made, and so sometimes the same monomers may lead to a more linear polymer or a more branched one. The prime example if polyethylene, which can form high-density polyethylene (HDPE) or low-density polyethylene (LDPE) depending on the conditions under which the ethylene is enchained.



In a branched polymer, smaller chains grow out like limbs along a tree trunk or leaves along a stem. We can take that arrangement a step further into something that looks more like a net. In what we call a crosslinked structure, branches connect one main chain to the next, tying them together into one big piece. Sometimes, this type of structure is called a thermoset.



The word "thermoset" is really a description of a physical property of a polymer, in contrast to "thermoplastic". A thermoplastic is a polymer that can be melted and reformed into new shapes after polymerization. In contrast, once a thermoset has been polymerized, it retains its shape even when heated; it doesn't melt. These terms have connotations about the topology of the material, nonetheless.

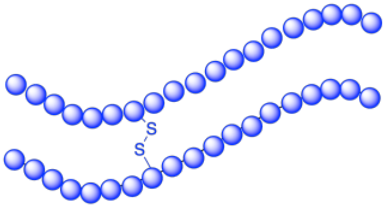
The reason thermoplastics can be melted and formed into new shapes is that they are made of separate molecules. The molecules may be very long, and they may even be branched, but at high enough temperatures these molecules can move completely independently of each other. They can melt and so the material that is comprised of these separate molecules take on new shapes.

In a thermoset, crosslinks connect the different chains in the material, forming bridges that span from chain to chain, essentially uniting the material into one big molecule. If it is one big molecule, the chains can never move completely independently of each other, and the material cannot form a new shape. Looked at in another way, those crosslinks tie the main chains in place. They may be able to move around some, but they can never get very far. If the amount of crosslinking is sufficient, they will always hold the material in the same basic shape.

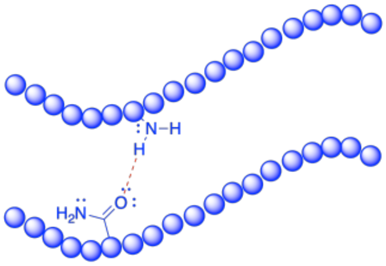
Of course, just a little bit of crosslinking may not have the same effect. You may have two or three chains tied together to form one big molecule, but they behave more like highly branched chains than like extended nets.

It's also worth noting that the term "crosslink" can actually mean different things when used in different ways. Sometimes, crosslinks refer to true covalent bonds connecting two chains together. These connections are called "chemical crosslinks"; the word chemical refers to the covalent bonds. Alternatively, chains can be connected to each other through strong intermolecular forces. That's not at all the same thing, of course, because these intermolecular forces can be overcome with sufficient energy, and so at some point, the chains may no longer be tied together. These connections are called "physical crosslinks" to distinguish them from permanent bonds.

To use a biology analogy, sulfide bonds in proteins would be an example of chemical crosslinks; they hold the protein firmly in one shape, and a chemical reaction is required to break that connection. The ordinary hydrogen bonds that are so prevalent in the protein are physical crosslinks. Because they can be overcome by adding heat, proteins are very sensitive to temperature.

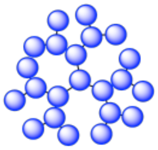


chemical crosslink



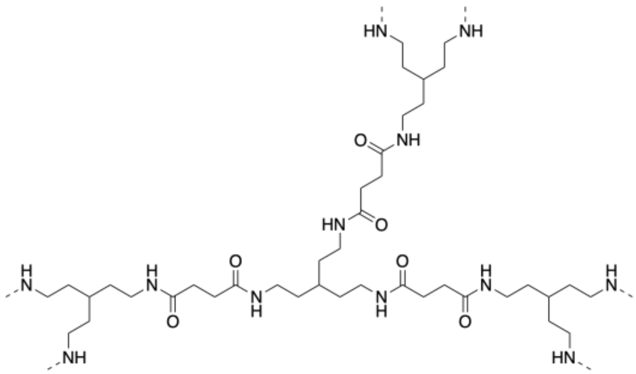
physical crosslink

Dendrimers are another type of branched structure; the term comes from the Greek *dendron* or tree. Dendrimers differ from regular branched polymers in that they have a much more regular branching pattern. A dendrimer will actually grow outward from the center, branching out at regular intervals.



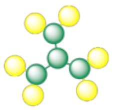
dendrimer

Many dendrimers are polyamides, although there are other types as well. Generally, at least one of the monomers is trifunctional, which introduces the branching in a predictable way.

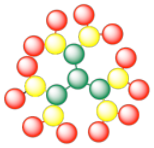


As dendrimers grow outward, layer by layer, they are often described in terms of generations. Suppose you start with a trifunctional monomer in the middle. That's generation 0. If the monomer is polymerized outward until there is another set of trifunctional monomers attached on the edge, we have a first generation dendrimer. If we keep going and add another layer of trifunctional monomers, we have a second generation dendrimer, and so on.

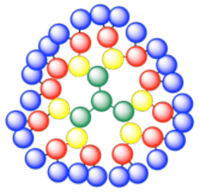
first generation



second generation



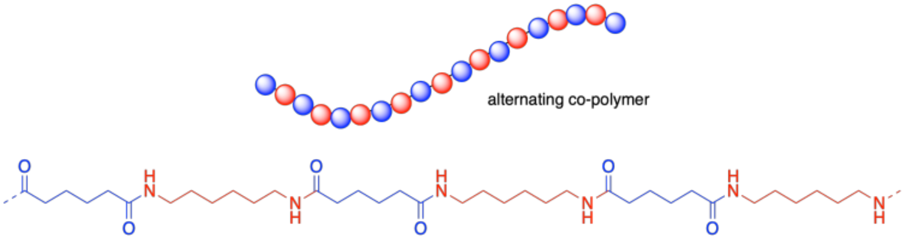
third generation



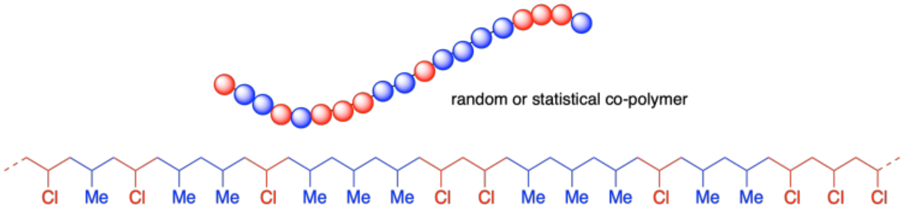
fourth generation

These dendrimers start to look circular on paper, like pancakes, but steric interactions between the groups forces things into three dimensions. As a result, dendrimers are roughly spherical in shape.

In some of the examples of polymers we have seen, the chain is actually composed of two different monomers. That's true in the case of polyamides such as nylon-6,6. In that example, the chain is composed of difunctional amines alternating with difunctional carboxyloids (such as carboxylic acids or acid chlorides). We can think of a polymer like that as being composed of two different monomers. Of course, because of their complementary reactivity they have to alternate: an amine and then a carboxyloid, to form an amide, and so on. We can think of these polymers as "co-polymers", meaning they are formed from more than one kind of monomer. We can go further and say that they are "alternating co-polymers" because the two different monomers alternate with each other along the chain.

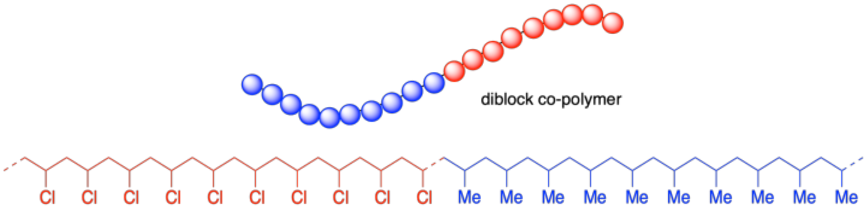


In some cases, there is no need for the two different monomers to alternate the way they do in nylon-6,6. If you take a mixture of alkenes that are capable of forming polymers and you polymerize them together, you may well get them randomly enchained into a growing polymer. This arrangement is called a "random co-polymer" or sometimes a "statistical co-polymer". For example, maybe you manage to get a random sequence of propene and vinyl chloride units along with the polymer.



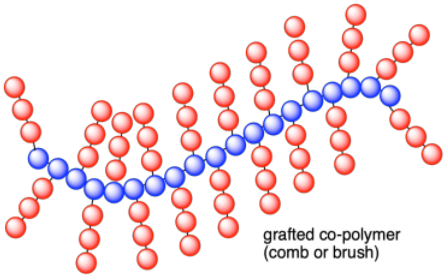
Notice that in the above example we still have the same zig-zag main chain in the polymer; all that changes between one monomer and the other is the group attached to that main chain. It is sometimes useful to think about this main chain or "backbone" separately from the attached or "pendant groups". In this case, we have what looks like a polyethylene backbone with pendant chlorides or methyls randomly attached.

A random arrangement isn't the only possibility. Maybe all of the vinyl chlorides polymerized in a row, and then all of the propenes were incorporated after them. The result would be a diblock co-polymer; there is a solid block of poly(vinyl chloride) at one end of the chain and a solid block of polypropylene at the other end.



There are a couple of ways that could happen. Maybe you waited until all of the vinyl chlorides were enchained before adding any propene so that all of the vinyl chlorides were enchained at the tail end and the propenes were added at the growing end later. Alternatively, maybe you added them all at once but the vinyl chlorides just underwent polymerization a whole lot faster than the propenes; the vinyl chlorides all became enchained before the propenes had a chance.

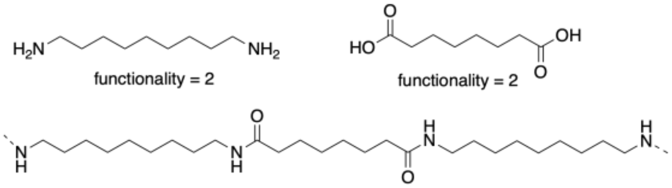
Those possibilities assume that the monomers are all enchained linearly. There are other possibilities. Maybe one set of monomers form the polymer backbone and the other set form pendant branches along the chain. That arrangement is called a "graft co-polymer", as though we have little apple trees grafted onto the trunk of another breed.



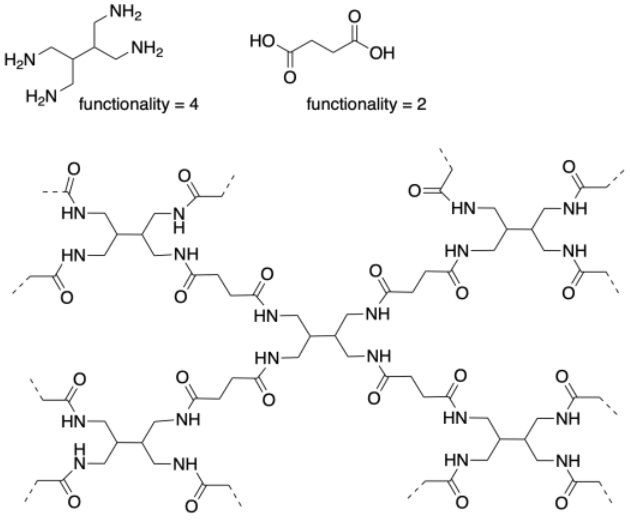
1.E: Solutions for Selected Problems

Problem MP1.1.

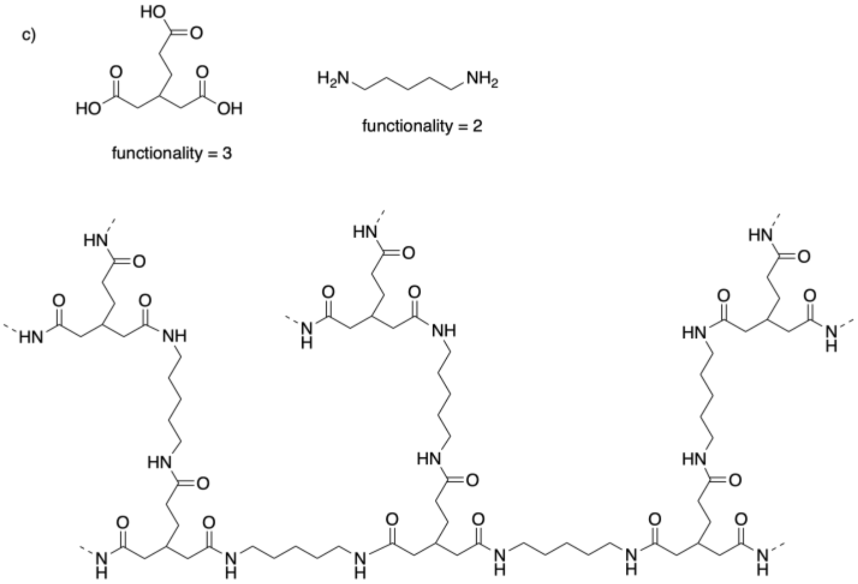
a)



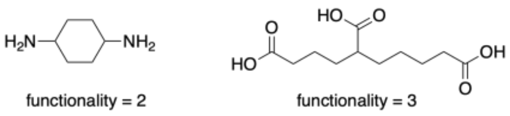
b)

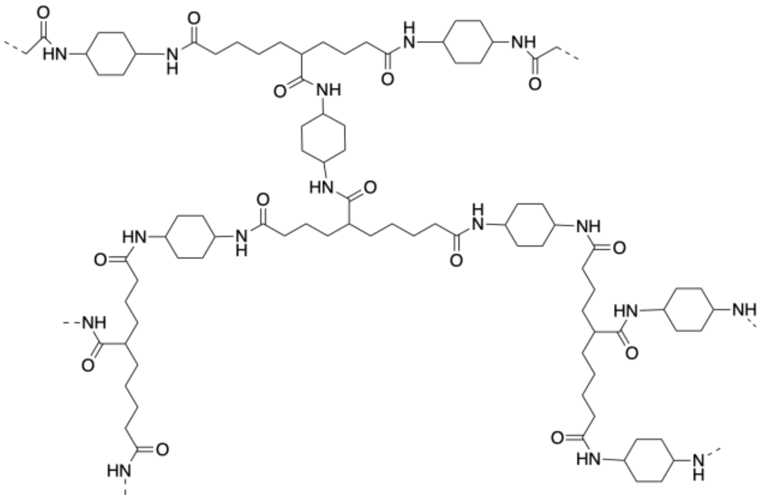


c)

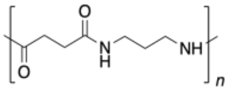


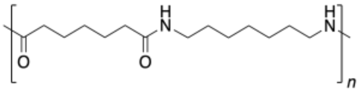
d)

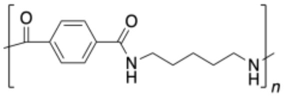


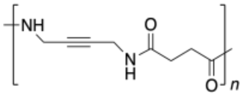


Problem MP1.2.

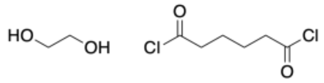
a)


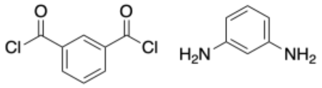
b)


c)


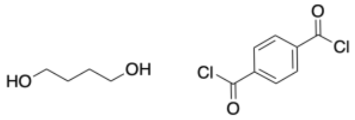
d)


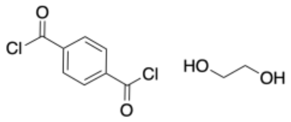
Problem MP1.3.

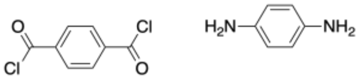
a)


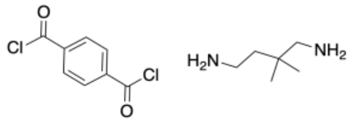
b)


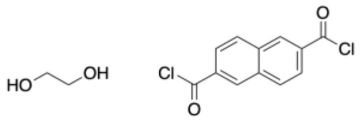
c)


d)


e)


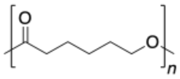
f)


g)


h)


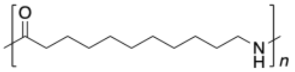
Problem MP2.1.

a)



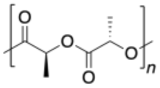
poly(caprolactone)

b)



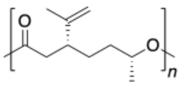
poly(laurolactam)

c)



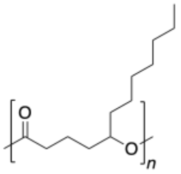
poly(*D*-lactide)

d)



poly(dihydrocarvide)

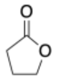
e)



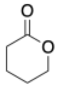
poly(δ-dodecalactone)

Problem MP2.2.

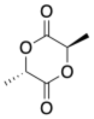
a)



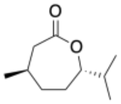
b)



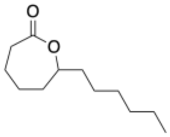
c)



d)

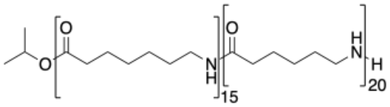


e)

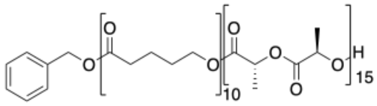


Problem MP2.3.

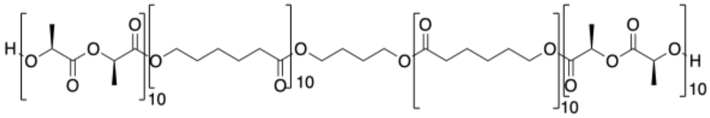
a)



b)

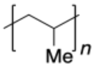


c)

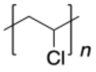


Problem MP3.1.

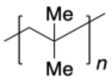
a)



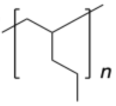
b)



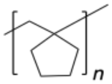
c)



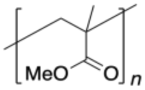
d)



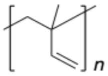
e)

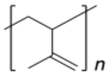


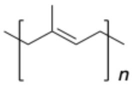
f)

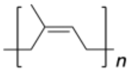


Problem MP3.2.









Problem MP4.1.

a)

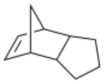
b)

c)

d)

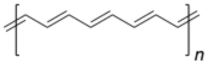
e)

f)

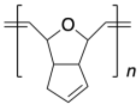


Problem MP4.2.

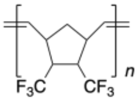
a)



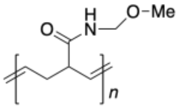
b)



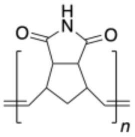
c)



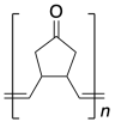
d)



e)

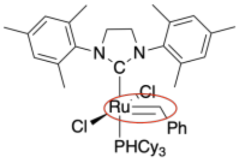


f)

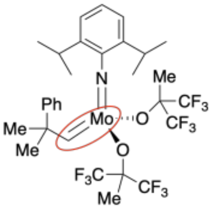


Problem MP4.3.

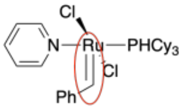
a)



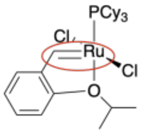
b)



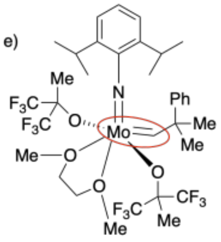
c)



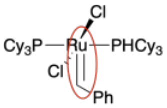
d)



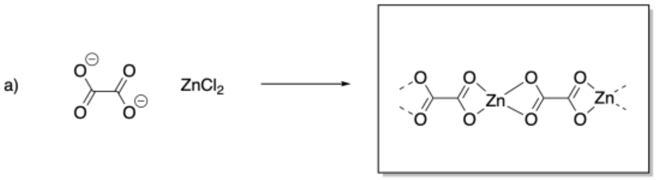
e)

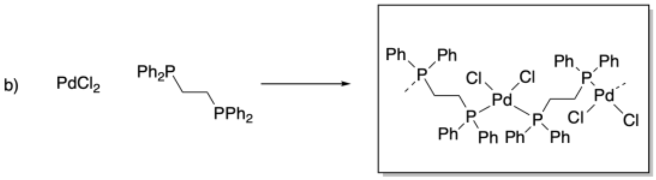


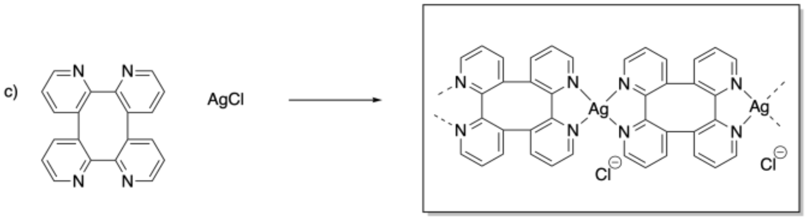
f)



Problem MP5.1.



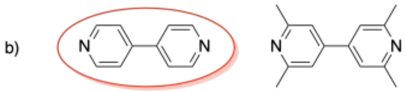




Problem MP5.2.

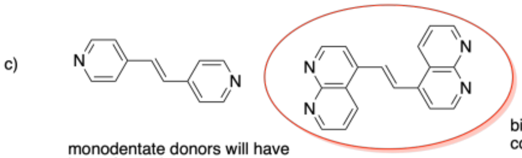
difunctional; could form polymer

monofunctional; will not
form polymer



more sterically crowded; will have lower formation
constant

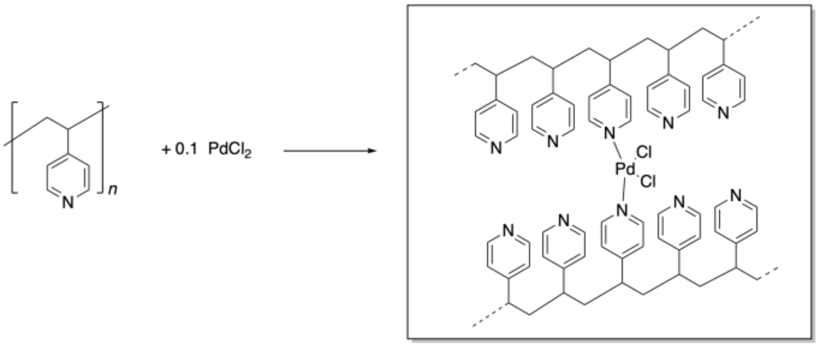
less sterically crowded; will have
higher formation constant



bidentate donors will have higher formation
constant

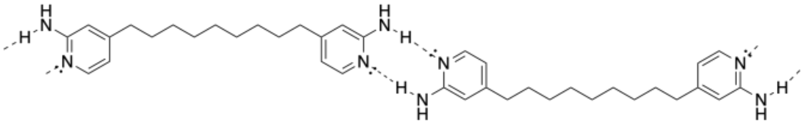
monodentate donors will have
lower formation constant

Problem MP5.3.

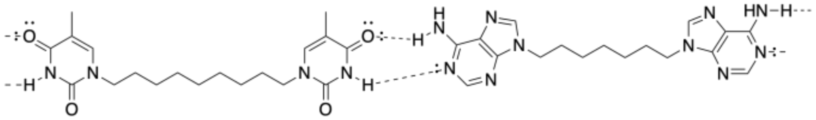


Problem MP6.1.

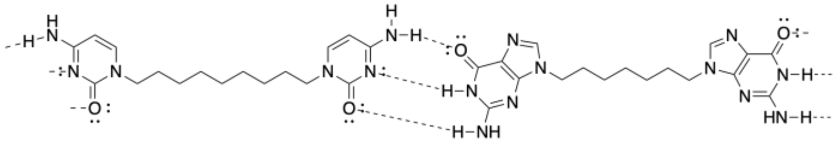
a)



b)

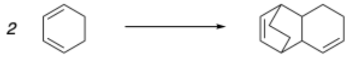


c)

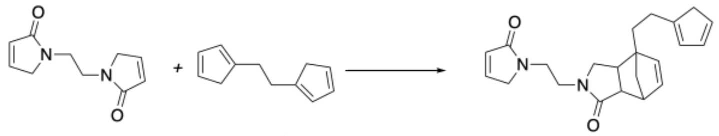


Problem MP7.1.

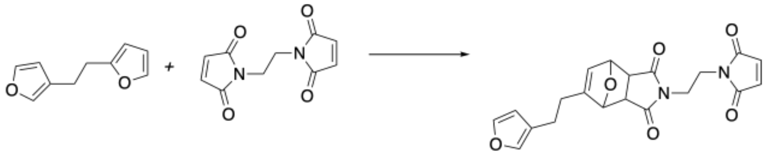
a)



b)

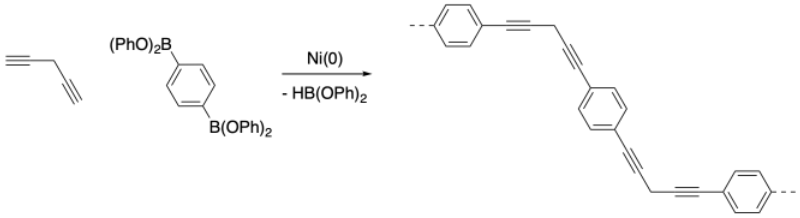


c)

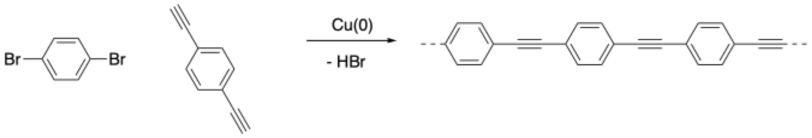


Problem MP7.2.

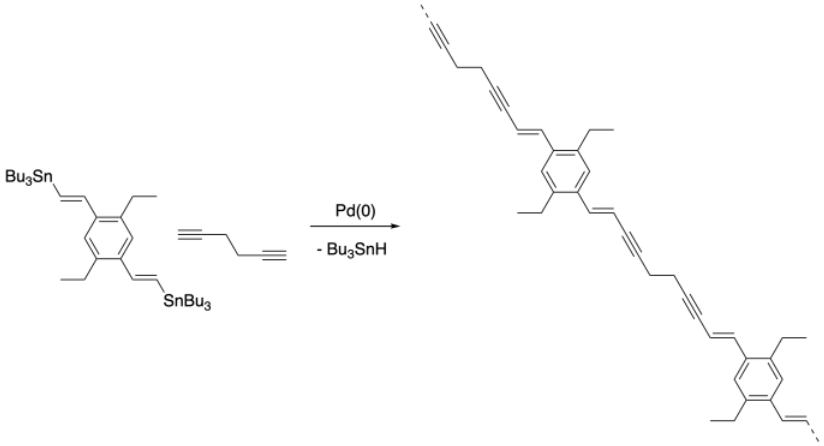
a)



b)



c)



CHAPTER OVERVIEW

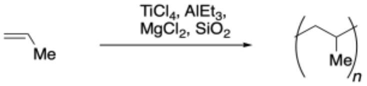
2: Synthetic Methods in Polymer Chemistry

2.1: Ziegler-Natta Polymerization

There are alkenes that do not give rise to cations stable enough for cationic polymerization, and don't form stable enough anions for anionic polymerization, either. The two most prominent examples are ethene and propene. Nevertheless, ethene and propene are the most common feedstocks for polymers, with about 100 millions tons of global polyethylene production annually, and around 50 million of polypropylene. So, how do we make such huge quantities of polyethylene and polypropylene?

These monomers are instead polymerized via an organometallic cycle of alkene associations and 1,2-insertions, so that the last alkene becomes part of a metal alkyl group ready to undergo insertion with the next alkene that binds the metal. This process was developed in 1952 by Karl Ziegler at the Max Planck Institute for Coal Research in Mulheim, Germany. The method was later improved by Giulio Natta at Milan Polytechnic.

Commonly used industrial conditions for Ziegler-Natta polymerization employ a multi-component system. There is always an early transition metal catalyst, from the left-hand side of the d-block of the periodic table. Typically this catalyst is $TiCl_4$ or $TiCl_3$; under the reaction conditions, $TiCl_4$ is probably reduced to $TiCl_3$ anyway. This catalyst is supported on other metal halides such as $MgCl_2$. In heterogeneous catalysis, a support is a layer which strongly interacts with the catalyst, tuning its properties; exactly how that works is somewhat complicated. The catalyst and support are deposited on a solid carrier, such as silica, SiO_2, which distributes the catalyst, increasing the usable surface area. In addition, the carrier may modify the three-dimensional space around the catalyst, providing a binding pocket for the catalyst and the substrate, for example. Finally, the system needs an activator, which is a p-block metal alkyl such as triethylaluminum. This compound transfers a starting alkyl group to the catalyst and may also reduce the transition metal species.



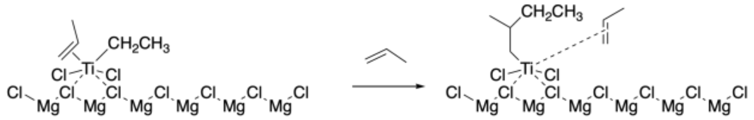
A Ti(III) rather than Ti(IV) catalyst has the advantage of being better able to bind the alkene substrate. Ti(IV) is a d^0 species, and d^0 metals are typically incapable of binding alkenes. The relatively weak π-bond donation to a metal is normally augmented by back donation from an occupied metal d orbital into the alkene π* orbital.

Exercise 2.1.1

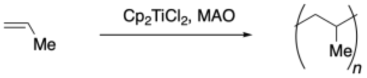
Let's take a look at some alternative Ziegler-Natta reagents. Identify each component as a possible catalyst, support, carrier or activator.

a. $ZrCl_4$
b. EtLi
c. $Mg(OEt)_2$
d. Al_2O_3
e. $AlMe_3$
f. $CrCl_6$
g. VCl_5
h. MgO

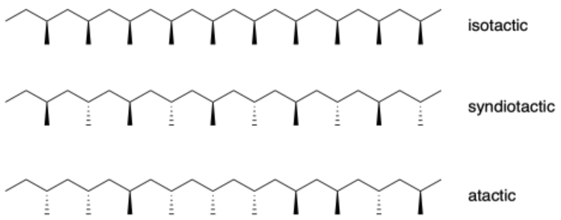
As indicated previously, once an alkene binds at the transition metal, an initial alkyl that was previously transfered from the aluminum is able to participate in a 1,2-insertion reaction. As a result, the alkene is incorporated into the alkyl chain. Subsequent alkene association and 1,2-insertion steps serve to extend the chain, eventually into oligomers and then polymers.



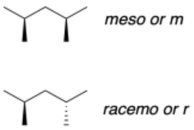
Homogeneous catalysts have also been used commercially for these polymerizations. These systems have been developed more recently by Walter Kaminsky at University of Hamburg, Germany and Hans-Herbert Brintzinger at University of Konstanz, Germany. These soluble catalysts have expanded the scope of stereochemical control over the polymerization of propene and other terminal alkenes or 1-olefins.



When propene is enchained into a polymer, a new chiral center is formed at every position where a methyl group branches from the backbone. Rather than trying to assign each of these chiral centers with stereochemical configurations (*R*) or (*S*), we instead describe the relative stereochemical relationships along the backbone. The term used to describe these relationships is "tacticity". If there is no apparent relationship between the projection of the methyl groups along the backbone, the polymer is termed "atactic". If the methyl groups alternate, pointing first one direction, then the other, all the way along the chain, then the polymer is termed "syndiotactic". If the methyl groups all project the same direction, the polymer is described as "isotactic".



Tacticity in polymers is frequently determined by NMR spectroscopy. Because diastereomers have different physical properties, they display slightly different shifts in the ^{1}H or ^{13}C NMR spectrum. In a polymer chain, we think about chiral centers in pairs, which we call "diads", because every pair of chiral centers has two possible diastereochemical relationships and therefore two possible chemical shifts. If the methyl groups are on the same side, the chiral centers have a "meso" relationship, whereas if they are on opposite sides, they have a "racemo" relationship.

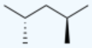


In principle, these are two different stereochemical relationships that could give rise to two different NMR signals. If the polymer is truly isotactic, we might only see the signal that comes from the meso diad, because all of the stereocenters would have that same relationship along the chain. If the polymer is truly syndiotactic, we might see only the signal from the racemo diad, at a slightly different chemcial shift as the meso. On the other hand, we might see two signals, and the relative integration of the two signals might indicate that the polymer is mostly syndiotactic, mostly isotactic, or completely atactic.

Exercise 2.1.2

Label the following diads.

a)



b)

We can expand from there to think about triads, a sequence of three chiral centers, considering the relationship between the first pair of chiral centers in the triad and then the next pair. We would then describe these relationships as mm, for two meso relationships in a row; rr, for two racemic relationships in a row; or mr, for a meso and a racemo relationship. We might be able to detect different signals for all of these relationships.

Given a big enough magnetic field strength an an NMR spectrometer, we may even be able to detect the difference between diads and tetrads, allowing us to see more detail along different segments of the polymer backbone.

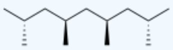
Exercise 2.1.1

Label the following triads and tetrads.

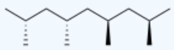
a)

b)

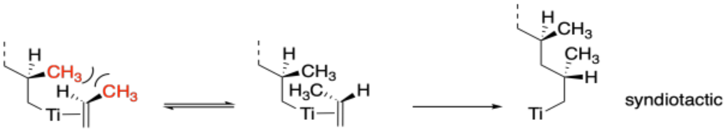
c)



d)

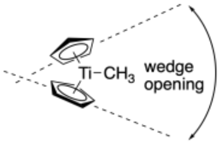


Control over polymer stereochemistry typically occurs in one of two ways. The first way is called chain end control. Given an existing stereocenter at the end of the chain, the approach of the next monomer will be influenced by how that existing chiral center projects in space. As a result, the last chiral center influences how the next one is formed. Conceptually, this idea is the same as saying that in a simple organic reaction, an existing chiral center may force an incoming group to one face of a molecule rather than another, leading to preferential formation of a particular stereochemistry where the new bond is made. In the case of polymers, it means the very first insertion reaction, when the first chiral center forms, determines all of the subsequent stereochemistries along the chain. Of course, there isn't a simple way to predict what that stereochemistry will be: syndiotactic or isotactic. However, the drawing below shows how such an interaction could lead to a syndiotactic polymer.

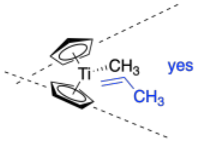


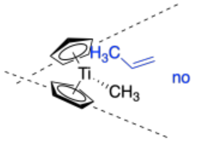
The second mechanism is called site control. In site control, the specific shape of the reagent or catalyst that facilitates the reaction also determines the stereochemictry. This idea is also seen in organic reactions. Chiral reagents or catalysts, whether for hydrogenations, hydroborations, or other reactions, will fit with the substrate in one way more easily than another, leading to preferential formation of one stereochemistry and not the other.

Site control is a topic of interest in homegeneous catalysis, so let's look at how it would work in a titanocene. The first basic lesson in titanocene chemistry is that the two cyclopentadienyls form an angle with each other, so that the molecule takes on a little bit of a wedge shape. One end of the titanocenes are closed together more, and the other end is more open. It's kind of like a clam shell.

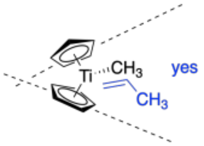


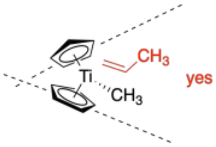
If another molecule, such as a propene, approaches to bind to the titanium, it will have to negotiate the wedge shape to minimize steric interactions. For example, keeping the methyl group away from the titanium, toward the opening on the wedge, would cause less crowding than if the methyl spun around to project deeper inside the wedge.



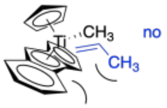


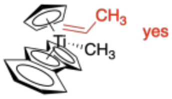
When discussing the formation of a new chiral center, the key idea is whether a new group will bind to one face of a molecule or the other face. We are going to show one face of the propene in blue and the other in red to emphasize this difference. So far, the methyl of the propene will remain further away from the titanium, but there is nothing to prevent the propene from flipping over; the methyl group could be either up or down in the picture.





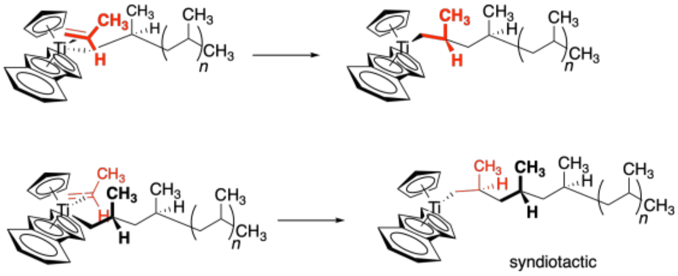
Much of the focus in these homogeneous catalysts has been on developing some kind of asymmetry in the catalyst. The catalyst shown below has C_s symmetry. The top is now different from the bottom. Specifically, the bottom is much more crowed, so that it is no longer very likely that the propene would approach with its methyl group down. It would be much easier to come in with its methyl group pointed up in this picture.





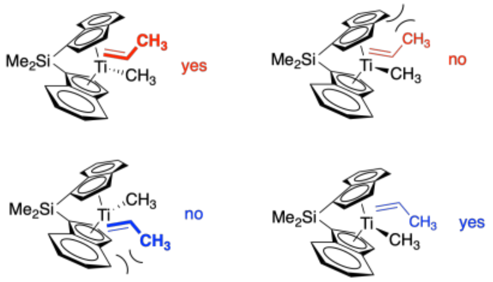
To add one more wrinkle, the propene isn't going to bind in the middle of the wedge, but will be off to one side or the other. That's because there should already be an alkyl group on the metal, which we have shown in this case as a simple methyl group. The propene could approach from the near side, in front of the methyl (shown on the left), or from the far side, behind the methyl (shown on the right).

If the propene is on the near side from our perspective, it is actually presenting its blue face to the alkyl chain. When the 1,2-insertion occurs, the alkyl will bond to the blue face, pushing the methyl and hydrogen of the propene towards us (seen in the top picture). However, if the propene is on the far side from our perspective, it really is presenting its red face to the alkyl chain. When the 1,2-insertion occurs, the alkyl will bond to the red face, pushing the methyl and hydrogen of the propene away from us.

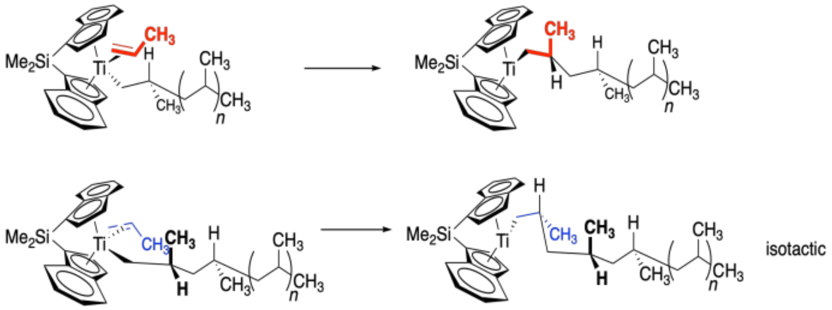


Which one really happens? Both. During the insertion, the alkyl chain shifts over to the coordinated olefin, opening up a coordination site. Notice in the top picture above, the propene is on a wedge and the alkyl is on a dash. After the insertion, the alkyl chain is on a wedge and a new coordination site opens up behind it. A new propene moves into that site. As a result, the new propene approaches first from one side, then the other, alternative every time. This windshield washer mechanism results in a syndiotactive stereochemistry.

What is we change the shape of the catalyst? In the picture below, we have a catalyst with C_2 symmetry. With this symmetry, the propene can approach with its methyl up only if it comes from the front. With its methyl down, it can only approach from the rear.



If you think about it, that means the propene is always presenting the same face to the metal. It only binds to the titanium through the blue face. That means the alkyl chain always binds to the blue face. If the alkyl always binds to the same face, it is always forming a new chiral center with the same configuration. It's making an isotactic polymer.

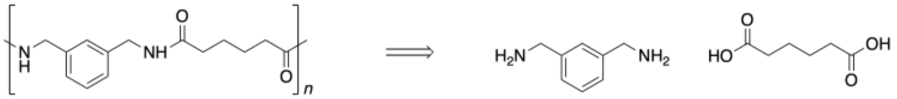


2.2: Solutions to Selected Problems

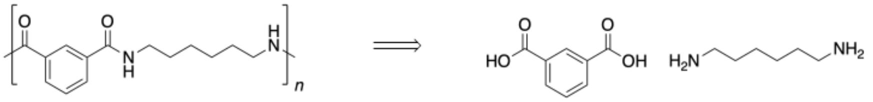
SM11. Solutions to Selected Problems

Problem SM1.1.

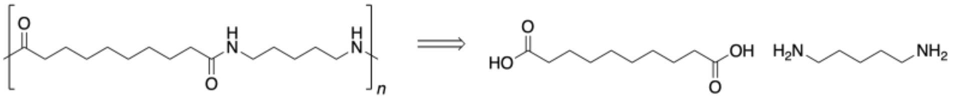
a)



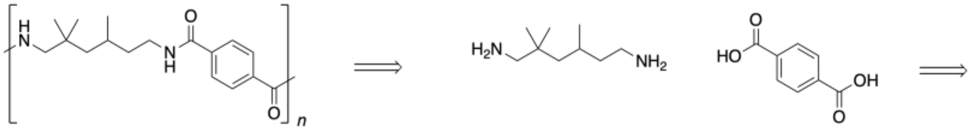
b)



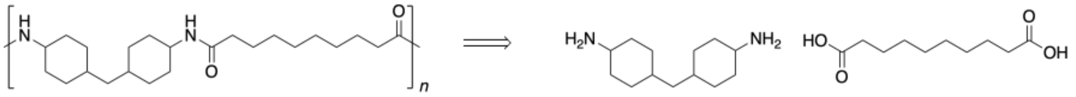
c)



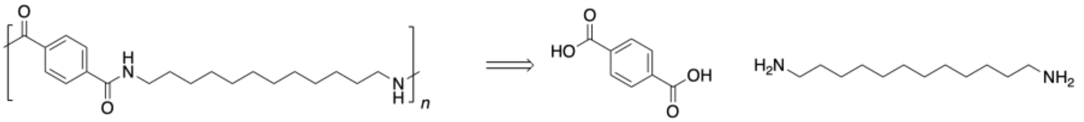
d)



e)



f)

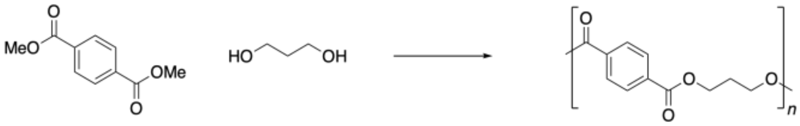


Problem SM1.2.

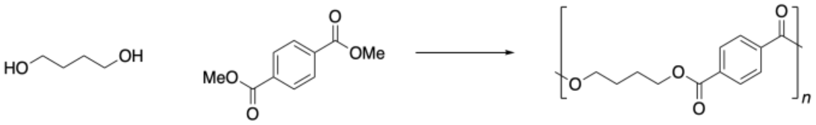
a)

b)

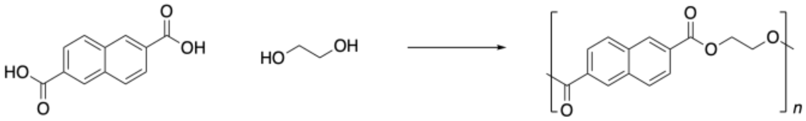
c)



d)

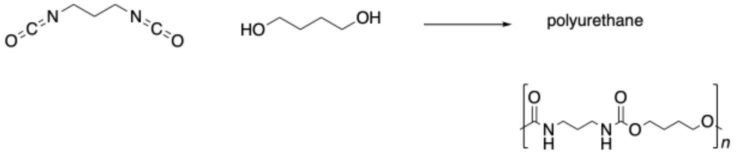


e)

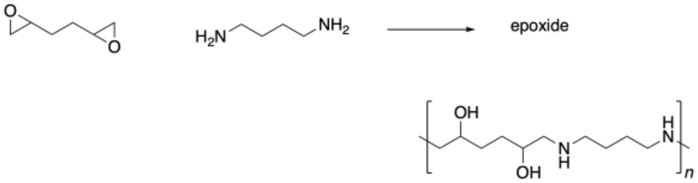


Problem SM1.3.

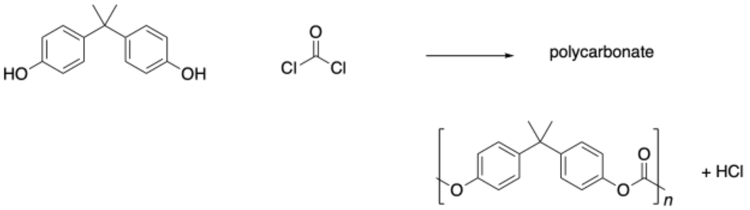
a)



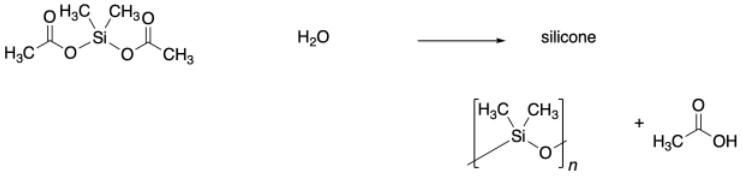
b)



c)

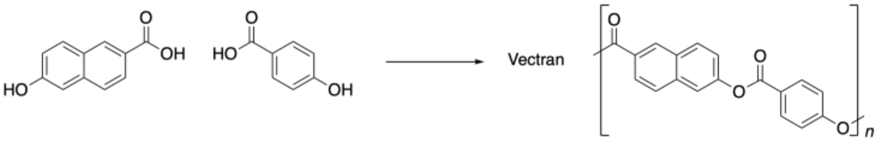


d)



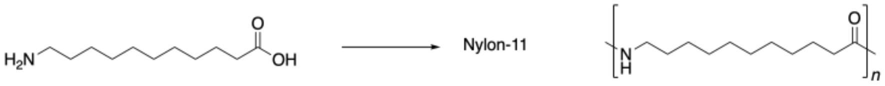
Problem SM1.4.

a)



b)

c)



Problem SM1.5.

a) After seven steps, the polymer will be 2^7 = 128 units long; MW = 128 x 150 g/mol = 19,200 g/mol.

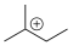
b) After sixteen steps, the polymer will be 2^{16} = 65,536 units long; MW = [(120 + 130)/2] x 65,360 g/mol = 8,192,000 g/mol.

c) After ten steps, the polymer will be 2^{10} = 1,024 units long; MW = [(100 + 105)/2] x 1,024 g/mol = 104,960 g/mol. One condensation will occur at the two ends of each monomer, except for the ones on the ends, but that's a loss of approximately 1,023 x 15 = 15,345 g/mol. The net molecular weight is 104,960 - 15,345 g/mol = 89,615 g/mol.

d) Chain growth occurs linearly, so the molecular weight is 30 x 105 g/mol + 65 g/mol (end group) = 3,215 g/mol.

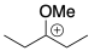
Problem SM2.1.

a)



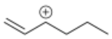
tertiary cation

b)



cation stabilized by pi-donation

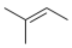
c)



cation stabilized by resonance delocalization

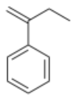
Problem SM2.2.

a)



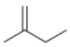
tertiary cation

b)



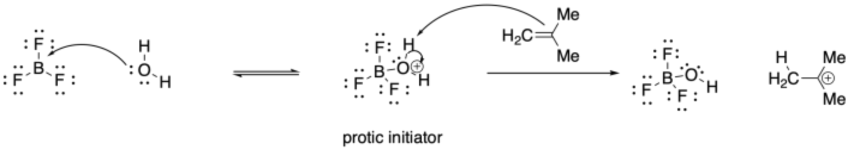
tertiary cation, resonance-stabilized

c)

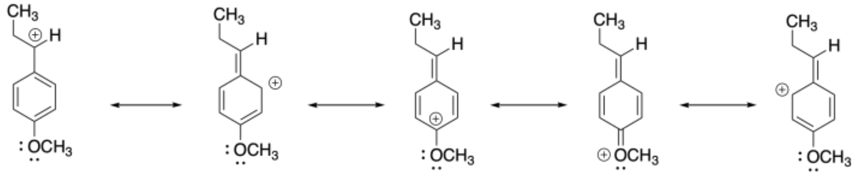


tertiary cation, without electron-withdrawing group

Problem SM2.3.



Problem SM2.4.



Problem SM2.5.

These large, highly charged anions are not very soluble, limiting their interaction with the growing polymer chains.

Problem SM3.1.

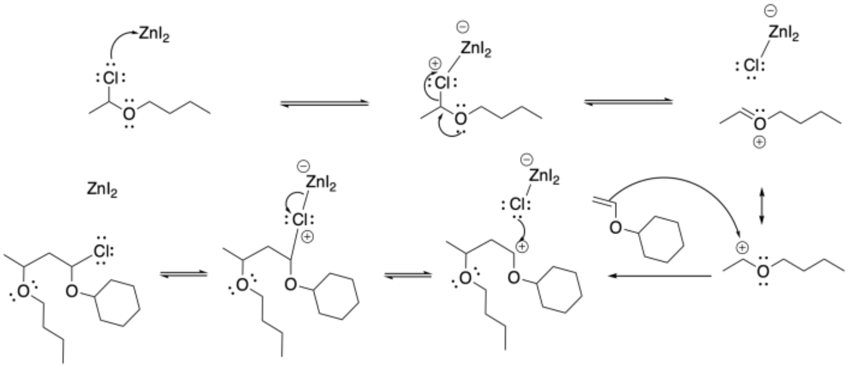
a) $GaCl_3$

b) $SnCl_4$

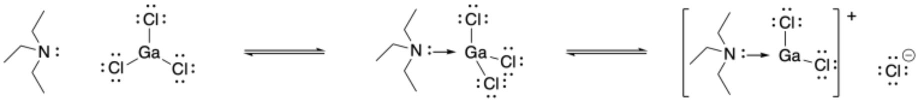
c) $ZnCl_2$

d) $FeCl_3$

Problem SM3.2.

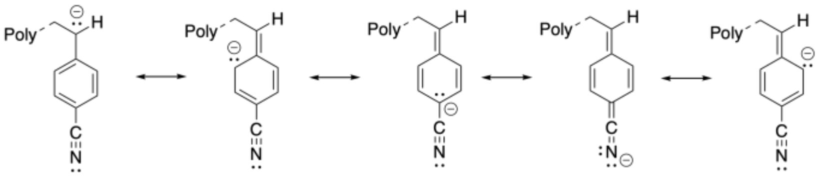


Problem SM3.3.



Problem SM4.1.

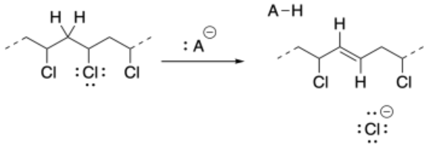
The additional resonance stabilization of the anion by the nitrile group makes anionic polymerization proceed smoothly.

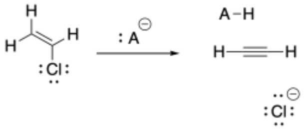


Problem SM4.2.

a) Vinyl chloride's electronegative chlorine might stabilize an anion on the adjacent carbon. However, that inductive effect may be offset by lone pair repulsion between carbon and chlorine.

b) Under these strongly basic conditions, 1,2-elimination may result from the growing polymer chain. Very basic conditions may even result in 1,2-elimination from viyl chloride to give acetylene (ethyne).





Problem SM5.1.

a) Li^+, Na^+, K^+

b) Be^{2+}, Mg^{2+}, Ca^{2+}

Problem SM5.2.

a) K^+, Na^+, Li^+

b) Ca^{2+}, Mg^{2+}, Be^{2+}

Problem SM5.3.

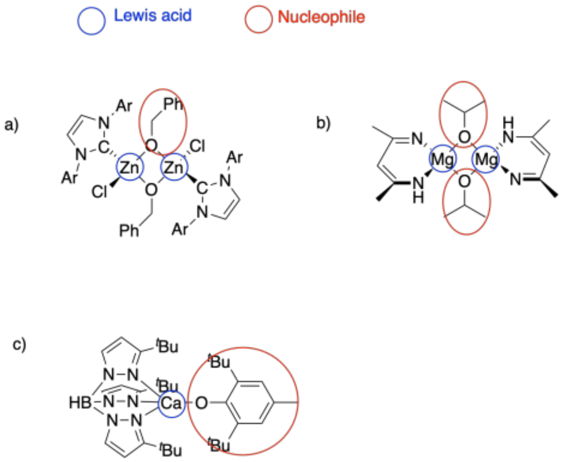
a) Et_3Al

b) Et_2Zn

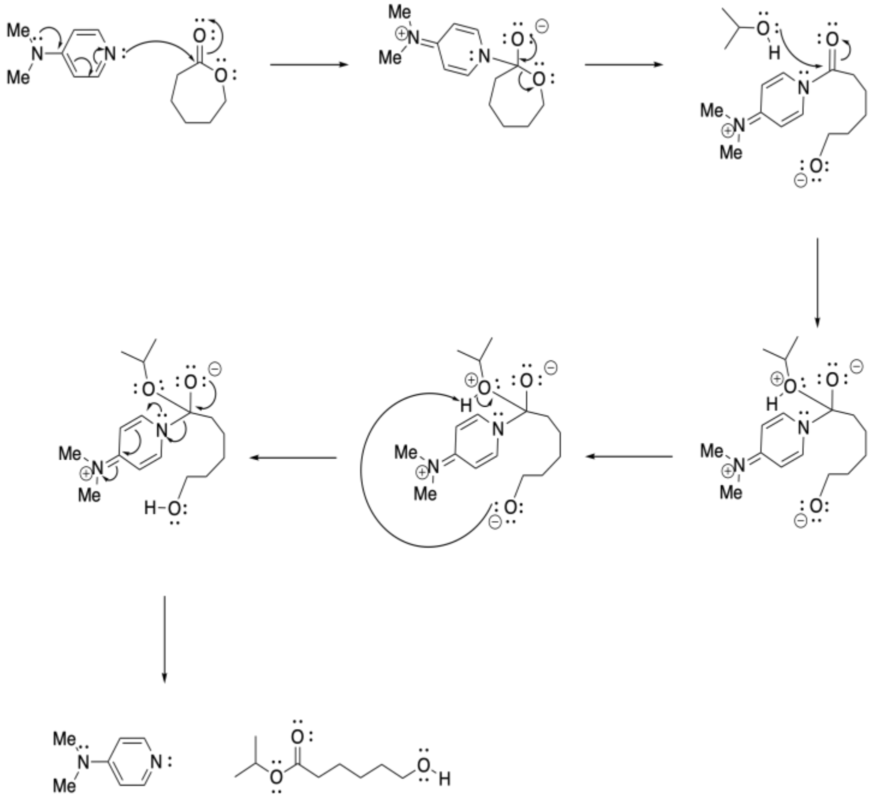
c) Ph_3B

d) $(CH_3O)_2AlCH_3$

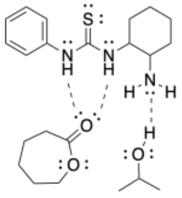
Problem SM6.1.



Problem SM6.2.

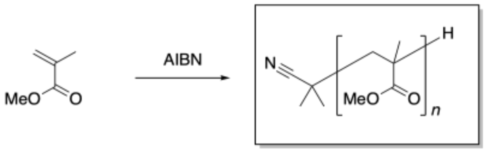


Problem SM6.3.

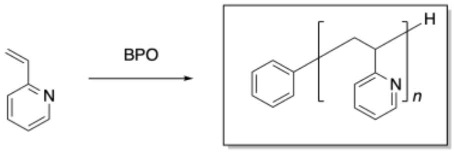


Problem SM7.1.

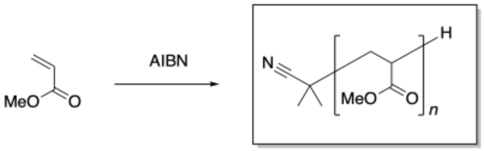
a)



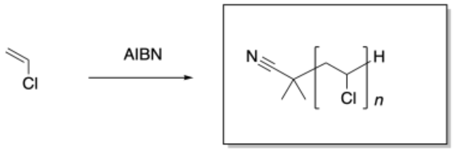
b)



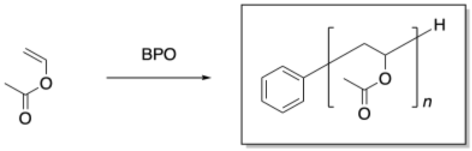
c)



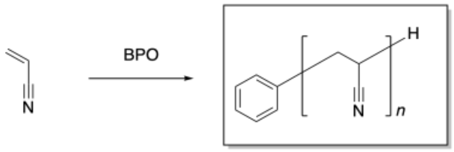
d)



e)

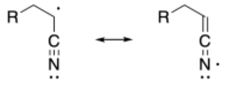


f)

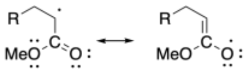


Problem SM7.2.

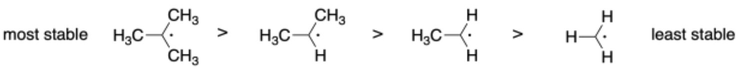
a)



b)

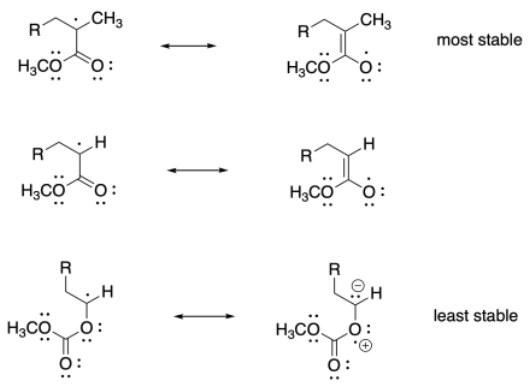


Problem SM7.3.



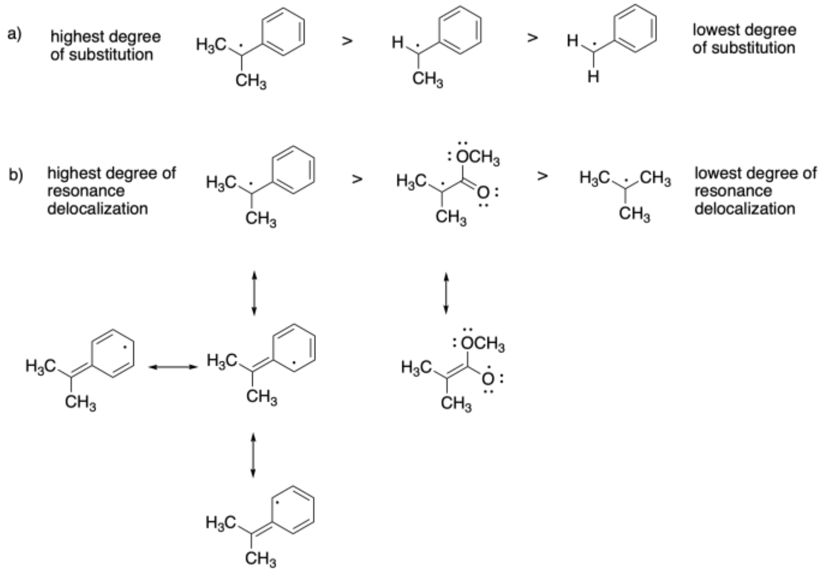
Problem SM8.1.

The more stable the radical, the more rapidly it will form from the monomer, leading to faster polymerization.



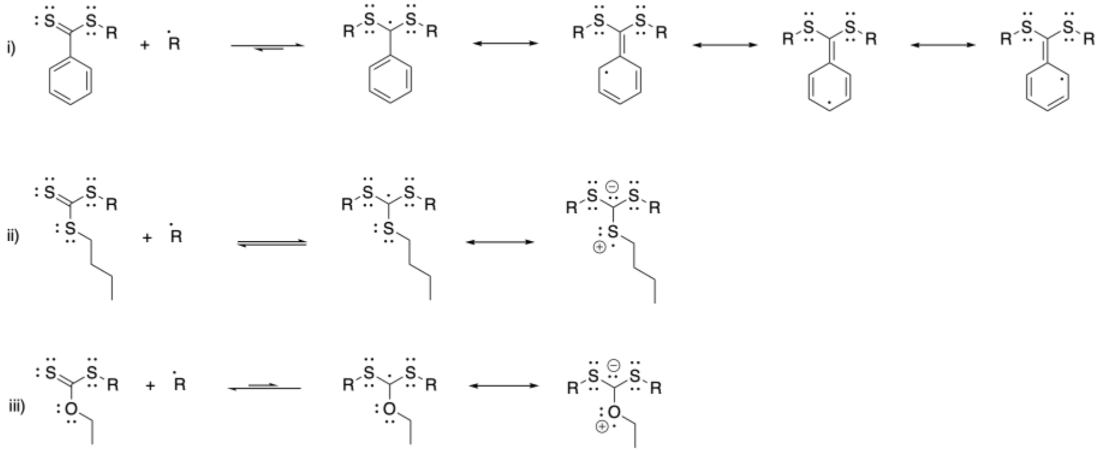
Problem SM8.2.

The more stable the radical generated upon fragmentation of R, the more the equilibrium will shift toward growing phase.



Problem SM8.3.

The more stable the radical formed, the more the equilibrium will shift toward the dormant phase.

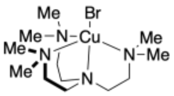


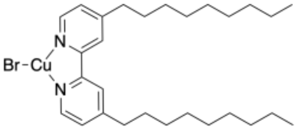
Problem SM8.4.

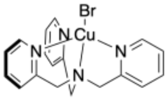
a) With a fast-polymerizing monomer like this one, we need a chain control agent that will provide a similarly stable radical, so that there is an appreciable equilibrium allowing chains to move into the dormant phase; hence the phenyl substituent. However, to get into a new growing phase, we need an R group that fragments very easily, such as this disubstituted benzyl.

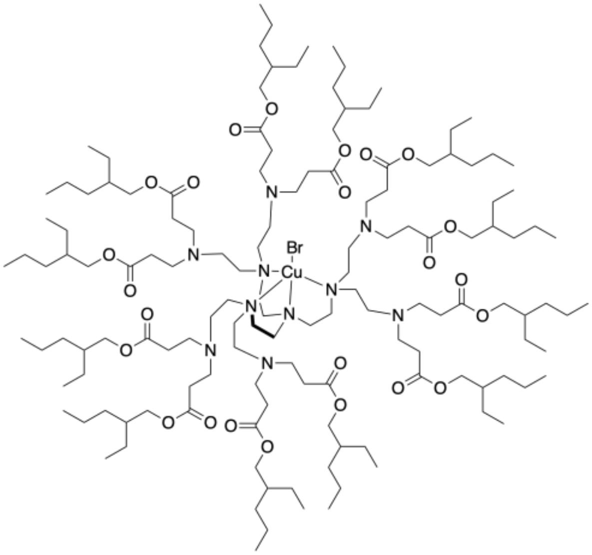
b) With a monomer on the lower end of radical stability, we need a chain transfer agent that isn't terribly stable as a radical, or else the chains will shift completely into the dormant phase. We also need an R group that will fragment at a rate comparable to the original radical chain, so we have one that will form a modestly stable radical.

Problem SM9.1.



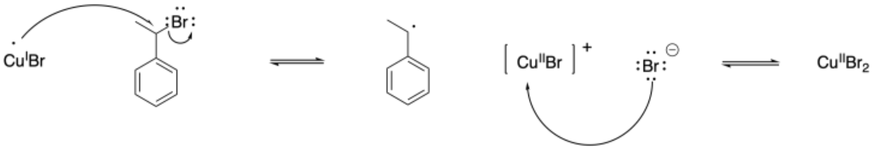




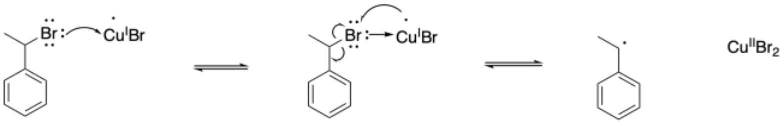


Problem SM9.2.

a)



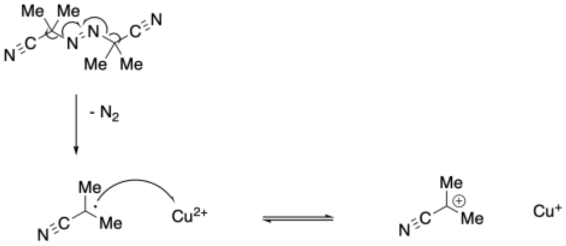
b)



Problem SM9.3.

Problem SM9.4.

a)

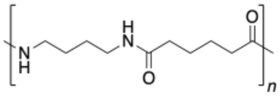


b) The radical generated in the first step may initiate new polymer chains instead.

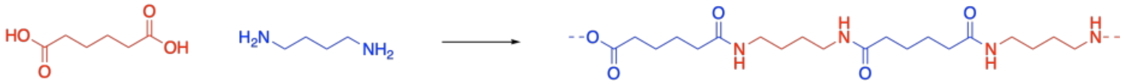
2.3: Step Growth and Chain Growth

Step growth and chain growth are two broad classes of polymerization methods. They use monomers with distinct characteristics and display some different growth patterns.

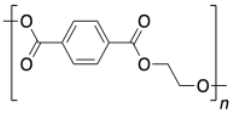
Condensation polymerizations take place via a step-growth process. In a classis condensation reaction, a carboxylic acid reacts with a neutral nucleophile, such as an alcohol or an amine. Substitution leads to formation of either an ester (from an alcohol nucleophile) ar an amide (from an amine nucleophile), with water as a side-product. For example, nylon-6,6 is a condensation polymer.



Nylon-6,6 is produced via a condensation reaction between 1,6-hexanedioic acid (or adipic acid) and 1,6-hexanediamine (or hexamethylenediamine). The amine end group of the nucleophile loses a proton and the carboxylic acid loses an OH group, for the formal loss of one water molecule each time an amide bond forms.

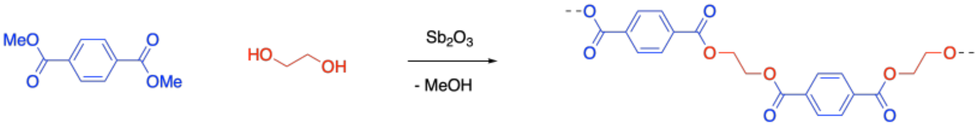


Poly(ethyleneterephthalate) or PETE is a very common example of a polyester.



poly(ethyleneterephthalate)

PETE is formed from the reaction of dimethyl terephthalate with 1,2-ethanediol (or ethylene glycol). Once again, a condensation reaction takes place, with a small molecule formed as a side product. An OMe group is displaced fron the carboxyl electrophile and a proton is lost from the nucleophilic alcohol group, adding up to the formal loss of methanol.



It's worth talking about the conditions used for these reactions. On paper, we might think about using more reactive monomers, such as acyl halide electrophiles, in order to have much faster reactions. However, these reactions are either exothermic in the case of the polyamide or thermoneutral in the case of the polyester, which is formed through a trans-esterification. Both reactions occur in equilibrium. Although they may be relatively slow, they should still get to product eventually, especially if the equilibrium can be shifted to the right. In both of these cases, that shift can be acheived through removal of the water or methanol side-products, which are relatively volatile compared to the other reactants.

Note also that the neutral nucleophile and the relatively poor leaving groups in these cases suggest the reaction will be pretty slow. To speed things up, a Lewis acid may be added (such as the antimony oxide, Sb_2O_3, employed in the second example).

The monomers used in step-growth polymerization usually have a couple of characteristics that we can see in these examples. Most often, there are two different monomers. Neither monomer would undergo polymerization on its own, but the two monomers are complementary to each other, so that each provides the other with an appropriate reactive partner.

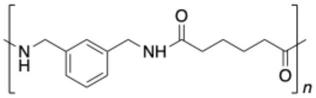
More importantly, each of the monomers we have seen here is mutlifunctional. In this context, functionality describes the number of reactive functional groups. Each of the monomers we have seen so far contains two functional groups; they each have a functionality of two, or they are each difunctional. Once a functional group has reacted on a difunctional monomer, it still has another one that can react. Every monomer can therefore make bonds with two others, allowing for chain formation.

This higher functionality is essential for step-growth polymerization. It isn't limited to difunctional monomers. Monomers could be trifunctional, tetrafunctional, and so on, leading to more highly branched or chemically crosslinked polymers, rather than simple chains.

Problem SM1.1.

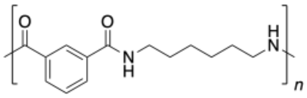
Identify the monomers that would be used to produce these polymers.

a)



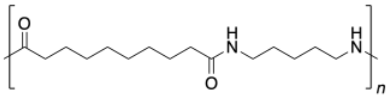
MXDX

b)



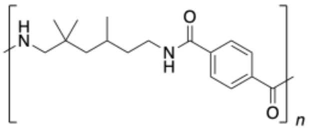
Nylon-6I

c)



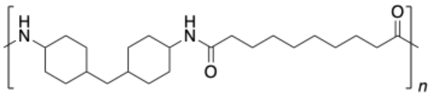
Nylon-510

d)



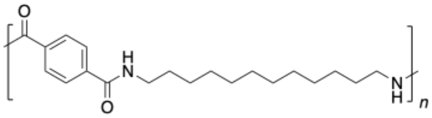
TMDT

e)



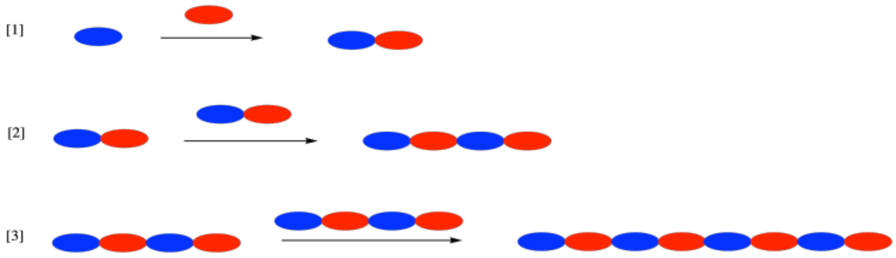
PACM12

f)

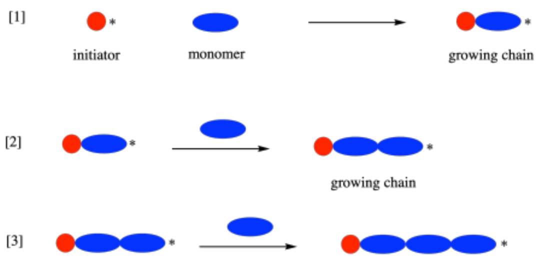


Nylon-12T

Because of difunctionality in the monomers, condensation polymers can grow in two directions at once. Two complementary monomers connect with each other to form a dimer. Now, suppose all the monomers are reacting at roughly similar rates (not quite true if you know about polymer molecular weight distribution, but close enough). When one end of the dimer goes to react again, chances are it will find another dimer, because most of the monomers have already reacted. That reaction will form a tetramer. The typical tetramer reacting another time will find another tetramer, forming an octamer, and so on.

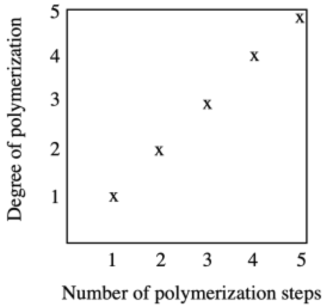


Most of the subsequent chapters in this text deal with a variety of ways of carrying out chain polymerizations. In chain polymerization, we usually start with just one kind of monomer, which is again unreactive by itself. This time, instead of adding a complementary monomer, we add an initiator. The initiator converts one monomer molecule into a reactive intermediate, capable of reacting with another monomer to form a new reactive intermediate, and so on. This is a chain reaction.

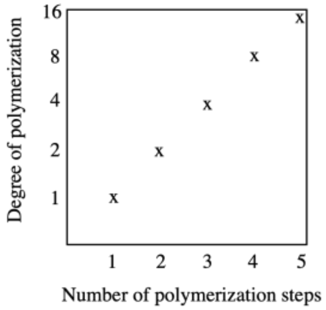


Notice the difference from step growth. In chain growth, the polymer chain always grows one monomer at a time. In step growth, the polymer chain doubles with each step. As a result, the rate of growth of the polymer chain is very different in these two cases.

Chain growth results in a steady increase in chain length with every coupling step. Growth is linear.



Chain growth is exponential, with chain length doubling at every coupling step. Notice that the y axis on this graph is logarithmic rather than linear.



What are the consequences of these two growth patterns? Let's take a look at how many steps it would take to form a high molecular weight polymer, maybe with a molecular weight of one million g/mol (sometimes expressed as one million Da in polymer chemistry; Da stands for Dalton). Starting with a monomer of molecular weight 100 g/mol and using step growth, in which chain length doubles every time a reaction takes place, it will take only thirteen or fourteen steps to reach a molecular weight of a million Da, because 2^{13} = 8,192 repeat units. Using chain growth, it would take ten thousand steps to reach the same molecular weight, assuming a monomer of similar size.

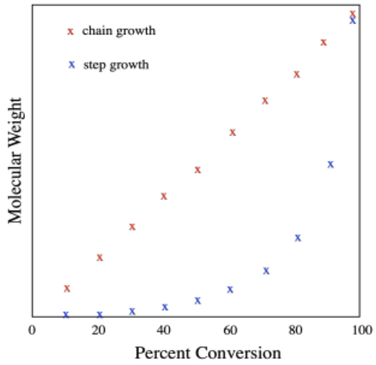
$$\begin{array}{c}\text{Monomer}\\ \text{MW = 100 g/mol}\end{array} \xrightarrow[\text{13-14 steps}]{\text{step growth}} \begin{array}{c}\text{Polymer}\\ \text{MW = 1,000,000 g/mol}\end{array}$$

$$\begin{array}{c}\text{Monomer}\\ \text{MW = 100 g/mol}\end{array} \xrightarrow[\text{10,000 steps}]{\text{chain growth}} \begin{array}{c}\text{Polymer}\\ \text{MW = 1,000,000 g/mol}\end{array}$$

That's a very approximate calculation, and it neglects the weight of side products during condensation polymerization, but we are looking at differences that are orders of magnitude apart.

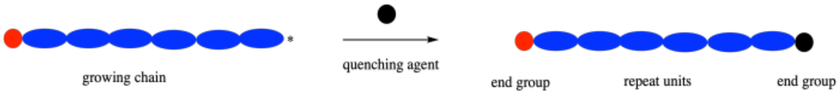
Why is this difference significant? For one thing, it doesn't matter that much if a condensation reaction is slow. If it only takes twenty (or even thirty) steps to reach a molecular weight of a million (not unheard of in a commercial polymer, but still pretty high), then there's no hurry. In chain polymerization, there is a much higher premium on speed. We need very fast reactions or sometimes very fast catalysts that can turn around and enchain monomer after monomer reliably.

If we take these two broad methods and look at them in a different way, we get new information. If, instead of thinking about the number of bonding events or reaction steps, we focus on the percent conversion, we get a graph that looks like this.

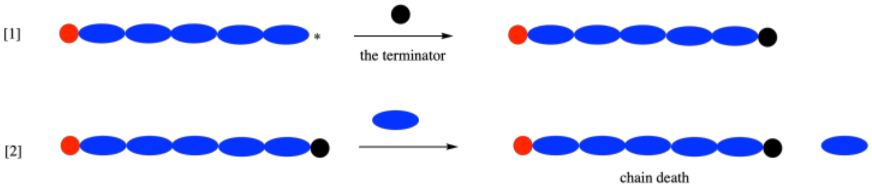


Looked at in this way, we see the linear nature of chain growth. Every time a new monomer is added, the polymer chain grows by the same amount (the weight or length of one new repeat unit, depending on whether we are thiniing in terms of molecular weight or chain length). Step growth works exponentially: doubling, quadrupling, and so on. Both modes of polymerization proceed, ideally, until all of the monomer has completely reacted; in other words, to 100% conversion. But what happens if growth is suddenly arrested because of some unwanted side reaction? In step growth, such an event happening even in the very late stages of polymerization might result in a chain length that is only half what we had expected. Such disastrous results in chain growth would result only if growth stopped after only consuming half the monomer. Arresting chain growth at 80 or 90% conversion still results in pretty long polymer chains, even if they aren't the expected length. Because of this feature, step growth polymerization requires very reliable chemistry. Otherwise, step growth would always result in relatively short chains.

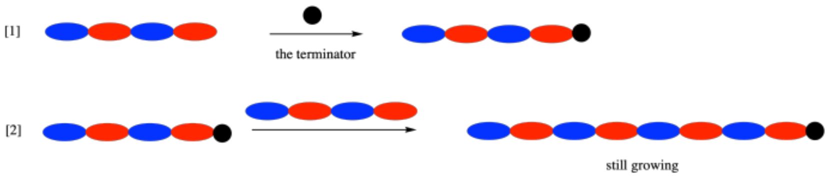
In either case, it's useful to know that polymerization is often followed by a quenching reaction to arrest the process once the polymer has reached the desired chain length. Usually that results in a polymer with two different groups at the end of the chain. The choice of those groups can occasionally be useful in modifying the properties of the polymer.



Imagine a case, however, in which this termination happens accidentally. In a chain growth, the polymer has a reactive intermediate at one end only. If something caps that end of the polymer chain, it stops growing altogether. Unexpected terminations can be a significant problems in chain growth.



Of course, they are also a problem in step growth, but remember that in step growth the polymer is growing from two ends. If one end gets capped, the other end can keep growing. The polymer will grow more slowly, but it won't stop altogether.

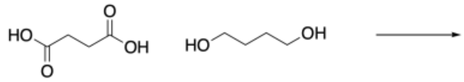


As a result, there is a great deal of interest in developing more reliable ways of carrying out chain growth. That's especially important because one wrong step and chain growth stops altogether. Chain growth is, in fact, a crucial way of making polymers, despite what may seem like some limitations here. A key reason is that step growth is mostly limited to condensation polymerization of carboxyloid compounds such as polyamides and polyesters, as well as a few related materials such as polyurethanes. Chain growth is used to polmerize a wide array of compounds that contain carbob-carbon double bonds (alkenes or olefins) as well as a variety of cyclic monomers. Both approaches are needed to make a range of useful materials.

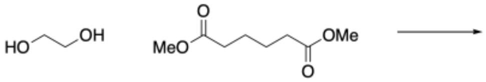
Problem SM1.2.

Provide structures of the polyesters made from the monomers as indicated.

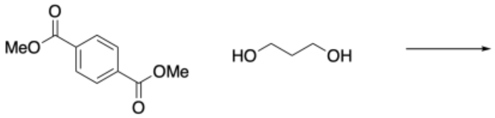
a)



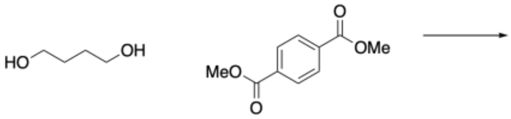
b)



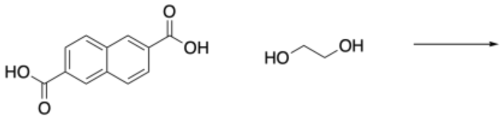
c)



d)



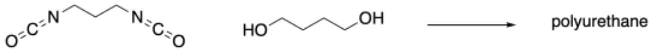
e)



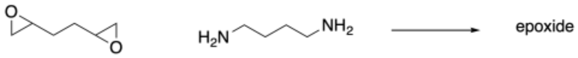
Problem SM1.3.

The following difunctional monomers would undergo polymerization together; in some cases the reaction happens without condensation of a side product. Show the product structures that result.

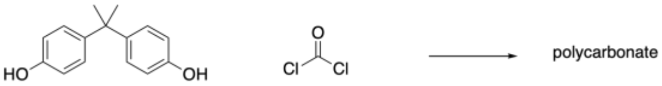
a)



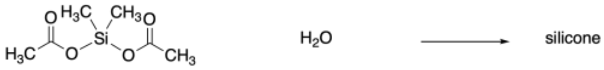
b)



c)



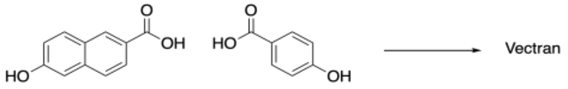
d)



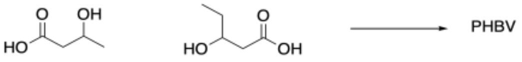
Problem SM1.4.

A few polymers are obtained from difunctional monomers that contain both nucleophilic and electrophilic sides. Show the polymers that result in these cases.

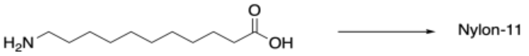
a)



b)



c)



Problem SM1.5.

Calculate the molecular weight of the polymer in each of the following cases.

a) Step polymerization involving monomers of molecular weight 150 g/mol, allowed to undergo seven polymerization steps.

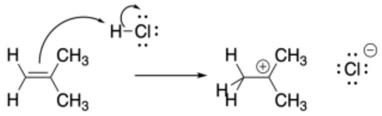
b) Step polymerization involving monomers of 120 and 130 g/mol, allowed to undergo sixteen polymerization steps.

c) Step polymerization involving monomers of 100 and 105 g/mol, allowed to undergo ten polymerization steps, producing a condensation product with molecular weight 15 g/mol.

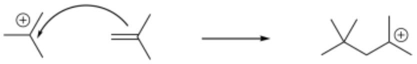
d) Chain polymerization of a monomer with molecular weight 105 g/mol, allowed to undergo thirty polymerization steps, using an initiator with molecular weight 65.

2.4: Cationic Polymerization

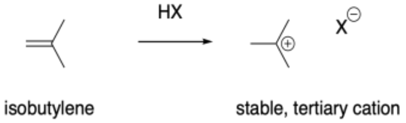
Alkenes, or olefins, are probably the most common polymer feedstock. The pi bonds of alkenes are inherently nucleophilic. The addition of an electrophile to an alkene results in cleavage of the pi bond, with the electrons drawn to the electrophile, and consequently a cation can be left on one end of the former double bond.



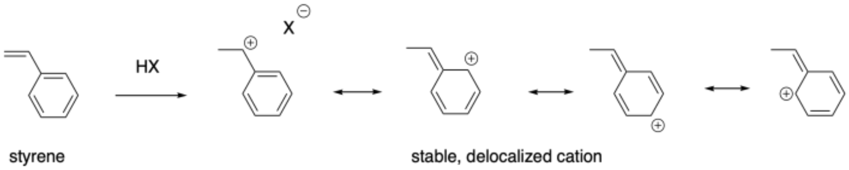
If the resulting cation interacts with another alkene, another electrophilic reaction occurs, and so on, leading to polymerization. Because of the presence of a key cationic intermediate along the reaction pathway, this method of polymerization is termed **cationic polymerization**. It is an example of a chain reaction that is initiated by a cationic species.



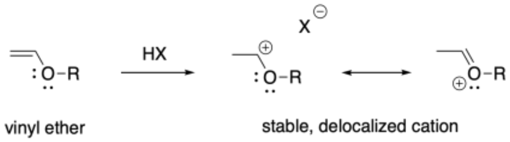
It stands to reason that alkenes that form stable cations would be particularly susceptible to polymerization via cationic methods. Cations are high-energy intermediates, so if a cation is relatively easy to form then the barrier for the process is lowered considerably. Isobutylene, $(CH_3)_2C{=}CH_2$, is a good example of an alkene that would form a stable cation upon protonation. The relative stability of more-substituted cations dictates that the positive charge is found at a tertiary position.



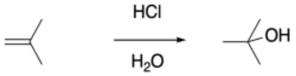
Degree of substitution is just one way that carbocations can be stabilized. Conjugation is also a major factor in cation stability. Alkenes that give rise to delocalized cations are also good candidates for cationic polymerizaton. Styrene, $PhCH{=}CH_2$, as well as butadiene, $CH_2{=}CHCH{=}CH_2$, and the related natural product isoprene, $CH_2{=}C(CH_3)CH{=}CH_2$, can all be polymerized using cationic methods.



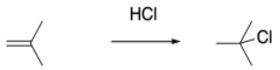
These examples are stabilized by allylic delocalization: the cation is part of a system that contains a $C{=}C{-}C^+$ feature, which is delocalized as $^+C{-}C{=}C$. Cations can also be stabilized via pi-donation. Oxygen and nitrogen are particularly good pi-donors towards carbocations, so oxygen and nitrogen substituents on alkenes render these compounds susceptible to cationic polymerization. Vinyl ethers, for example, can be polymerized this way.



The obvious way to initiate these polymerizations is through addition of a strong acid. Protonation of the alkene should certainly result in formation of a carbocation. However, most common strong acids are mineral acids, typically found in aqueous media. The presence of nucleophilic water would quickly cap the carbocation before polymerization could take place.

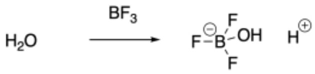


Of course, hydrogen chloride does not require water as a solvent. The addition of dry HCl gas to the olefin of interest should result in cation formation without subsequent hydration. Unfortunately, just the presence of the chloride ion, which can also act as a nucleophile, dooms polymerization to an early death.

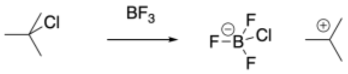


There are other, less nucleophilic acids that are not as strongly prone to classical addition across an alkene compared to the extent that we associate with HCl. Sulfuric acid and various sulfonic acids come to mind. Even in these cases, however, polymerization is limited by eventual collapse of the nucleophile with the cationic chain end.

Instead of using strong Brønsted acids to inititate polymerization, it is actually very common to use Lewis acids. Lewis acids cannot initiate cationic polymerization directly, but they can co-initiate the reaction in the presence of a water impurity, for example. The Lewis acid activates the water towards release of a proton. The proton then initiates the reaction. Traces of HCl can also act as the initiator when a Lewis acid co-initiator is employed, because the Lewis acid ties up the chloride ion so that it cannot connect with the growing cationic chain end.



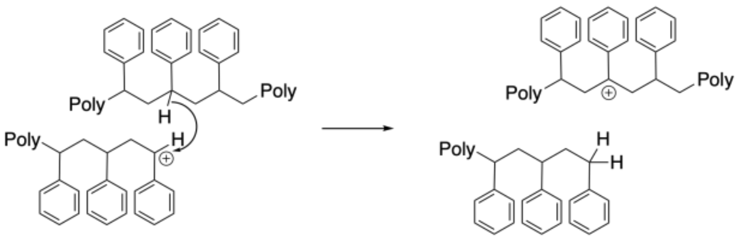
Protic initiators are not strictly required for cationic polymerization. Strong Lewis acids are also capable of activating alkyl halides. The carbocation that results can then initiate the polymerization chain reaction.



Even in these systems, there are chain-termination events that destroy the reactive intermediate and stop polymerization. As indicated previously, combination of a nucleophilic anion with the cationic chain end is a common fate of growing polymers. Halide ions, released in equilibrium from the Lewis acid-base complex, are still a possible problem, even though this event is much less likely in the presence of Lewis acidic co-initiators. Other, similar anions, such as hydroxide anions in water-initiated polymerizations, can play a similar role.

Anionic species can also carry out beta-eliminations on cationic chain ends. Beta-elimination results in the loss of the cationic intermediate, replacing it with a cain-end elkene. That event results in the production of a new initiator, and although it could be argued that the initiator might just re-initiate the same polymer chain, given relative concentrations it is much more likely that the initiator transfers the proton to a new monomer. In that case, a new growing chain starts from scratch and begins to accumulate monomers.

Surprisingly, chain-transfer events are another common mode of termination. In these cases, a hydride must be transferred from one chain to another, or from one position along the backbone to the growing chain end. This unusual hydride transfer is probably facilitated by very close contact distance between two chains, or between two segments of one chain, in a concentrated polymerization milieu. As a result, one chain end stops growing, and the chain begins growing from a new position along its backbone. This event results in chain branching, changing the morphology and properties of the polymer.



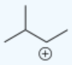
Normally, assuming a relatively rapid initiation step (formation of a cation from the first monomer), growth of tandem polymer chains will proceed at roughly the same rate, so that all of the chains reach similar lengths by the time all monomers have been consumed. What happens if some of those chains die prematurely? Other chains continue to grow to longer lengths. As a result, there is a wider distribution of chain lengths, or molecular weights, than there would be otherwise. A wider molecular weight distribution means that physical properties of the material may be less reproducible.

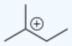
In a typical polymerization process, the reaction is followed by quenching, in which some agent is added that will stop further polymerization. In cationic polymerizations, quenching might be accomplished through addition of aqueous acid, because either the water or the conjugate of the acid will destroy the cation. The material is usually precipitated in a solvent that can dissolve any remaining monomer, but not polymer. Because some chains may have died very early, they might also remain in solution, leaving only larger chains in the precipitate.

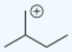
Exercise 2.4.1

Choose the most stable cation from each of the following groups. Provide a reason for the stability of that cation.

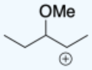
a)

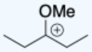


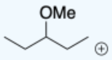




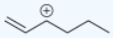
b)

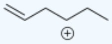






c)

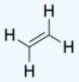


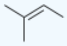


Exercise 2.4.2

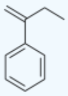
In each group, select the alkene most suitable for cationic polymerization.

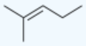
a)

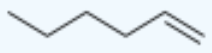




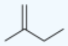
b)

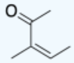






c)



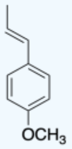


Exercise 2.4.3

Provide a mechanism for the formation of a protic initiator from the interaction of boron trifluoride with water.

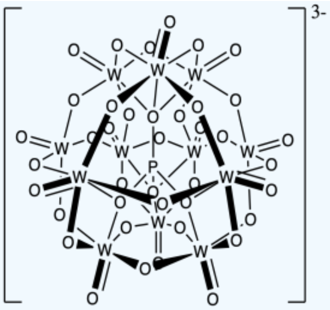
Exercise 2.4.4

Anethole in a naturally-occuring compound that has been used in cationic polymerizations. Show why anethole should be a good monomer for this method.



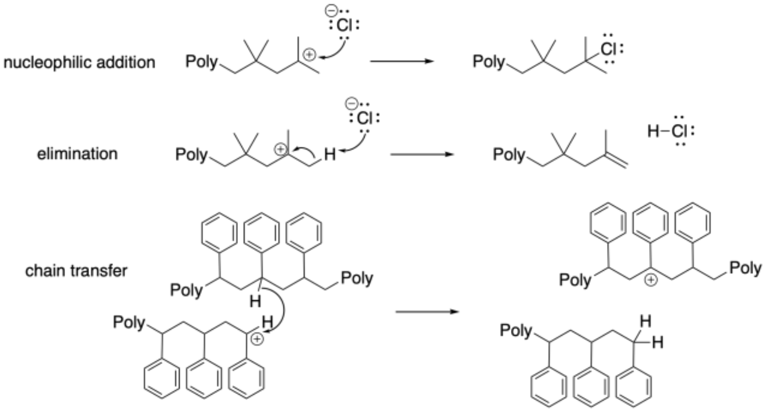
Exercise 2.4.5

Phosphotungstates such as $H_3PW_{12}O_{40}$ have been used as cationic initiators and do not show much termination by the counterion, below. Propose a reason for the low nucleophilicity of this counterion for the growing cationic chain.

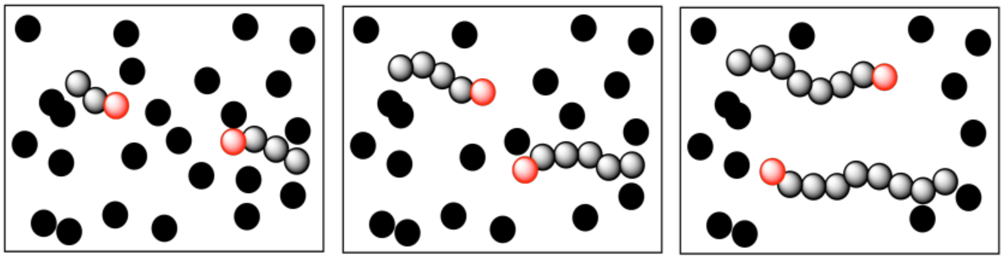


2.5: Living Cationic Polymerization

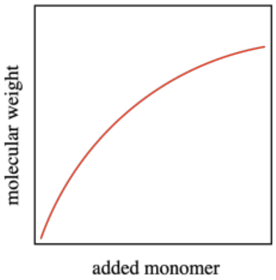
Alkenes are a common polymer feedstock, used to make a range of very familiar plastics in everyday use. Because their properties depend strongly on their molecular weights and molecular weight distributions, it is very important to be able to control the growth of these long-chain polymers from their alkene monomers. Termination events, such as combination of the cation with a nucleophile, elimination, or chain transfer, all contribute to a widening disperity between chains that have undergone these events and those that continue to grow.



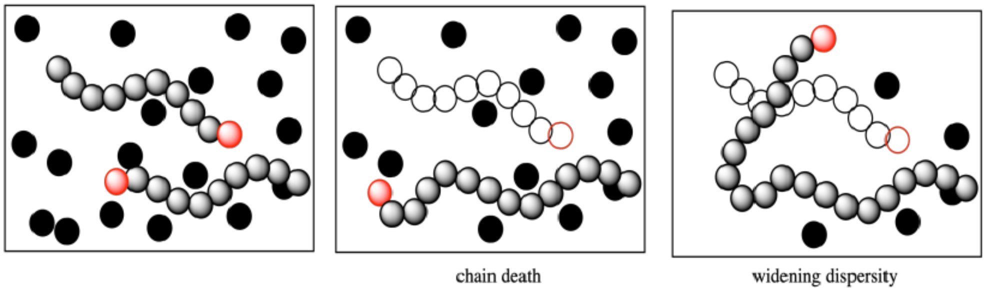
In any polymerization, as in any other reaction, we are dealing with thousands of reactions involving thousands of different molecules all happening at the same time. Several reactive chains growing in tandem would be expected to grow at similar rates, and ultimately they would reach similar degrees of polymerization. That means they would all have the same number of monomers incorporated into the final polymer chain and so they would all have similar molecular weight.



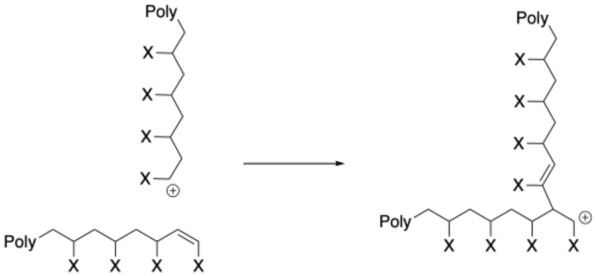
What happens when one of these growing chains undergoes some kind of termination event? Chain death, as this problem is commonly called, has a couple of direct consequences. Obviously, the chain that stopped growing does not keep up with the others, so its molecular weight is lower than the rest. That fact alone might lead us to believe the average molecular weight would be lower than we had expected in this polymerization. If we added more and more polymer to the polymerization over time, we wouldn't expect the molecular weight to keep increasing, because the reactive sites keep getting quenched.



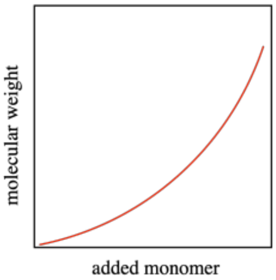
More subtly, that growing chain had been slated to enchain a certain number of monomers, some of which are still left in the system when it dies. What happens to them? Of course, the other growing chains will each get some extra monomers. That means the dispersity problem gets even worse; one chain stops growing and is shorter than anticipated, but others gobble up the extra monomers and become longer than anticipated. Dispersity, the distribution of molecular weights, gets wider.



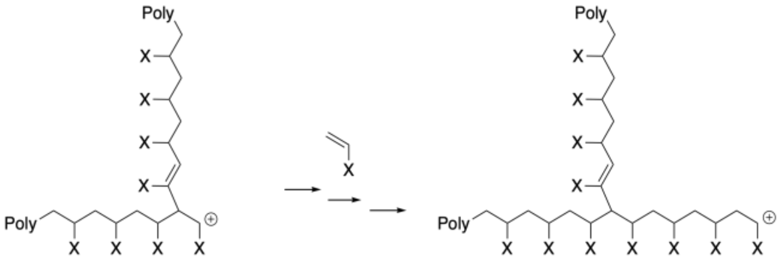
The problem can be even worse when a termination occurs through elimination, resulting in the formation of a new alkene. Because that new alkene is already found at the end of a polymer chain, when it combines with a cationic chain end the polymer molecular weight effectively doubles.



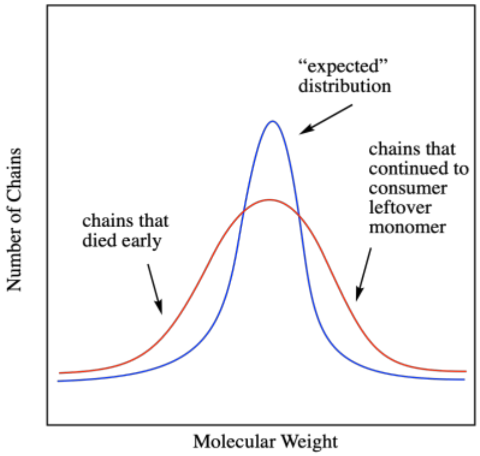
In other words, although we would reasonably expect molecular weight to stop increasing as chains die, resulting in lower molecular weight than expected, the opposite can also happen. We can observe an increase in molecular weight, because the chains that are left are consuming all of the monomer, becoming much bigger, and occasionally two chains are combining to dramatically increase molecular weight. Molecular weight increase is proceeding in an uncontrolled and somewhat unpredictable way.



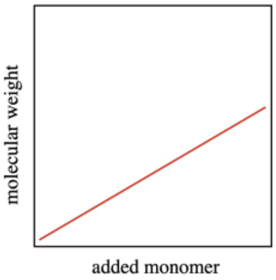
Furthermore, the reaction of a cationic growing chain with a macroalkene results in a sudden shift in polymer morphology. Instead of a straight chain, we now have a dramatically branched polymer. That change in morphology has a severe impact of polymer properties.



All of these factors mean that the distribution of molecular weights gets broader when chain reactions undergo unexpected termination. The term for the width of molecular weight distribution is dispersity (D), sometimes called polydispersity index (PDI). In the graph below, the red line describes a sample from a polymerization that was not as well controlled as the one described by the blue line. There are a lot more polymer chains that are both longer and shorter than the average.



In an ideal polymerization, growing chains wouldn't die unexpectedly. They would continue to grow, and we could easily predict how long each chain would become based on how much monomer and initiator we added. Each initiator molecule would start one growing chain, and each growing chain would enchain its portion of the monomers. The molecular weight would be predicted easily because the polymer chains would grow linearly with added monomer. A polymerization in which there is a linear relationship between added monomer and molecular weight, even as the molecular weight becomes very high, is called a "living polymerization".



A second feature of living polymerization is that dispersity (or PDI) stays relatively constant throughout the course of a reaction. Because there are no chain terminations, the reactive chains all continue to grow at the same pace, and the polymers that result are of uniform molecular weight.

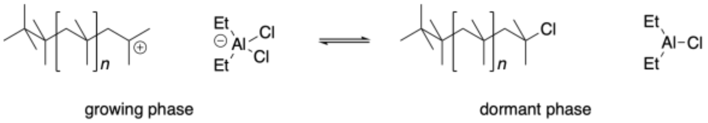
In order to achieve a living cationic polymerization, we would have to prevent unwanted terminations steps. There are a variety of systems that accomplish this goal, but they share some common features. Essentially, these methods intentionally allow a nucleophile to combine with the cationic chain end, but use a Lewis acid to reactivate the resulting compound and regenerate the growing chain end.

Like other cationic polymerizations, these processes could be initiated by addition of a protic acid to an alkene to generate a cation. That initial cation would then begin reacting with the nucleophilic alkenes around it, generating subsequent cations that sustain a chain reaction. In practice, it's instead very common to add an ionizable compound, such as a tertiary alkyl halide, along with a Lewis acid co-initiator. The Lewis acid promotes ionization of the initiator, forming a cation.

Once that cation has formed, regardless of how it got there, it can begin to react with the monomers around it. The chain reaction will continue, consuming more and more monomers, resulting in a longer growing chain with higher molecular weight.

Lewis acid-base adducts always form reversibly, however. At some point, the adduct can give back to the cationic chain end the same anionic group that it once extracted from the initiator. The chain stops growing, because it no longer contains a reactive site.

However, just as the Lewis acid once extracted an anionic group from the initiator, it can extract it from this polymer chain. When it does, the cationic chain end will start reacting with more monomers, and the chain will grow again.



Living cationic polymerization depends on an equilibrium between a reactive, growing phase and an unreactive, dormant phase. There is an inherent trade-off here. The concentration of reactive cationic chain ends is lowered because a large fraction of the chains are always dormant. That low concentration of cations means there is less opportunity for chain termination events; that's helpful in keeping dispersity low. On the other hand, that low concentration of cations also means the polymer grows much more slowly than it would otherwise.

This trade-off works to our advantage because of kinetic conditions that hold true throughout most of the duration of the polymerization. Termination steps depend on the collision between two species that are both held at relatively low concentration, whether it is a cationic chain end and an anionic base or two different growing chains. Propagation depends on the concentration of reactive chain ends and the concentration of monomer. Although one of those concentrations is very low, the other one is very high all the way up until nearly the end of the polymerization. That means propagation remains fast relative to termination.

For example, if your target is a polymer of molecular weight 100,000 Da and the monomers have molecular weight of 100 Da, then you would conduct the polymerization with one initiator for every thousand monomers. Each time a monomer was consumed, the relative monomer concentration would change very, very little, and it would remain high enough to keep the polymerization reaction moving forward at a reasonable pace. Only near the end of the polymerization would the monomer concentration drop significantly enough to slow the reaction down drastically.

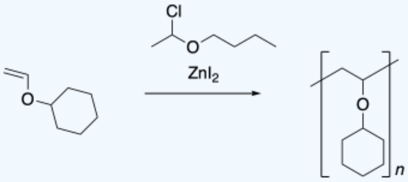
Exercise 2.5.1

Choose the best Lewis acid from each of the following pairs.

a. NCl_3 $GaCl_3$
b. $SnCl_4$ Cl_2
c. CCl_4 $ZnCl_2$
d. $FeCl_3$ $XeCl_2$

Exercise 2.5.2

Provide a mechanism for this polymerization. Show chain control using equilibriu between a growing phase and a dormant phase.



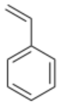
Exercise 2.5.3

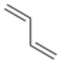
Living cationic polymerizations are sometimes promoted when a weakly basic molecule is added to the reaction mixture. Although different reasons have been proposed for the role of the Lewis base, it is well-established that adding a neutral Lewis base to a Lewis acid can result in a more active, cationic Lewis acid. Show how this stronger Lewis acid forms using triethylamine and gallium chloride.

2.6: Anionic Polymerization

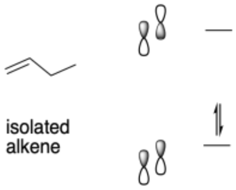
If you have studied some organic chemistry, then it seems obvious that cationic methods would be employed for the polymerisation of alkenes. After all, alkenes are nucleophilic, and so they should react readily with cationic initiators. It might be surprising that there are a number of alkene polymerisations that work very well using anionic initiators.

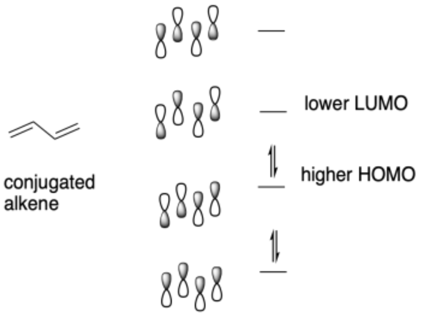
One of the most common scenarios for this approach is in the polymerisation of conjugated hydrocarbons, such as styrene. From the point of view of Lewis structures, this seems like a funny combination. There is no obvious electrophile in an alkene; not even in a conjugated one. Why would it interact with an anionic initiator?


styrene

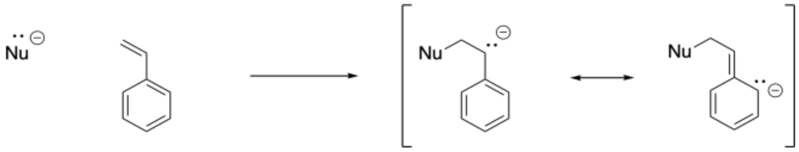

butadiene

A molecular orbital treatment of conjugated systems provides an answer. When alkenes are conjugated, several things happen. There is at least one extended π-bonding orbital that moves to lower energy because of conjugation, and we think of that factor to explain the relative stability of conjugated alkenes toward electrophiles, compared to the reactivity of isolated alkenes. At the same time, there are also π-bonding orbitals that are raised a little in energy as well as corresponding π*- or π-antibonding orbitals that are lowered in energy by conjugation. This feature explains the well-known shift in optical absorption of conjugated alkenes toward the visible region of the spectrum; we see that in brightly coloured compounds such as carotene and xanthophylls in autumn leaves. It is partly that lowering of the Lowest Unnocupied Molecular Orbital (LUMO) that leads to the increased electophilicity of conjugated alkenes compared to regular alkenes.

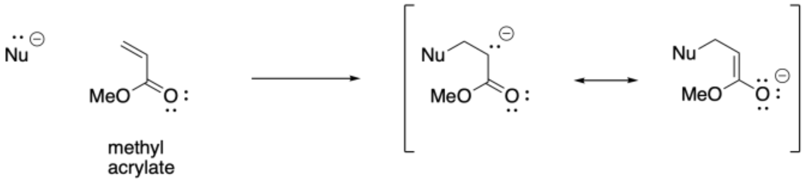




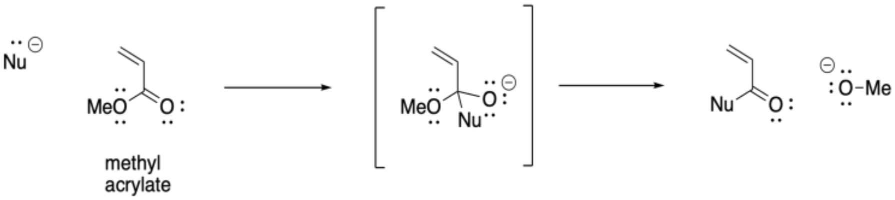
Once an anionic initiator has added to a conjugated alkene, the conjugated alkene itself becomes an anion. That leads to the second part of the explanation. If you look at the anion that results, you will find resonance stabilisation. That delocalisation is always a powerful factor that allows ions to form more easily. In fact, we can easily choose an anionic initiator that is more reactive than that delocalised one, so that there is a driving force toward polymer initiation. Alkyllithiums, such as butyllithium, are good candidates.



There may be other alkenes that come to mind as being potentially suitable for anionic polymerisation. Again, if you have studied organic chemistry, you might thing of 1,4-addition of nucleophiles to conjugated enones. Anionnic initiation of these kinds of monomers is also possible. Acrylate polymerisation, involving monomers that contain a C=C-CO_2 unit, is commercially very important.



The 1,4-addition of anionic initiators does not proceed as smoothly as we might expect, however. This approach is prone to a number of side reactions. For example, Claisen condensations result in the loss of an alkoxide leaving group and chain death.

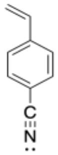


On the other hand, the presence of α-hydrogens along the polymer can lead to a different problem, with equilibrium proton transfer resulting from "back-biting". This phenomenon leads to uncontrolled branching of the polymer chain.

The potential for side reactions means that anionic polymerisations are prone to poor molecular weight control. Chains that die early will have lower molecular weight than those that continue to grow, leading to broad molecular weight distributions. Like cationic polymerisations, anionic polymerisations can be greatly enhanced through the use of living methods.

Problem SM4.1.

Anionic polymerization of *p*-substituted styrene proceeds very well when the substituent is an electron-withdrawing group such as nitrile. Explain the reason for the success of this approach.



Problem SM4.2.

Vinyl chloride (CH2=CHCl) might be expected to be a good candidate for anionic polymerization, but side reactions make it unsuitable.

a) Explain why the resulting anion might be expected to show some stability.

b) Show the side reaction that would result under anionic polymerization conditions.

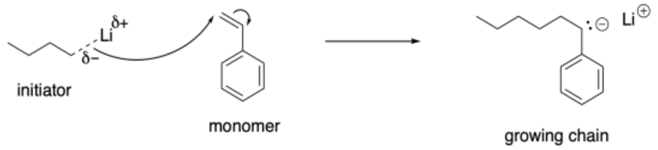
2.7: Living Anionic Polymerization

Unwanted side reactions in anionic polymerization, such as back-biting or Claisen reactions with acrylate chains, lead to early chain death and a broadening of the molecular weight distribution. This problem is intrinsic to polymer growth. Because reactive chain ends are needed to enchain additional monomers, there is always the potential that these relatively high-energy species will go off track and lead to different products.

Living polymerization describes any system in which early chain death is limited, so that polymer chains can continue to grow uniformly. In these systems, the molecular weight increases linearly with the percent conversion of monomer to polymer. In addition, dispersity remains low even at high percent conversion.

The reactive chain ends in anionic polymerizations are nucleophilic carbon anions. If you have studied these kinds of compounds before, the idea of covalency might come to mind. Carbon anions are easier to work with if they are not really anions, but instead share their electrons with their counterions to some degree. So, for example, we might choose to employ lithium counterions with these anionic chain ends, rather than sodium or potassium. The smaller, more electronegative lithium (at least compared to sodium or potassium) can form a polar covalent bond with carbon, stabilizing the nucleophile.

Of course, even an alkyllithium is a strong enough nucleophile to initiate anionic polymerization, provided the resulting anion is more stable than the initial one. In general, it can initiate the formation of growing chains if the resulting anion is delocalized.

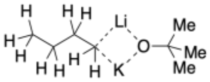


We can think of the growing chains as being in equilibrium between having covalent lithium-carbon bonds and forming ion pairs. The ion pair would be more ready to react with the next monomer. That equilibrium could form a basis for a dormant state and a growing state. Just as in living cationic polymerization, the growing state is necessary for polymer chain growth but is susceptible to unwanted side reactions. The dormant state protects the growing chain by limiting the growing chain concentration, consequently limiting the degree of side reactions.

So, just using a lithium counterion, for instance, might be expected to promote living polymerization, keeping dispersity low. For that reason, it may be surprising that one of the strategies used for chain control in anionic polymerizations is to add potassium alkoxides along with the alkyllithium initiator. If lithium bases have greater covalency and offer greater control, why would you add potassium bases?

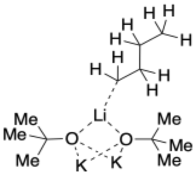
That question has even more merit if you explore the history of mixed-metal bases. Schlosser's base is a well-precedented example. Typically, it's a mixture of butylllithium and potassium tert-butoxide. Developed by Manfred Schlosser at EPF (ETH) Lausanne in Switzerland, mixtures of alkylithiums and potassium alkoxides form powerful bases capable of deprotonating hydrocarbons such as toluene. The mechanism of achieving such high base strength is believed to involve transfer of an alkyl anion from lithium to potassium. From the point of view of making growing chains more covalent, providing a dormant state, this doesn't seem like a good idea. Nevertheless, it works. How?

One of the other features of these mixtures (Schlosser called them LiCKOR bases, noting the mix of lithium and potassium components) is a high level of aggregation. Aggregates are clusters of molecules that stick together. For Schlosser's base, the simplext aggregate would be one alkylithium molecule bound to one potassium tert-butoxide molecule.



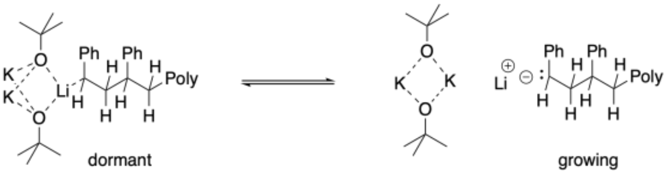
What holds aggregates like this together? The anions can bridge between alkali metals. With the alkoxide ion, that's easy to imagine: the oxygen atom has more than one lone pair, so it can donate one to lithium and one to potassium. It's a little harder to see how the alkyl anion, with only one lone pair, could do that. However, that sort of interaction in which one lone pair is shared between two or more lithium ions, although rare, is pretty well-documented in some alkyllithiums. It's like the alkyl anion has been caught midway between two lithiums, transferring from one to another.

Bigger aggregates could form if additional molecules stuck together. We can easily picture this happening if one alkyllithium combined with two potassium alkoxides.

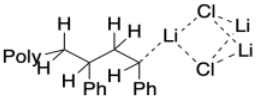


You can probably imagine even larger aggregates. Maybe two alkoxides come together with one alkyllithium, held together by bridging oxygens. In fact, these structures seem to be very dynamic. They can come apart in solution, and they can come together to make even bigger structures. In reality, a number of different aggregation states will exist in equilibrium with each other, and some might contain eight or twelve alkali cations together with their accompanying anions.

So, what is the role of aggregation in producing a dormant state? It may cap the end of the growing chain temporarily, so that the anionic chain end is less likely to interact with monomers. Reaction would occur only when the aggregate broke up, freeing an anionic chain end.



Aggregate formation can also be promoted by other anions, including simple halides such as chloride and fluoride. As a result, the addition of simple lithium salts can be effectine in promoting living anionic polymerization. The alkoxide base needn't play a role.



An alternative strategy for living anionic polymerization involves the addition of Lewis acidic compounds as chain control agents. In these cases, the equilibrium between dormant and growing chains would involve coordination of the anionic chain end to the Lewis acidic atom. Because Lewis acid-base complexes occur in equilibrium, some fraction of the polymers would always exist in the growing phase, but a greater fraction would always be found in the dormant phase.

Exercise 2.7.1

Rank the following ions in terms of covalency with oxygen (most covalent to least covalent).

a. Na^+, Li^+, K^+
b. Mg^{2+}, Ca^{2+}, Be^{2+}

Exercise 2.7.2

Coordination number can vary with the size of a cation. Rank the following ions from largest to smallest.

a. Na^+, Li^+, K^+
b. Mg^{2+}, Ca^{2+}, Be^{2+}

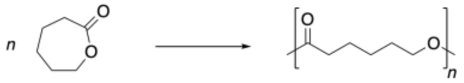
Exercise 2.7.3

Which compounds would be expected to stabilize growing anionic chains?

a. Et_3N or Et_3Al
b. Et_2Zn or Et_2O
c. Ph_3B or Ph_3N
d. $(CH_3O)_2AlCH_3$ or $(CH_3O)_2CHCH_3$

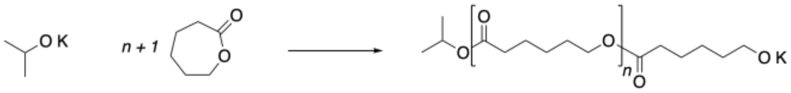
2.8: Ring-Opening Polymerization

On an earlier page, we saw that polyesters and polyamides are typically obtained via condensation polymerization. Ring-opening polymerization (ROP) offers a second approach to these kinds of materials. Using this method, cyclic esters (lactones) or amides (lactams) are opened up to make extended chain structures. The reaction is typically driven by the release of ring strain. For example, caprolactone is ring-opened to produce polycaprolactone.



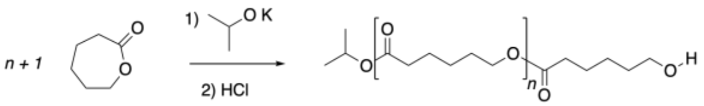
Caprolactone and other ROP monomers are different from the monomers used in condensation polymerization in a couple of ways. First of all, ROP monomers contain only one functional group, not two. Furthermore, they don't need a complementary monomer. These monomers just react with each other. Also, when they react, they don't form a new functional group, as was sometimes the case in condensation reactions. The monomers were esters and the products are esters, too. This swapping of esters leads to the more specific term "ring-opening trans-esterification polymerization" (ROTEP) when lactone monomers are used.

Let's take a look at how these monomers can be enchained together without the need for complementary monomers. The transformation is instead carried out using a chain reaction. An initiator is needed. In this case, an alkoxide nucleophile can be added to open the first monomer, but when that happens, the substitution reaction at the carboxyloid carbon displaces an alkoxide leaving group. The new alkoxide can then add to the next monomer, propagating the chain reaction.

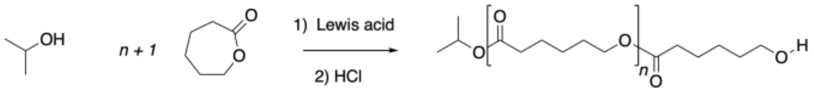


In this drawing, you can explicitly see the new ester linkage formed between two monomers, replacing the ester linkage in the monomer.

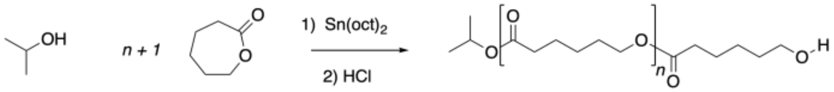
Ring-opening polymerizations like this one are typically quenched with acid to convert the alkoxide nucleophile into a less reactive alcohol, arresting polymerization.



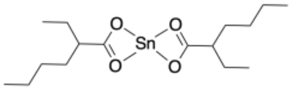
Caprolactone and other cyclic esters can be polymerized via anionic methods, but that isn't the only way. It's very common for these polymerizations to be performed via Lewis acid catalysis instead.



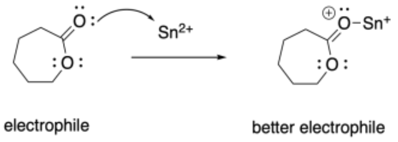
A range of Lewis acids can be used for this purpose, and common examples include iron, zinc, tin and aluminum compounds. This example uses the commercially available tin octoate as a catalyst.



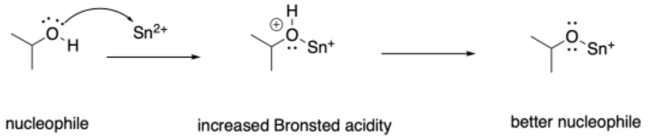
Sn(oct)$_2$ =



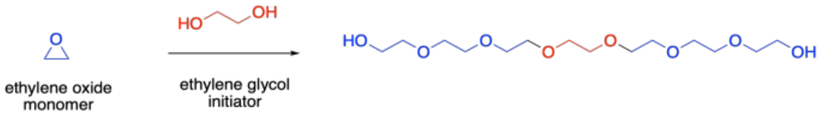
The role of the Lews acid can be twofold. It can accelerate the reaction via electrophilic activation, in which it binds the carbonyl oxygen of the ester, making it more electrophilic.



In addition, when neutral alcohols bind to Lewis acids such as tin octoate, they are more easily deprotonated, becoming better nucleophiles. Both of these effects probably add up to very rapid ring-opening polymerization under these conditions.



Usually, ring-opened polymers grown either through anionic or Lewis acid conditions have a single growing end, but that doesn't have to be the case. If a difunctional initiator is used instead of a simple alcohol, two monomers would be initiated, allowing growth in two different directions. For example, ring-opening polymerization of ethylene oxide is often accomplished with ethylene glycol as an initiator. The ethylene glycol unit becomes enchained in the middle of the polymer chain, rather than at the end.

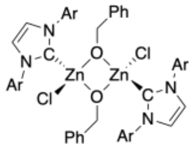


This type of structure, with two growing ends, is sometimes called a "telechelic" polymer. It can be very useful in the synthesis of triblock copolymers, because a different kind of monomer can be added to both ends of an existing polymer, leading to an ABA structure.

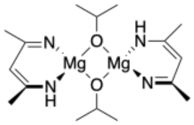
Problem SM6.1.

Some catalysts for ring-opening polymerization contain both a Lewis acid and a nucleophile for initiation of chain growth. Identify these two components in the following catalysts.

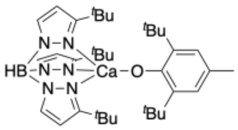
a)



b)

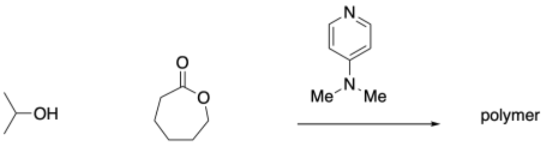


c)



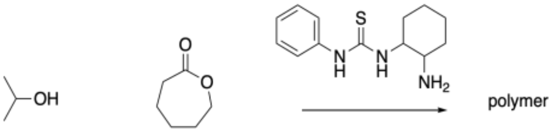
Problem SM6.2.

Some organocatalysts promote ring-opening polymerization of cyclic esters through nucleophilic catalysis, acting as an initial nucleophile. Show the mechanism for the following reaction.



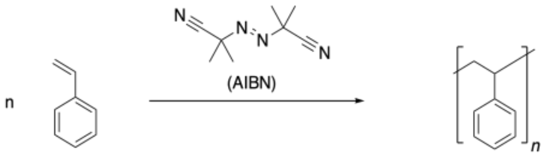
Problem SM6.3.

Some organocatalysts can activate both the nucleophile and the electrophile, and also use a catalytic approximation strategy. Provide a structure that illustrates these features in the following system.

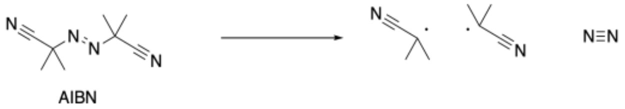


2.9: Radical Polymerization

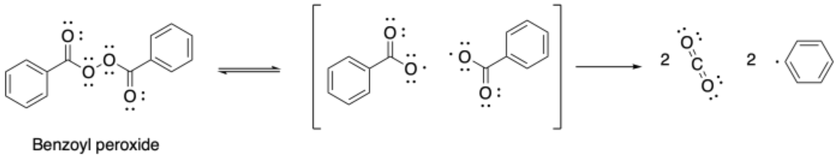
Radical polymerization is a very common approach to making polymers. There are a number of very reliable methods of carrying out radical polymerization, leading to high molecular weight materials. A typical example is the formation of polystyrene under the influence of the radical initiator, azoisobutyronitrile (AIBN).



Radical reactions start with an initiation reaction, in which radicals first come into being. When AIBN is used as an initiator, the compound decomposes partly because of the strong N-N triple bond that is formed, and partly because of the relatively stable radical that results. This radical is both tertiary and delocalized.

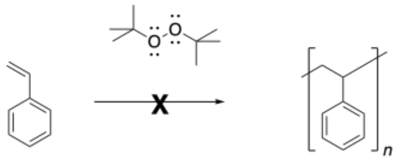


Other initiators can also be used in radical polymerizations. Benzoyl peroxide (BPO) is one common example. In this case, the initiation reaction is sparked by the weak O-O single bond. The benzoate radical that forms from that homolysis further decomposes via decarboxylation, rapidly giving rise to a phenyl radical.

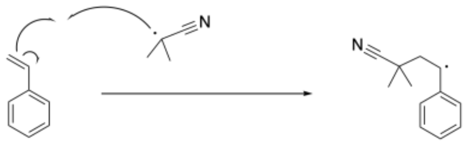


Phenyl radicals and isobutyronitrile radicals are both able to initiate the polymerization of styrene. Not just any radical will peform that task. Simple peroxides are not very good at initiating radical polymerization, despite the fact that they also contain O-O bonds that are readily cleaved.

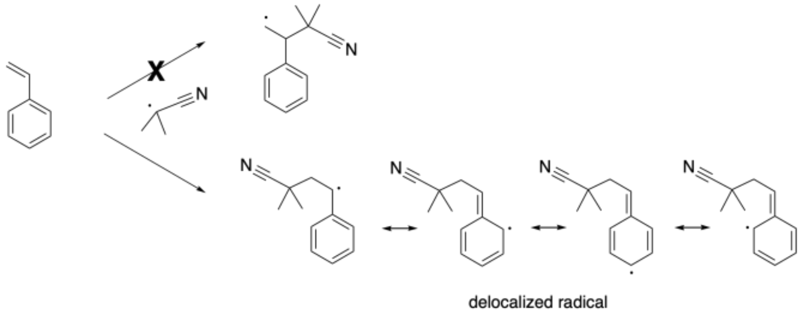
Oxygen-centered radicals do not typically add to double bonds. It's much more common to see them abstract hydrogen atoms. Accordingly, tert-butyl peroxides and other such peroxides would not be used to initiate the polymerization of styrene.



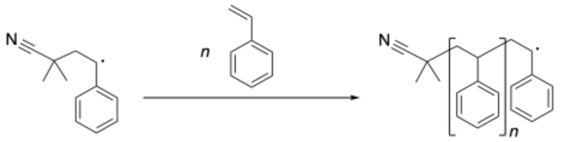
The radical formed via initiation induces cleavage of the pi bond in styrene, resulting in a benzylic radical. This is an example of a propagation step, because old radicals have disappeared and new radicals have appeared.



Note that this step takes place with regioselectivity. There are two possible radicals that could result, but only one actually forms. That's the more stable one. It is stabilized by delocalization because of the benzene ring.

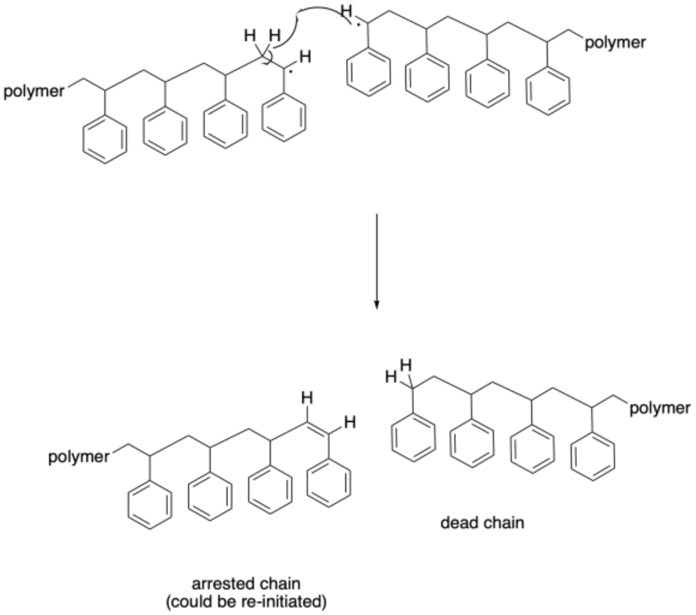


Once that benzylic radical forms, it can continue to propagate, enchaining more styrene molecules. Each time a new styrene molecule is enchained, it forms a new benzylic radical.

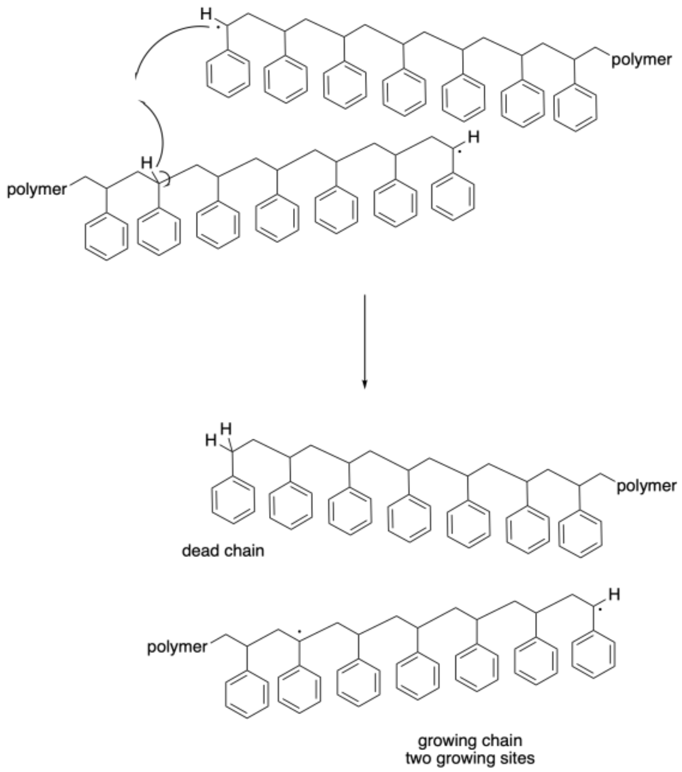


Eventually, radical reactions undergo termination, in which two radicals combine in some way so that neither one is a radical anymore. The most obvious way for that to happen is if two growing chains meet head-to-head, with two benzylic radicals connecting to make a bond.

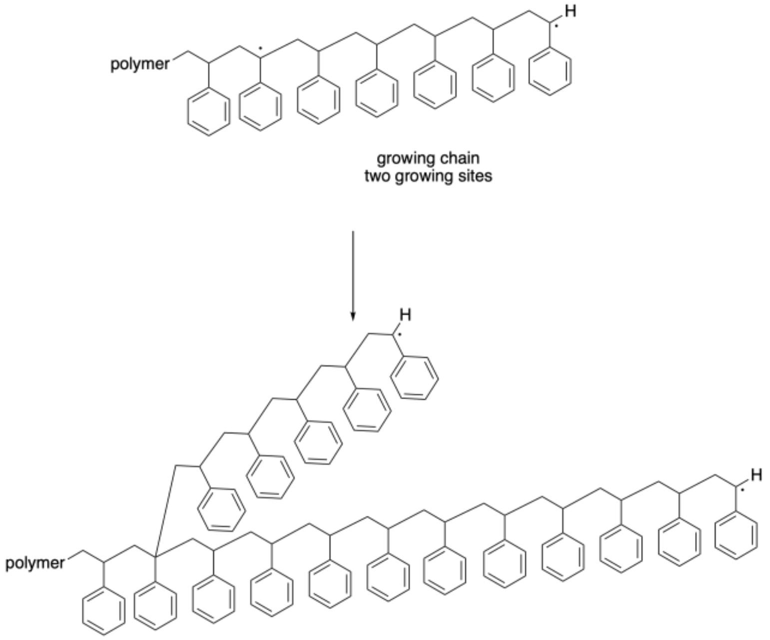
Other termination events are also prevalent in radical polymerizations. Hydrogen atom abstraction is pretty common, with one growing radical stealing a hydrogen atom alpha to the radilca at the head of another chain. The reason that may happen is that it results in the formation of two new bonds: a C-H bond and a C-C pi bond. In that case, both chains stop growing. The one that contains the new pi bond could eventually be re-initiated, of course, but in the meantime it will lag behind most of the other chains that will continue to grow without it. That lag will lead to a broadening molecular weight disctribution.



Partly because of the immense size of the molecules involved, hydrogen atom abstraction need to necessarily take place alpha to another radical. One growing chain may pass another in such a way that its benzylic radical grazes a hydrogen atom along the backbone of another. Hydrogen atom abstraction may occur more randomly in this case, although it may still result in a new benzylic radical.



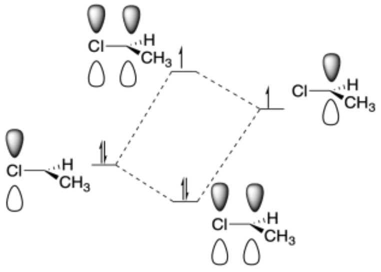
In this case, one chain becomes dead; it stops growing altogether, just like one of the chains in the previous case. However, the other chain continues to grow. In fact, with two radical sites, it will begin to grow twice as quickly as the rest of thegrowing chains. Once again, this development leads to a dramatic broadening of the molecular weight distribution. What's more, this "back-biting" event leads to a change in morphology of the growing chain. Because it is now growing from two different sites, this chain becomes branched, unlike all of the other chains that are growing in a linear fashion. Not only do we now have chains of vastly different lengths, but we also have chains of vastly different shapes, and their properties are becoming less well-defined.

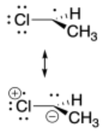


These termination steps are important because they result in the death of growing chains and therefore have an impact on the polymers that result. In later sections, we will see some strategies that limit these termination steps, leading to more uniform molecular weight distribution and more reliable polymer properties.

So far, we have focused on polystyrene as an example of radical polymerization, because of the obvious stability of the benzylic radical. Other monomers can also be polymerized under similar conditions. Like styrene, they may give rise to resonance-delocalized radicals. In other cases, the radical stability may be less obvious, such as in the case of vinyl chloride. Vinyl chloride (CH_2=CHCl) is a pretty candidate for radical polymerization because radicals are stabilized by adjacent halogen atoms.

That may come as a surprise. This stability results from a hyperconjugation effect, in which overlap between the radical electron and a nonbonding pair on the halogen results in a net stabilization. This idea is similar to the one behind the stability of highly substituted radicals, such as radicals on tertiary carbons.



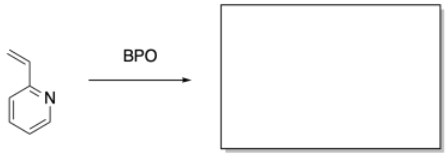


Problem SM7.1.

Show the polymers that would result from radical polymerization of the following monomers.

a)

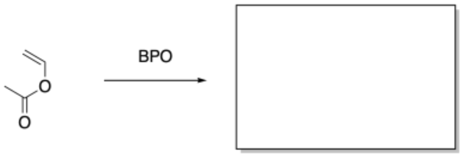
b)



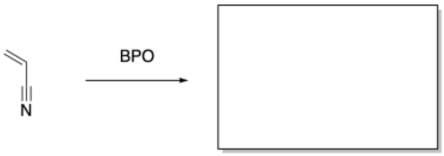
c)

d)

e)



f)



Problem SM7.2.

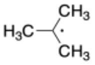
Show why radicals formed from the following monomers are relatively stable:

a) acrylonitrile, $CH_2{=}CHCN$

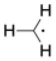
b) methyl acrylate, $CH_2{=}CHCO_2Me$

Problem SM7.3.

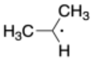
Apart from resonance delocalization, degree of substitution is also a modest stabilizing factor for radicals. Indicate the order of stability of the following radicals:



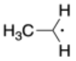
tert-butyl



methyl



iso-propyl



ethyl

2.10: Living Radical Polymerization- RAFT

The termination of radical polymerizations can lead to broadening molecular weight distributions and divergent morphology, with branched structures eventually adding in to the mixture of linear chains that were already growing. There are several methods commonly used to prevent these random terminations. All of them work by keeping the concentration of growing chains low. That strategy limits the chance that radical chain ends encounter other chains and undergo termination reactions.

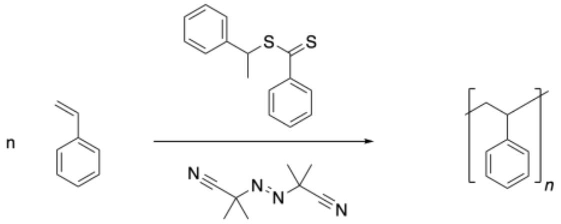
The underlying argument for this strategy is that the kinetics of chain growth and chain termination steps depend differently on the concentration of growing chains. A propagation step requires only one growing chain to encounter a highly abundant monomer molecule. A termination typically requires two growing chains to encounter each other. Consequently,

Rate propagation = $k\,[\text{polymer}^{\cdot}][\text{monomer}]$

Rate termination = $k\,[\text{polymer}^{\cdot}][\text{polymer}^{\cdot}] = [\text{polymer}^{\cdot}]^2$

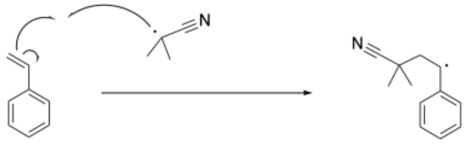
There is a trade-off. Limiting the concentration of growing chains results in slower polymer growth. At the same time, it results in dramatically slower rates of chain termination.

Reversible addition-fragmentation chain transfer (RAFT) polymerization is a common strategy used to limit the concentration of polymer chains at any given time, while ensuring a steady supply of these growing chains in the long run. The strategy has been described as putting growing chains in suspended animation, waking them up periodically to continue polymerization. The key component of this strategy is the chain transfer agent, sometimes called a chain control agent. Usually, these chain transfer agents are thiocarbonylthio compounds like the one shown below.

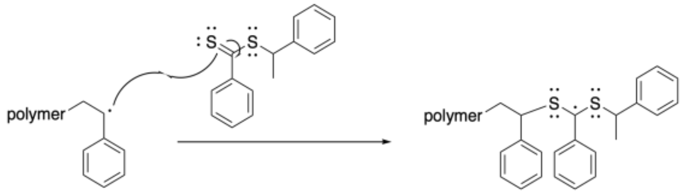


Note that the conditions are otherwise very similar to a regular radical polymerization. The process starts with initiation of radicals, in this case through decomposition of the AIBN.

The isobutyronitrile radical then propagates the radical to the first styrene molecule. So far, nothing different has happened compared to a regular radical polymerization. The resulting benzylic radical propagates with additional styrene monomers, one at a time, enchaining them into the polymer.



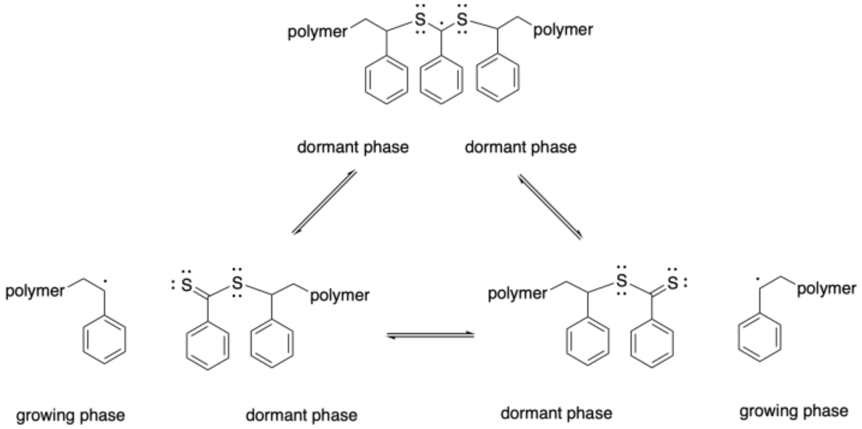
After a few of those propagation events, the growing chain encounters a molecule of the chain transfer agent. Insetad of adding to the pi bond of the styrene, the radical adds to the pi bond of the thiocarbonyl. The new radical is centered on the carbon between the sulfur atoms. If you have encountered sulfur and phosphorus chemistry before, you will know that these large main group atoms have a knack for stabilizing species next to them that would otherwise be very reactive. That's true with radicals, too. The result is that the radical has found a stable resting state. While it sits there, no polymerization can occur, but no terminations will happen, either.



This step happens reversibly, so the growing chain can be released again. It is useful to think of this equilibrium as partitioning the polymers between a growing phase, in which chains can grow but they may also die, and a dormant phase, in which chains are safely sleeping but will not grow.

The structure of these particular chain transfer agents leads to a second possible equilibrium. Rather than releasing the original growing chain from the dormant phase, a radical could be released by cleaving the other sulfur-carbon bond, forming a new thiocarbonyl. The radical that is released is then free to propagate, forming a new polymer chain.

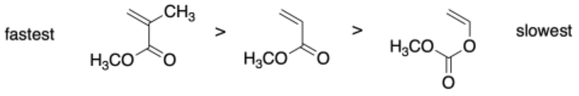
As a result, we can think of this chain control agent as participating in multiple equilibria, with two chains that can each be either dormant or growing. The quilibrium constants are typically chosen so that the chains spend more of their time in a dromant state, but at any given time one of them may be released and start growing again.



As a result, the rate of termination is cut down drastically. Molecular weight distribution (or dispersity) is much narrower and consequently the polymer has much more well-defined properties. Furthermore, the low chance of termination means that the polymer chain can continue to grow until it reaches very high molecular weight.

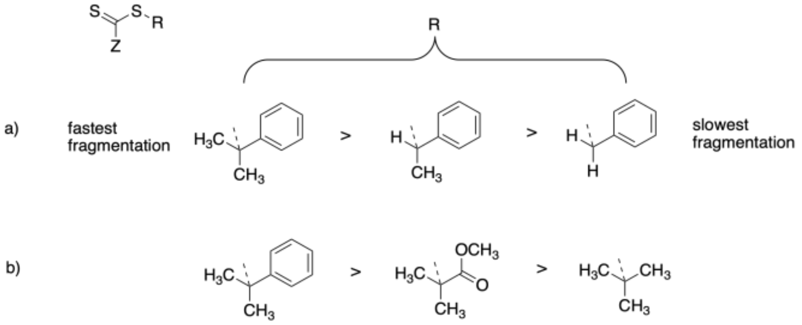
<u>Problem SM8.1.</u>

Relative rates are very important in controlling polymerization via RAFT. Rationalize the relative radical polymerization rates for the monomers below.



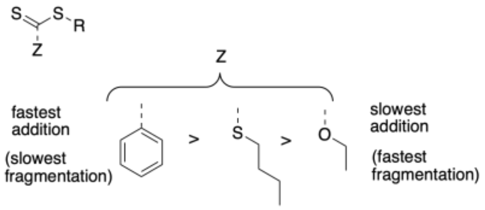
Problem SM8.2.

Relative rates of fragmentation of the chain control agent are important in releasing the growing phase during polymerization. Rationalize the relative fragmentation rates for the chain control agents below.



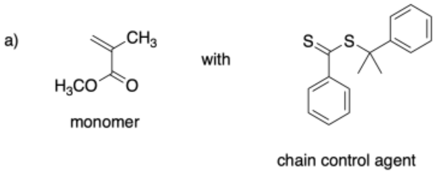
Problem SM8.3.

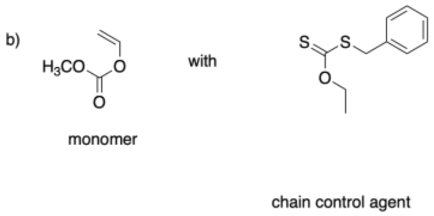
Relative rates of addition of radical to the chain control agent are important in controlling the concentration of the growing phase during polymerization. Rationalize the relative addition rates for the chain control agents below.



Problem SM8.4.

Effective chain control by RAFT requires selective matching between monomer and chain control agent so that there is an appreciable equilibrium between growing phase and dormant phase. Explain the choice of reagents here.



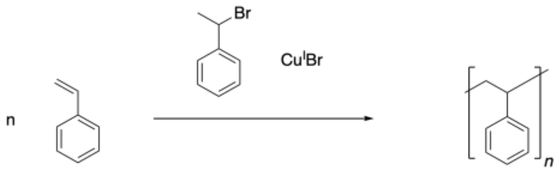


2.11: Living Radical Polymerization- ATRP

SM9. Living Radical Polymerization: ATRP

Atom transfer radical polymerization (ATRP) is another common method of carrying out living polymerization. This method, like RAFT and other methods, sets up an equilibrium between a dormant phase of polymer chains and a growing phase. In the dormant phase, radicals have been trapped and are protected from termination, but are also unable to participate in polymerization. In the growing phase, radical chains have been released and can continue to grow by adding monomers in a radical mechanism. The idea is to release just a few radical chains at a time, recapturing them before they have a chance to undergo chain termination events.

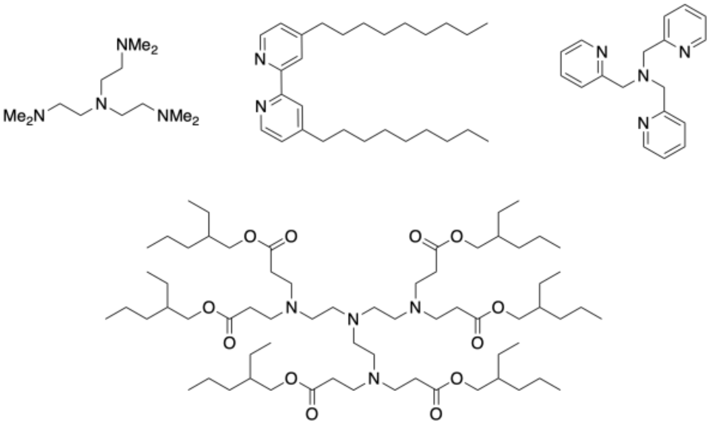
ATRP is initiated in a very different way from other radical polymerizations. It does not depend on a typical initiator such as AIBN or benzoyl peroxide. Instead, the initiator is an alkyl halide. On its own, the alkyl halide seems more suited for polar reactions such as nucleophilic substitutions than radical reactions. The second component of the chain control agent, usually a copper(I) halide, is required in order to activate the initiator, turning it into a radical. Polymerization ensues.



In the initiation step, a halogen atom is transferred from the alkyl halide to the copper(I) ion, leaving behind a radical. In formal terms, the copper has become copper(II), so mechanistically this step appears to involve an electron transfer.

Because the halogen atom on the alkyl halide has lone pairs, it is likely that the electron transfer takes place via an inner-sphere mechanism after the alkyl halide has coordinated to the copper. However, if something prevents the alkyl halide from coordinating to the copper, an outer-sphere electron transfer would still be possible.

There is always an additional component to the chain control system. The copper salts themselves are pretty insoluble. A chelating ligand is added to bind the copper ion and help get it into solution, where it can much more readily participate in the polymerization reaction. A few examples of these ligands are shown below.



Problem SM9.1.

Show CuBr binding with each of the ligands shown above.

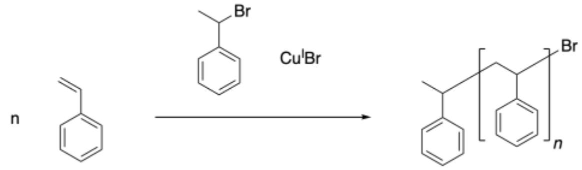
Problem SM9.2.

Show a mechanism of initiator activation via

a) outer-sphere electron transfer

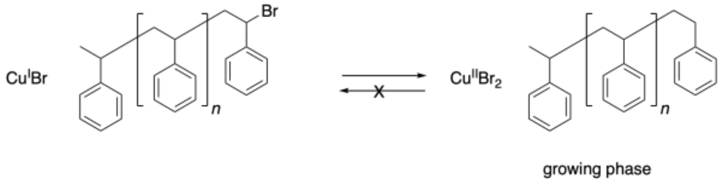
b) inner-sphere electron transfer

Once the initiator has been activated, it can add to the first styrene molecule. The radical continues to propagate, building up a long polymer chain. In the final polymer, both end groups come from the initiator.

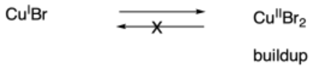


Chain control once again relies on an equilibrium between a dormant phase and a growing phase. In the dormant phase, the radical chain end has been capped with a bromine atom. In the growing phase, the radical chain end is free and able to add to additional monomers.

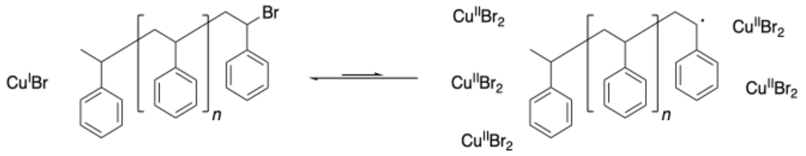
One problem that can arise in living polymerizations is that at some point a termination may still occur. Of course, that results in a dead chain that will no longer grow. An additional consequence is that the chain can no longer go back into the dormant phase, and if the chain cannot go back, then neither can the copper(II).



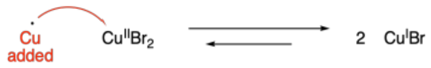
Thus there is a buildup of copper(II) in the system.



What happens when there is a buildup of copper(II)? The job of copper(II) is to deactivate the radical, sending it back into the dormant phase. If copper(II) starts building up, the equilibrium shifts, driving all of the polymer chains into the dormant phase. Polymerization grinds to a stop.



There are a couple of clever solutions to this problem. Perhaps the simplest method uses copper metal to reduce the copper(II) to copper(I). This method has been coined "supplemental activation reducing agent" or SARA.



Problem SM9.3.

In addition to SARA, there are other methods of converting deactivated copper back into its active form in order to shift chains back into the growing phase. Initiators for continuous activator regeneration (ICAR) uses organic reducing agents to convert Cu^{II} back into Cu^{I}. Provide a mechanism for this reaction using phenylhydrazine ($PhNHNH_2$) as the reducing agent.

Problem SM9.4.

Activators regenerated by electron transfer (ARGET) is a similar method to SARA and ICAR, but relies on the addition of the thermal initiator, AIBN, to the polymerization.

a) Provide a mechanism for how AIBN regenerates Cu^{I} ion.

b) Explain the disadvantageous side reaction that can result under these conditions.

CHAPTER OVERVIEW

3: Kinetics and Thermodynamics of Polymerization

3.1: Thermodynamics of Polymerization

Polymerization is the process of taking individual monomers and enchaining them into a macromolecule. Thermodynamically, there are always two factors to consider in a reaction: enthalpic contributions and entropic contributions.

$$\Delta G = \Delta H - T\Delta S$$

Entropic changes in chain polymerizations tend to be qualitatively similar in different cases. Because a large number of monomers are being enchained together in a macromolecule, the number of degrees of freedom is always decreasing, regardless of the specific polymerization process under consideration. Consequently, the entropy change associated with polymerization is always negative.

$$\Delta S = k_B \ln\left(\frac{W_f}{W_i}\right)$$

in which k_B is Boltzmann's constant and W is the number of microstates available in the final or initial state. If $W_f < W_i$, then $\Delta S < 0$ because the natural log of a fraction is a negative number.

Free energy correlates positively with enthalpy and negatively with entropy. That means that a negative entropy change translates into a positive, and unfavorable, free energy change. Polymerization is always entropically disfavored, regardless of the circumstances. However, because entropy changes are generally rather small compared to enthalpy changes, polymerization proceeds despite this handicap. The entropy factor begins to dominate the equation only at higher temperatures, because the entropy contribution scales with temperature (in Kelvin) in the expression for free energy.

As a result, thermodynamically, chain polymerizations should be run under cooler conditions in order to maximize the degree of polymerization. Nevertheless, there are certain polymerizations (such as ring-opening polymerization of cyclic esters) that are frequently run at elevated temperatures because of a significant barrier to the reaction. Of course, in these cases there tends to be a maximum extent of polymerization before the process bottoms out in an equilibrium between polymer and monomer.

In general, this entropic problem in entropy gives rise to the term "**ceiling temperature**", which is the temperature above which polymerization of a particular monomer will not occur.

In condensation polymerizations, the entropy of reaction is more subtle. The formation of condensation side products, such as water or methanol, means that there are not overall changes in the number of molecules before and after polymerization. For example, *n* co-monomers are converted into 1 polymer chain and *n*-1 water molecules. There may still be entropy changes in the reaction, but the sign of the entropy change is not as easy to predict compared to chain polymerization.

Since the entropy for chain polymerizations is always positive, then all chain polymerizations must be exothermic, because otherwise they would never proceed. The reasons for these enthalpically-favored reactions varies from one case to another.

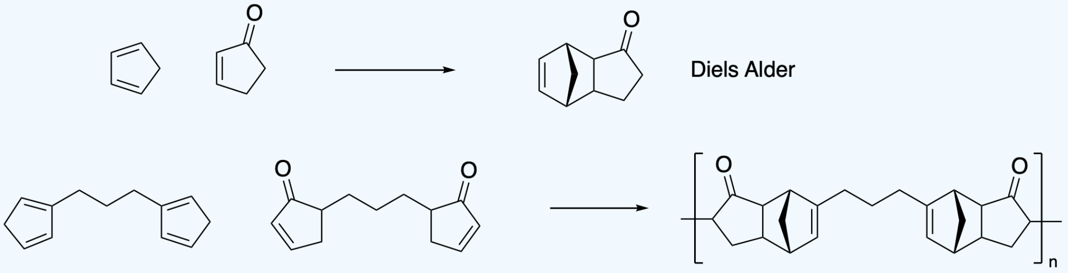
In olefin polymerization (alkene polymerization), the enthalpy of reaction has been measured in a wide range of cases; it is usually around -20 kcal/mol. This negative ΔH value can be partly attributed to the exchange of one C=C π bond for one C-C σ bond for every alkene monomer enchained. The strength of an average C=C double bond is approximately 147 kcal/mol, whereas the strength of an average C-C bond is about 83 kcal/mol. By difference, the strength of a C=C π bond is about 64 kcal/mol. Thus, it costs 64 kcal/mol to break the π bond but we drop 83 kcal/mol for each σ bond made, for a net decrease of around 20 kcal/mol.

Bond	Bond Energy (kcal/mol)	Bond	Bond Energy (kcal/mol)	Bond	Bond Energy (kcal/mol)
C-C	83	C-N	73	C=C	147
C-O	86	C-Cl	81	C=O	178
N-H	93	Cl-H	102	O-H	111

To be sure, there are other factors that contribute to the enthalpy change. C-H bond strengths change significantly with hybridization changes. Intramolecular steric interactions are drastically different in standard monomers compared to polymers. In alkene polymerization in particular, phase changes between gas phase or liquid phase starting material and solid product is appreciable, although still small compared to the bond strength issues. Nevertheless, at first glance we would expect a moderately exothermic reaction, and that's what has been measured experimentally.

Exercise 3.1.1

Diels Alder polymerization depends on a [4+2] cycloaddition. Thermodynamic studies on the parent reaction indicate ΔH = -40 kcal/mol. Explain this observation in terms of bond strengths.



Taking a second example, the ring-opening polymerization of cyclic esters is considered to be exothermic because of ring strain. Values of ΔH are strongly dependent upon ring size, which is intimately connected with ring strain. For γ-butyrolactone, a five-membered ring containing a carbonyl, ΔH = -1 kcal/mol; that's not enough to compensate for a negative entropy of reaction, so that this monomer can only be polymerized at low temperatures. On the other hand, for δ-valerolactone, ΔH = -3 kcal/mol, whereas for ε-caprolactone, ΔH = -7 kcal/mol. These six- and seven-membered lactones are much more readily polymerized because of increasing ring strain.

Exercise 3.1.2

The Ceiling temperature can be calculated from an assumption that $\Delta G = 0$, at which point polymerization is readily reversible. A kinetic approach to equilibrium gives the relation:

$$T_c = \frac{\Delta H}{\Delta S + R \log[M]}$$

in which R is the ideal gas constant, 1.98 cal K^{-1} mol^{-1} (or 8.314 J K^{-1} mol^{-1})

Calculate the ceiling temperature for caprolactone polymerization if ΔH = -7 kcal mol^{-1} and ΔS = -8.6 cal K^{-1} mol^{-1}. The concentration of neat caprolactone is 8.7 M. (Data from: Olsen, P.; Odelius, K.; Albertsson, A.-C. *Biomacromolecules* **2016**, *17*, 699-719.)

Given a less pronounced entropic bias against condensation polymerization, endothermicity becomes less crucial. Indeed, some condensation polymerizations are effected through simple trans-esterifications, which ought to be close to thermoneutral. As pointed out in the condensation section, these reactions are frequently driven to completion by removal of the condensation side product, small molecules such as methanol or water.

Exercise 3.1.2

Some polyamides are made industrially from the corresponding difunctional amines and acid chlorides, releasing HCl. Calculate the enthalpy change for this reaction

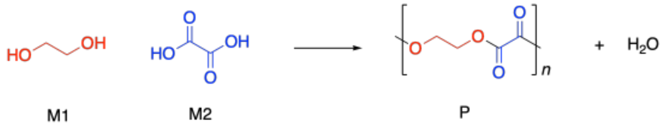
---

3.2: Kinetics of Step-Growth Polymerization

KP2. Kinetics of Step-Growth Polymerization

It is important to understand how reactions proceed over time. This information can tell us how long it will take for a polymer to reach an optimum length. It can also provide insight into how the polymerization occurs, just as kinetics can provide insight into other reaction mechanisms.

Condensation polymers grow through a a step-growth process. The reaction generally involves substitution at a carboxyloid. For example, polyester formation often involves the substitution of an alcohol functional group at a carboxylic acid, making an ester. The drawing below illustrates that action using ethylene glycol and oxalic acid, to use common names prevalent in industry. Oxalic acid is not typically used in making polyesters, but it is drawn here as a very simple example structure.



If you know some basic kinetics, you know that we can express the rate of a reaction as the rate of change of product concentration per change in time. In this case, the product is the polymer, abbreviated P. Alternatively, we could express the rate of the reaction as the rate of change of monomer concentration per change in time. Just by looking at the equation of reaction, we expect that every time a polymer molecule is made, a monomer molecule is used up. In this case, we have a co-polymer, made of two different monomers, so that's why we could express the reaction rate as the rate of change of either monomer concentration. The negative sign in the rate suggests we are looking at the rate of disappearance of monomer; as polymer appears, monomer disappears.

$$\text{Rate} = \frac{d[P]}{dt}$$

$$= -\frac{d[M1]}{dt}$$

$$= -\frac{d[M2]}{dt}$$

If you know something about organic reaction mechanisms, you may know that the very first step in an esterification is the donation of a lone pair from an alcohol oxygen on the diol to a carbonyl carbon on the dicarboxylic acid. (It could actually be the second step, but we'll get to that later.) That first step in the mechanism is an elementary reaction. All of the other steps you would draw in a mechanism are also elementary reactions. The nice thing about elementary reactions is that we always know the rate law of each one: it's a rate constant times the concentrations of all of the species leading into that step. In this case, this first step is also the rate-determining step, so the entire reaction is governed by the rate law of that first step. It requires both monomers, so we get a simple rate law.

$$\text{Rate} = k\,[M1]\,[M2]$$

$$\text{but if} \quad [M1] = [M2] = [M]$$

$$\text{then} \quad \text{Rate} = k\,[M]^2$$

Note that, based on the stoichiometry (the ratio of monomers in the equation of reaction), we would probably run this polymerization with equal amounts of diol and dicarboxylic acid. Instead of worrying about M1 and M2 separately, we can call them both [M].

So, what we have here is a simple second-order rate law. This form of the rate law is called the differential rate law, because it is expressed in terms of the rate of change of one thing with the rate of change of the other. If that isn't exactly what you are interested in, and you just want to see what happens to concentrations over time, you may want to integrate this expression to obtain the integrated from of the rate law.

$$\text{Rate} = \frac{-\,d[M]}{dt} = k[M]^2$$

$$\frac{-\,d[M]}{[M]^2} = k\,dt$$

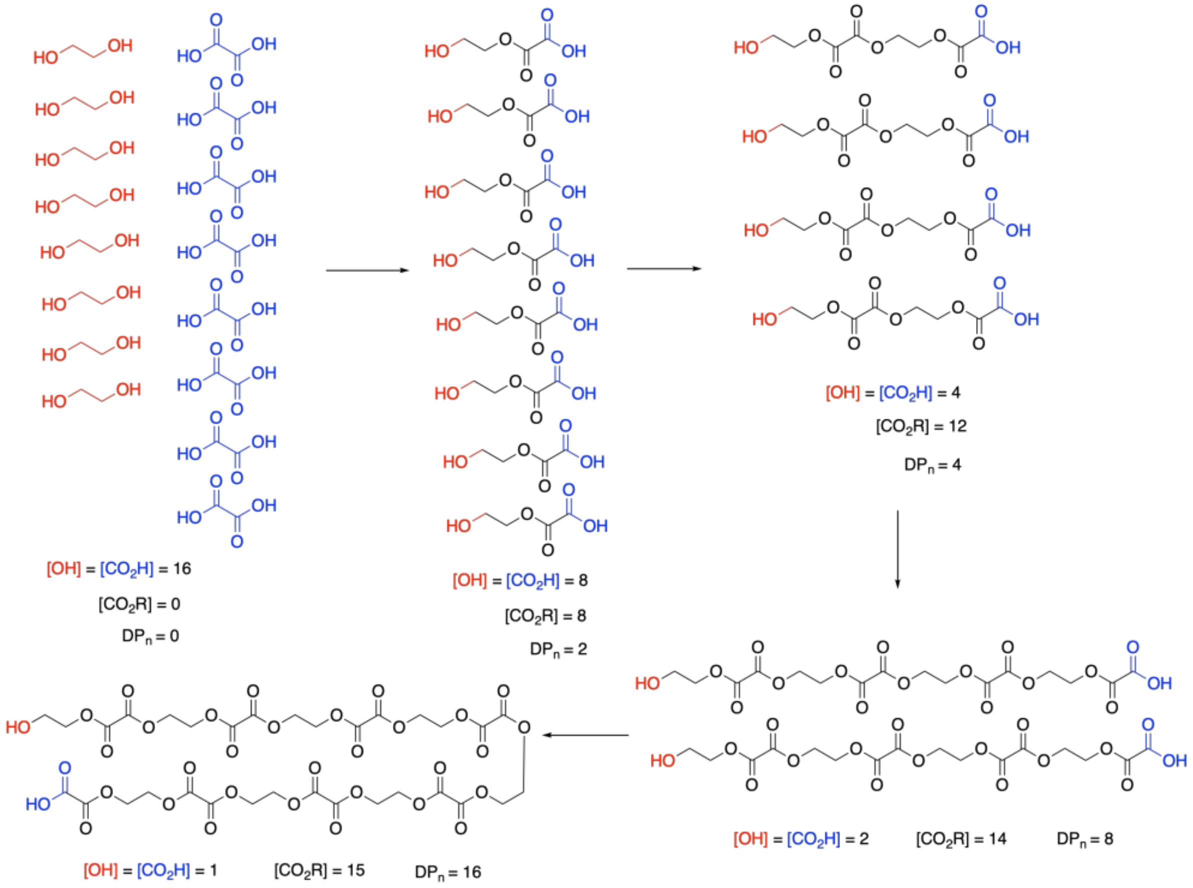
Integrating:

$$\int_{c_0}^{c_t} \frac{-\,d[M]}{[M]^2} = \int_{t=0}^{t} k\,dt$$

$$\frac{1}{[M]} - \frac{1}{[M]_0} = k\,t$$

If we were to measure monomer concentration periodically during the polymerization and plot its inverse over time, we would obtain a straight line. The slope of the line would be the rate constant, and the intercept would reflect the inverse of the monomer concentration with which we had started the reaction.

At this point, we need to pause and talk about what we actually mean by monomer concentration. Because of a very specific feature of condensation polymerizations, it isn't really the concentration of ethylene glycol or oxalic acid. Take a look at this drawing of this step-growth process and we will talk about why that is.



Remember that, in step-growth polymerization, the majority of molecules are probably reacting at roughly similar rates. Two monomers link together to form dimers, two dimers form tetramers, two tetramers form octamers, and so on. It won't go as perfectly as we see in this picture; there will inevitably be some stragglers that throw the averages off. But notice what this means: the monomers disappear right away. Nobody is really interested in how quickly the monomers turn into dimers. They want to know how the gowth of the polymer chain is progressing.

So, in the above expression, [M] doesn't refer to the concentrations of those two monomers at all. It refers to the concentration of the reactive functional groups in those monomers. After all, once the monomers are gone, the same esterification reaction keeps happening, and it's really the concentration of alcohol and carboxylic acid groups that matters, whether they are found on monomers, dimers, tertramers, or whatever. In these rate expressions, sometimes people will explicitly use [OH] and [CO_2H] in the rate expression, underscoring that they are really following the disappearance of those functional groups.

And notice what's happening to those functional groups. Their concentration is smoothly dropping over time. Furthermore, ester concentration, representing the new functional group in the polymer, is growing in at the same rate. [OH] and [CO_2H] drop by 8 (or in half) in the first step; [CO_2R] increases by 8, and so on. SO the rate of consumption of reactant functional groups equals the rate of appearance of product functional groups.

The other thing we are interested in here is the degree of polymerization: the number of monomers incorporated into the chain. The polymer is growing at a certain rate, but how long is it getting? Just looking at the simple scheme of polymer growth above, we see the average degree of polymerization increasing (written as *DP* or sometimes as X_n; a bar over the symbol signals that we are looking at an average). If you look carefully, you will see that the degree of polymerization is always the original monomer concentration divided by the remaining monomer concentration. That turns out to be a very important relationship.

$$\text{degree of polymerization} \quad DP_n = \bar{X}_n = \frac{[M]_0}{[M]}$$

Note that this relationship is just the inverse of the fraction of monomer remaining (or, really, the fraction of those monomer functional groups left over).

$$\text{fraction monomer remaining} = \frac{[M]}{[M]_0}$$

The opposite quantity is the fraction of monomer converted. That describes the functional groups already converted into esters. Because we are dealing with fractions, the fraction converted is just one minus the fraction remaining. If we do a little algebra, we get a variation on that piece of information.

$$\text{fraction monomer converted} \quad p = 1 - \frac{[M]}{[M]_0}$$

$$\text{or} \quad 1 - p = \frac{[M]}{[M]_0}$$

$$\text{or} \quad \frac{1}{1 - p} = \frac{[M]_0}{[M]}$$

Why did we do that last part? Because now we have arrived back at the expression for degree of polymerization. So, now we have an equivalent way of expressing degree of polymerization in terms of the fraction converted. This relationship is called the Carothers equation, in honor of Wallace Carothers, the DuPont chemist who invented nylon.

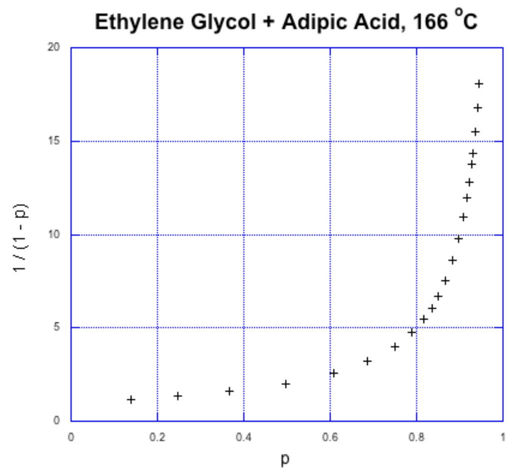
$$\text{but} \quad \bar{X}_n = \frac{[M]_0}{[M]}$$

$$\bar{X}_n = \frac{1}{1 - p} \qquad \text{(Carothers Equation)}$$

Problem KP2.1.

Predict the degree of polymerization if 75% of monomer end groups have been converted to polymer.

So, what does that relationship look like? Here's some data from Paul Flory, another DuPont chemist and Nobel laureate, obtained during the period between the World Wars when this kind of chemistry was just getting started (Flory, P. J. *J. Am. Chem. Soc.* **1937**, *59*, 466-470).



That's fraction converted on the x axis and the expression for degree of polymerization on the y axis. This is exponential growth. The degree of polymerization is starting to shoot upward dramatically. We already knew that from our introduction to step growth, but what stands out from the data is how a higher degree of polymerization, and high molecular weight, doesn't really occur until very late in the reaction. If we need high molecular weight condensation polymers, the chemistry better be pretty reliable; otherwise, if things go wrong, we'll be left with some short-chain goo instead of long-chain materials.

Now let's take these new relationships and look at them in the context of our second-order kinetics. We're starting with that same integrated rate law, but we have mulitplied everything on both sides of the equation by the starting monomer concentration. That's fair game in algebra, remember. The reason for doing that is to get a term that resembles our relationships that describe degree of polymerization.

$$\frac{[M]_0}{[M]} - \frac{[M]_0}{[M]_0} = [M]_0\, k\, t$$

$$\frac{[M]_0}{[M]} - 1 = [M]_0\, k\, t$$

$$\text{but} \quad p = 1 - \frac{[M]}{[M]_0}$$

$$\text{or} \quad 1 - p = \frac{[M]}{[M]_0}$$

$$\text{or} \quad \frac{1}{1 - p} = \frac{[M]_0}{[M]}$$

$$\text{so} \quad \frac{1}{1 - p} - 1 = [M]_0\, k\, t$$

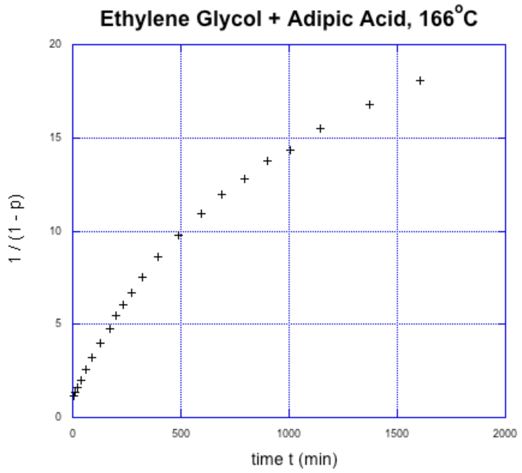
So far, we have taken the ratio we obtained in the first line and worked out its relationship to fraction converted, which we substituted in the last line. Now we bring in the Carothers equation to recall that this is really telling us how degree of polymerization changes over time. This relationship indicates the degree of polymerization should increase linearly over time.

$$DP_n = X_n = \frac{[M]_0}{[M]}$$

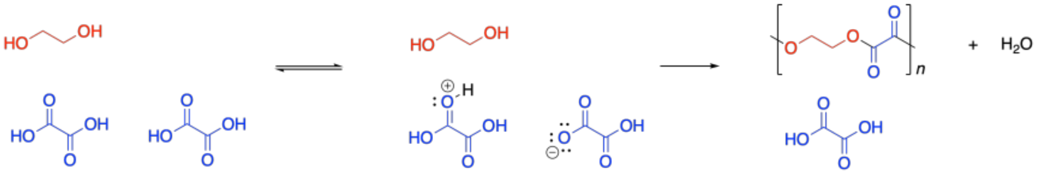
$$\text{and} \quad \frac{[M]_0}{[M]} - 1 = [M]_0\, k\, t$$

$$\text{so} \quad X_n - 1 = [M]_0\, k\, t$$

This relationship indicates the degree of polymerization should increase linearly over time. Once again, we're going to use Flory's data to illustrate the relationship, using the fraction conversion data. He could measure that data easily, and knew how it was related to degree of polymerization.



It was supposed to be linear. But don't worry; Flory knew what went wrong. You might know, too, if you remember a few things about substitution at carboxloids. The trouble is, we are dealing with a neutral nucleophile and a fairly unreactive electrophile. That reaction should be really slow. It isn't that slow, thoough, because it is self-catalyzed. One carboxylic acid monomer can activate another, making it a better electrophile.



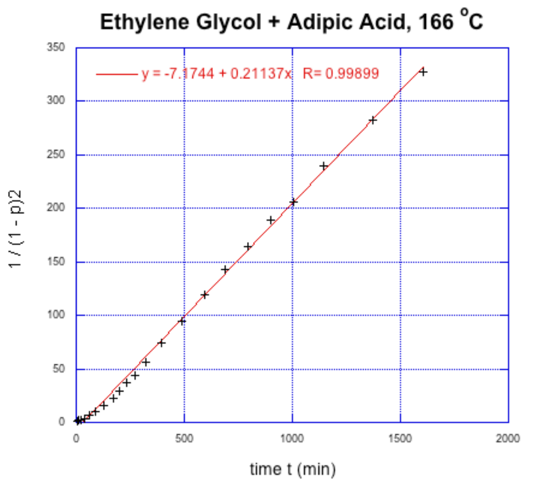
That means the coupling of the alcohol with the carboxylic acid isn't the first elementary step of the reaction, but the second. Before the alcohol and carboxylic acid can come together, two carboxylic acids need to have collided already. That means we have a third order reaction. As it happens, the integrated form of a third order rate law isn't all that much more complicated, and we can do some similar algebra with it to see how the degree of polymerization would vary with time given this new information.

$$\frac{1}{[M]^2} - \frac{1}{[M]_0^2} = 2\,k\,t$$

$$\frac{[M]_0^2}{[M]^2} - \frac{[M]_0^2}{[M]_0^2} = 2\,[M]_0^2\,k\,t$$

$$\frac{1}{(1-p)^2} - 1 = 2\,[M]_0^2\,k\,t$$

We can take Flory's data again and give it this new treatment.



This time, we get a linear relationship. That correction illustrates one of the fundamental uses of kinetics, which is a tool that lets us probe how reactions happen. In this very specific case, kinetics showed that there was an extra (pre-rate determining) step in the reaction. In addition, we found that it is the square of the degree of polymerization that is increasing linearly with time.

Problem KP2.2.

Given an initial alcohol group concentration $[M]0 = 17$ M, determine the rate constant from Flory's data in $L^2mol^{-2}s^{-1}$.

Flory also established a statistical basis for predicting molecular weights and molecular weight distributions in polymers. For example, once we have the degree of polymerization, it is a simple step to calculate the approximate molecular weight. That's just the degree of polymerization times the molecular weight of the monomer; in other words, the number of monomers in the chain times the weight of each one. (This approach neglects any small molecules such as water that are lost during the condensation reaction.)

$M_n = DP \text{ x } M_0$

$M_n = M_0 / (1 - p)$

This is called the number average molecular weight. It's based on taking one average value for the chain length and converting that into the chain molecular weight. Of course, some chains may be much shorter (Flory actually shows, based on probability, that there will be a number of monomers left over) and as such they contribute less to the overall sample.

A second way to approach the average chain molecular weight is to assess the fraction of the total weight contributed by each chain length. The average chain molecular weight would then be given by:

$M_w = \Sigma \pi_x x M_0$

in which π_x is the fraction of chains of length x.

What is the fraction of chains of length x? The approach starts with considering the probability that a chain will be *x* units long. As noted above, a chain x units long has x-1 ester linkages and 2 unreacted chain ends. We know the probability of a chain end being converted to a polymer linkage is p, and in a chain x units long that will have to happen x-1 times, for a probability p^{x-1}. We also know that the probability of a functional group being left unreacted is 1-p, and that has to happen twice here, for a probability $(1-p)^2$. The probability of having a chain of length x is:

$\pi_x = x\, p^{x-1}(1-p)^2$

That means:

$M_w = \Sigma\, x\, p^{x-1}(1-p)^2\, x M_0$

$M_w = (1-p)^2 M_0\, \Sigma\, x^2\, p^{x-1}$

The series on the right is reducible to:

$\Sigma\, x^2\, p^{x-1} = (1 + p) / (1 - p)^3$

So that:

$M_w = (1\text{-}p)^2 M_0(1 + p) / (1 - p)^3$

$M_w = M_0(1 + p) / (1 - p)$

That provides a straightforward prediction of the weight-average molecular weight based on the fraction converted in condensation polymerization. Although M_n and M_w presented here are essentially theoretical predictions of molecular weight, these quantities can also be measured experimentally using different methods.

The ratio between these two quantities has always been used as an expression of the breadth of the molecular weight distribution, called the polydispersity index or simply the dispersity:

$D = M_w/M_n$

In the case of condensation polymerization,

$D = [M_0(1 + p) / (1 - p)]/[M_0 / (1 - p)]$

$D = 1 + p$

Because p is always a fraction, the result is that the dispersity of a condensation polymerization is statistically expected to be less than 2.0.

Problem KP2.3.

Given 99% conversion of monomers with average molecular weight 120 g/mol, calculate M_w, M_n and D.

3.3: Kinetics of Chain Polymerization

The polymerization of alkenes occurs in a very different way than monomers that undergo condensation reactions. Whether it occurs through an anionic, cationic, or radical mechanism, polymerization of alkenes involves a chain reaction. Chain reactions are classically illustrated by radical chemistry, so we will look at a treatment of radical chain polymerization to see some of the factors that influence polymerization rates.

A typical radical polymerization starts with the thermal decomposition of a radical initiator to provide two radicals. The rate of decomposition depends only on the decomposition rate constant and the concentration of the initiator.

$$\mathrm{I} \xrightarrow{k_d} 2\,\mathrm{R}^{\cdot}$$

$$\frac{-\,\mathrm{d[I]}}{\mathrm{dt}} = \frac{1}{2}\frac{\mathrm{d[R^{\cdot}]}}{\mathrm{dt}} = k_d\,\mathrm{[I]}$$

Once the radicals have been generated, they are able to undergo radical addition to a monomer double bond. Of course, radical addition to a double bond results in a new radical where the double bond used to be. Although this is formally a radical propagation step, in polymer chemistry it is termed the initiation step, because it is the first time a monomer has undergone radical addition. This step consumes the first monomer and produces a new radical species which will become the growing radical chain. It requires a collision between the radical and a monomer, so the rate of initiation depends on those two concentrations and the chain initiation rate constant, k_i.

$$\mathrm{R}^{\cdot} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}^{\cdot}$$

$$\frac{-\,\mathrm{d[M]}}{\mathrm{dt}} = \frac{\mathrm{d[M^{\cdot}]}}{\mathrm{dt}} = k_i\,\mathrm{[R^{\cdot}][M]}$$

That rate law depends on a reactive intermediate. It's not a very helpful rate law, because the reactive intermediate isn't something that we have directly measured out and added to the reaction, and it might not even occur at high enough levels that we can measure its concentration as the reaction progresses. We usually look for ways to express the rate law in ways that do not include reactive intermediates. In this particular situation, the way of getting around this situation is to assume that the decomposition of the initiator is the rate determining step. Making the radicals in the first place is probably the slow part because it is heavily dependent on bond breaking, which is energy intensive. Once we have radical, it probably undergoes addition to a monomer fairly quickly, initiating chain growth. If that's true, we can assume that the chain initiation step proceeds very quickly afterward, so that the rate really depends only on the rate of the decomposition step.

$$k_i \gg k_d$$

$$\frac{\mathrm{d[M^{\cdot}]}}{\mathrm{dt}} = \frac{\mathrm{d[R^{\cdot}]}}{\mathrm{dt}} = 2\,k_d\,\mathrm{[I]}$$

In practice, polymer chemists add another factor to the rate law. This factor, *f*, takes into account the fact that only some of the radicals from the initiator actually react with monomers to initiate growing chains. The rest decay through some other side reactions. Usually, *f* is assumed to be around 0.5.

$$\frac{\mathrm{d[M^{\cdot}]}}{\mathrm{dt}} = 2\,f\,k_d\,\mathrm{[I]}$$

$$f = 0.3 \text{ to } 0.8$$

Once the first monomer has been initiated into a radical, it can react with another monomer to enchain it and make a new radical. This is the principal propagation step of the chain reaction. That step will keep repeating, adding more monomers into the chain. The rate constant for this step, k_{prop} or k_p, is identical no matter how many monomers have been enchained, but is distinct from k_i because of the different nature of the radical intermediates in the two different steps. For example, the radical obtained from addition to styrene looks pretty similar whether it is the first in the chain or the tenth. Each time, the rate of consumption of monomer depends on the propagation rate constant, the concentration of the monomer, and the concentration of the propagating radical. Notice that in the rate law we just write that propagating radical the same way (M dot) no matter how long the chain grows.

$$M^{\cdot} + M \xrightarrow{k_p} M\text{-}M^{\cdot}$$

$$\frac{-\,d[M]}{dt} = k_p\,[M][M^{\cdot}]$$

There is one last process, or group of processes, to complete the chain reaction cycle. In termination, two radicals combine in some way to form closed-shell products. There are a variety of ways that can happen in a radical polymerization. The simplest event conceptually is coupling, in which two radical chains come together and form a bond. That idea is shown below.

$$M^{\cdot} + M^{\cdot} \xrightarrow{k_t} M\text{-}M$$

$$\frac{-\,d[M^{\cdot}]}{dt} = \frac{2\,d[M\text{-}M]}{dt} = 2\,k_t\,[M^{\cdot}]^2$$

Of course, that rate depends on the termination rate constant and the concentrations of both growing chains. The same would be true if the reaction terminated by conproportionation, in which one radical abstracted an alpha hydrogen from the other, forming one saturated and one unsaturated product.

Once again, these last two rates -- of propagation and of termination -- depend on concentrations of reactive intermediates, which we do not typically know. This time we will use a very standard assumption, which is that the concentration of this reactive species remains constant, being consumed as soon as it is generated. The usual way that we apply the steady state approximation is to assume zero change in concentration of the reactive intermediate. That means that the sum of all the rates for processes generating the intermediate equal the sum of all the rates consuming the intermediate. In polymer chemistry, we take a slight shortcut, and just assume that the rate of appearance of the radical in the first place equals its rate of disappearance. We already have expressions for both of those rates.

$$\text{Rate}_{\text{term}} = \text{Rate}_{\text{init}}$$

$$2\,k_t\,[M^{\cdot}]^2 = 2\,f\,k_d\,[I]$$

$$[M^{\cdot}] = \left(\frac{f\,k_d\,[I]}{k_t}\right)^{1/2}$$

By rearranging, we can get an expression for the reactive chain end concentration. Then we can just substitute the result into our expression for propagation rate:

$$\frac{-\,d[M]}{dt} = k_p\,[M][M^{\cdot}]$$

$$= k_p[M]\left(\frac{f\,k_d\,[I]}{k_t}\right)^{1/2}$$

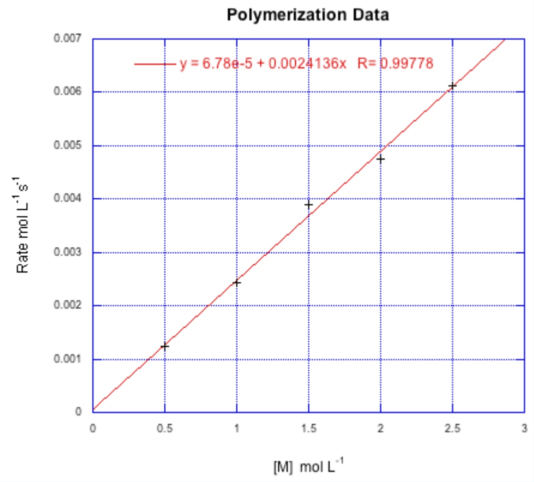
The result sums up the factors that control the growth rate for the polymer. The growth rate increases linearly with the concentration of monomer, and as the square root of the initiator concentration. The rest of the factors are just constants, so we can think of the rate law as one combined constant and those two concentration dependences. Sometimes an aggregate constant of this type is just designated k'.

Note that the propagation rate varies linearly with the concentration of growing chains, but that the termination rate varies with square of the concentration of growing chains. That difference is significant, and it underlies the strategy of living polymerization, which is to keep the concentration of growing chains low. Doing so has the adverse affect of slowing the rate of propagation, but the effect on the termination rate is much greater, making this trade-off worth it to achieve enhanced molecular weight control.

✓ Example 3.3.1

Suppose the following data were obtained for a radical polymerization conducted at various starting concentrations of monomer. If all of the data were conducted at an initiator concentration of 0.25 mmol L^{-1}, calculate k'.

Solution



Kinetics can also be used to establish a theoretical polymer chain length. This quantity is called kinetic chain length, represented by "vee bar". In principle, it's just the ratio of the chain propagation rate to the chain initiation rate. That should tell us the number of monomers per each chain initiated. Because of our earlier assumption about the initiation rate equaling the termination rate, we can substitute the terms for those two rates and simplify the result.

$$\bar{\nu} = \frac{\text{Rate}_{\text{prop}}}{\text{Rate}_{\text{init}}}$$

but at steady state $\text{Rate}_{\text{init}} = \text{Rate}_{\text{term}}$

$$\bar{\nu} = \frac{\text{Rate}_{\text{prop}}}{\text{Rate}_{\text{term}}}$$

$$\bar{\nu} = \frac{k_p[\text{M}][\text{M}^\cdot]}{2k_t[\text{M}^\cdot]^2} = \frac{k_p[\text{M}]}{2k_t[\text{M}^\cdot]}$$

Substituting our earlier expression for the concentration of the growing radical chain ends gives a new expression.

$$\bar{\nu} = \frac{k_p[\text{M}]}{2\,(f\,k_t\,k_d\,[\text{I}])^{1/2}}$$

That means that we can theoretically control the length of polymer chains, because the average length should vary linearly with the concentration of monomer and inversely with the square root of initiator concentration.

As chain reactions, cationic and anionic polymerizations have some characteristics in common with radical polymerizations. One key difference is that the initiator does not fragment into two pieces, each capable of initiating a chain; instead, one added initiator starts polymerization of one chain, without the prior decompositions step seen in radical reactions. Also, termination steps in radical reactions are dominated by radical recombinations (as well as other variations), but in anionic and cationic terminations it is more likely that the growing chain encounters an impurity and reacts with that.

✓ Example 3.3.2

Given that for a cationic polymerization:

$$\text{Rate}_{\text{init}} = k_i\,[\text{M}][\text{I}] \text{ and } \text{Rate}_{\text{term}} = k_t[\text{M}^+]$$

Provide a steady state expression for the concentration of growing cationic chain.

✓ Example 3.3.3

If the propagation step in a cationic polymerization is written as follows:

$\text{M}^+ + \text{M} \rightarrow \text{M-M}^+$

Provide the rate expression for cationic polymerization.

✓ Example 3.3.4

By analogy to radical polymerization, the kinetic chain length in cationic polymerization can be expressed as the ratio of propagation rate to initiation rate. Provide an expression in terms of constants and known concentrations.

✓ Example 3.3.5

In a living polymerization, chain length simplifies to $[M]_0/[I]_0$ because all initiation leads to polymerization and there are no terminations steps. Given a radical polymerization with $[M]_0 = 4.5$ M and $[I]_0 = 1.25$ mM, compare chain length in the following situations:

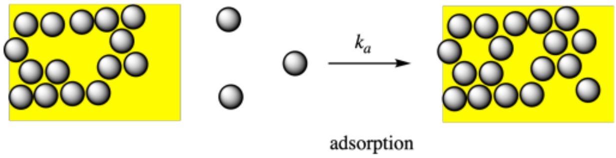
a. a living polymerization
b. a non-living polymerization with $f = 0.5$; $k_p = k_t = 0.003$ s^{-1}; $k_d = 0.0001$ s^{-1}.
c. a non-living polymerization with $f = 0.5$; $k_p = 0.003$ s^{-1}; $k_t = 0.3$ s^{-1}; $k_d = 0.0001$ s^{-1}.
d. a non-living polymerization with $f = 0.5$; $k_p = 0.003$ s^{-1}; $k_t = 0.003$ s^{-1}; $k_d = 0.1$ s^{-1}.

3.4: Kinetics of Catalytic Polymerization

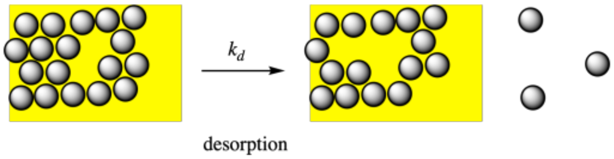
KP4. Kinetics of Catalytic Polymerization

The Ziegler-Natta polymerization of alkenes is conducted under catalytic conditions. In most cases, the process involves heterogeneous catalysis, in which the reaction takes place on the surface of a solid. The kinetics of catalyzed reactions have some features that are different from other reactions and that are worth exploring.

The fact that the reaction is taking place on the surface of a solid is a key feature that must be stressed in the kinetics of heterogeneous catalysis. The treatment of rates therefore uses an approach developed by Irving Langmuir, a long-time scientist at General Electric who was awarded the Nobel Prize for the study of surfaces. One of the things that makes metal catalysts so useful is their ability to adsorb molecules on their surfaces (think of the precious metals used in catalytic hydrogenation, adsorbing alkenes and hydrogen; or the iron in the Haber-Bosch synthesis of ammonia, adsorbing dinitrogen and hydrogen, to cite two important examples). "Adsorption" refers to the adhesion of molecules to a surface. Langmuir thought of this adsorption process as a dynamic one, with molecules landing on and sticking to open spots on a surface even as other molecules lifted off to create vacancies.



Desorption, on the other hand, refers to the process of molecules leaving the surface.



In terms of kinetics, the rate of desorption of a molecule would depend on some rate constant, k_d, and the fraction of the surface covered by these molecules, θ (that's the Greek letter, theta). The greater the surface fraction covered by molecules, the greater the chance that you will encounter one desorbing.

$\text{Rate}_d = k_d\,\theta$

On the other hand, the rate os adsorption of a molecule onto a surface will depend on some rate constant k_a, the concentration of the molecule to be adsorbed, and the fraction of the surface still available. That last part is 1 - θ, because the fraction covered plus the fraction uncovered would equal the whole. Note that Langmuir was interested in gas phase molecules adsorbing onto a surface, and so he expressed things in terms of pressure rather than concentration.

$\text{Rate}_a = k_a\,(1 - \theta)\,[\text{M}]$

At equilibrium, these two rates will equal each other:

$k_d\,\theta = k_a\,[\text{M}] - k_a\,\theta\,[\text{M}]$

$\theta\,(k_d + k_a\,[\text{M}]) = k_a\,[\text{M}]$

$\theta = k_a\,[\text{M}] / (k_d + k_a\,[\text{M}])$

Now we have an expression for the fraction of the surface covered by the substrate. This term is called the "Langmuir isotherm" and it shows up in various surface and catalytic phenomena. It is usually expressed slightly differently, in terms of an equilibrium constant for adsorption:

$$\theta = \frac{K_{eq}[\text{M}]}{1 + K_{eq}[\text{M}]} \qquad K_{eq} = \frac{k_a}{k_d}$$

The rate of a reaction catalyzed on that surface will depend on the catalyst concentration as well as a rate constant for enchainment, k_{prop} or simply k_p, and the amount of surface covered by monomer (unbound monomer will not undergo propagation). An additional factor, x*, takes into account the fact that only a fraction of the catalyst is active.

$$\text{Rate}_p = k_p[\text{Cat}]\text{x}^*\theta$$

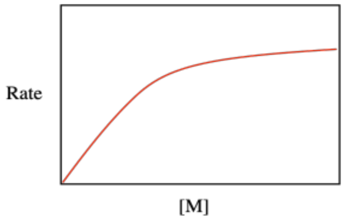
[Cat] = catalyst concentration
x* = fraction of catalyst that is active

$$\text{Rate}_p = \frac{k_p K_{eq}[\text{M}][\text{Cat}]\text{x}^*}{1 + K_{eq}[\text{M}]}$$

Superficially, the form of the rate law has something in common with the Michaelis-Menten equation, with which you may already be familiar. The Michaelis-Menten equation relates the rate of an enzyme-catalyzed reaction to enzyme concentration, the rate constant for the catalytic reaction, and rate constants for reversible substrate binding with the enzyme.

$$\text{Rate} = \frac{k_{cat}[\text{E}]_0[\text{S}]}{1 + K_m[\text{S}]} \qquad K_\text{m} = \frac{k_r + k_{cat}}{k_f}$$

Maybe that resemblance shouldn't be too surprising. After all, both equations describe catalytic processes, in which either the surface or the binding site must accomodate the substrate so as to carry out a subsequent series of reactions. Both equations take the form of a saturation curve, indicating that the rate of reaction will level out if the surface or binding site becomes fully occupied.



Problem KP4.1.

One way to evaluate multi-term relationships is to consider what happens under different conditions. What happens to the rate law for catalytic polymerization if monomer concentration is very low, so that $1 >> K_{eq}[\text{M}]$?

Problem KP4.2.

What happens to the rate law for catalytic polymerization if monomer concentration is very high, so that $K_{eq}[\text{M}] >> 1$?

3.5: Solutions to Selected Problems

KP5. Solutions to Selected Problems

Problem KP1.1.

Two C-C σ bonds and one new π bond are made. Three old π bonds are lost.

ΔH = bonds broken - bonds made

ΔH = (3 x 64) - ((2 x 83) + 64) kcal/mol

ΔH = -38 kcal/mol

Problem KP1.2.

$T_c = \Delta H / (\Delta S + R\log[M])$

$T_c = -\ 7{,}000\ \text{cal mol}^{-1}\ (-8.6\ \text{cal K}^{-1}\ \text{mol}^{-1} + 1.98\ \text{cal K}^{-1}\ \text{mol}^{-1} \log(8.7))$

$T_c = -\ 7{,}000\ (-8.6 + 1.98\ (0.939))\ \text{K}$

$T_c = -\ 7{,}000\ (-6.74)\ \text{K}$

$T_c = 1038\ \text{K} = 765\ °\text{C}$

Problem KP1.3.

For each amide bond, a C-N bond and a H-Cl bond are made. A C-Cl and a N-H bond are lost.

ΔH = bonds broken - bonds made

= (C-Cl + N-H) - (C-N + H-Cl)

ΔH = (81 + 93) - (73 + 102) kcal/mol

ΔH = -1 kcal/mol

Problem KP2.1.

75% conversion means 0.75 in terms of fractions.

DP = 1 / (1 - p)

DP = 1 / (1 - 0.75)

DP = 1 / 0.25

DP = 4

Problem KP2.2.

$\text{slope} = 2\ [M]_0\ k = 0.717\ \text{s}^{-1}$

$k = 0.717\ \text{s}^{-1} / (2 \text{ x } 17\ \text{mol L}^{-1})$

$k = 0.021\ \text{L mol}^{-1}\text{s}^{-1}$

Problem KP2.3.

$M_n = M_0 / (1 - p)$

= 120 g/mol / (1 - 0.99)

= 120 g/mol / 0.01

= 12,000 g/mol

$M_w = M_0(1 + p) / (1 - p)$

= 120 g/mol (1 + 0.99) / (1 - 0.99)

= 120 g/mol (1.99) / 0.01

= 23,800 g/mol

$D = 1 + p$

$= 1 + 0.99$

$= 1.99$

Problem KP3.1.

$\text{Rate} = k' [\text{M}][\text{I}]^{1/2}$

$\text{slope} = k' [\text{I}]^{1/2}$

$0.0024136 \text{ s} = k' (0.00025)^{1/2}$

$k' = 0.015 \text{ s}^{-1}$

Problem KP3.2.

At steady state:

$\text{Rate}_{\text{init}} = \text{Rate}_{\text{term}}$

$k_i [\text{M}][\text{I}] = k_t[\text{M}^+]$

Rearranging:

$[\text{M}^+] = (k_i/k_t) [\text{M}][\text{I}]$

Problem KP3.3.

$\text{Rate}_{\text{prop}} = k_p [\text{M}^+][\text{M}]$

Substituting the steady state expression for $[\text{M}^+]$:

$\text{Rate} = (k_i k_p/k_t) [\text{M}]^2[\text{I}]$

Problem KP3.4.

$\bar{v} = \text{Rate}_{\text{prop}}/\text{Rate}_{\text{init}}$

$\bar{v} = k_p [\text{M}^+][\text{M}] / k_i [\text{M}][\text{I}] = (k_p / k_i)[\text{M}^+] / [\text{I}]$

but $[\text{M}^+]$ is not a known quantity. Alternatively, at steady state, $\text{Rate}_{\text{init}} = \text{Rate}_{\text{term}}$

$\bar{v} = \text{Rate}_{\text{prop}}/\text{Rate}_{\text{term}}$

$\bar{v} = k_p [\text{M}^+][\text{M}] / k_t [\text{M}^+] = (k_p / k_t)[\text{M}]$

Problem KP3.5.

a) $\bar{v} = [\text{M}]_0/[\text{I}]_0 = 4.5 / 1.25 \text{ x } 10^{-3} = 3{,}400$

b) $\bar{v} = (k_p/2f\, k_t\, k_d)([\text{M}]/[\text{I}]^{1/2})$

$\bar{v} = (0.003 / 2(0.5)(0.003)(0.0001))(4.5/(1.25 \text{ x } 10^{-3})^{1/2}) = (1/0.0001)(4.5/0.035) = 128/0.0001 = 1{,}280{,}000$

c) $\bar{v} = (k_p/2f\, k_t\, k_d)([\text{M}]/[\text{I}]^{1/2})$

$\bar{v} = (0.003 / 2(0.5)(0.03)(0.0001))(4.5/(1.25 \text{ x } 10^{-3})^{1/2}) = (0.01/0.0001)(4.5/0.035) = 128/0.01 = 12{,}800$

d) $\bar{v} = (k_p/2f\, k_t\, k_d)([\text{M}]/[\text{I}]^{1/2})$

$\bar{v} = (0.003 / 2(0.5)(0.003)(0.1))(4.5/(1.25 \text{ x } 10^{-3})^{1/2}) = (1/0.1)(4.5/0.035) = 128/0.1 = 1{,}280$

Problem KP4.1.

The key point is that, when two terms are added together and one is much larger than the other, the sum is approximately the same as the larger of the two terms. You can ignore the smaller one.

$$\mathrm{Rate_p} = \frac{k_p K_{eq}[\mathrm{M}][\mathrm{Cat}]\mathrm{x}^*}{1 + \underset{\sim 0}{\cancel{K_{eq}[\mathrm{M}]}}}$$

$$\mathrm{Rate_p} = \frac{k_p K_{eq}[\mathrm{M}][\mathrm{Cat}]\mathrm{x}^*}{1}$$

$$\mathrm{Rate_p} = k_p K_{eq}[\mathrm{M}][\mathrm{Cat}]\mathrm{x}^*$$

Problem KP4.2.

$$\mathrm{Rate_p} = \frac{k_p K_{eq}[\mathrm{M}][\mathrm{Cat}]\mathrm{x}^*}{\underset{\sim 0}{\cancel{1}} + K_{eq}[\mathrm{M}]}$$

$$\mathrm{Rate_p} = \frac{k_p K_{eq}[\mathrm{M}][\mathrm{Cat}]\mathrm{x}^*}{K_{eq}[\mathrm{M}]}$$

$$\mathrm{Rate_p} = k_p[\mathrm{Cat}]\mathrm{x}^*$$

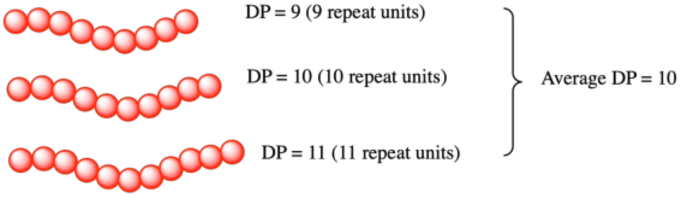
CHAPTER OVERVIEW

4: Polymer Properties

4.1: Molecular Weight of Polymers

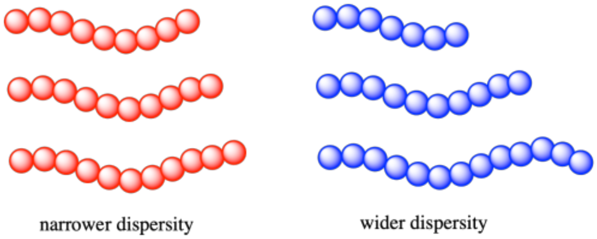
Molecular weight is one of the most central aspects of polymer properties. Of course, all molecules have molecular weights of their own. It might seem obvious that molecular weight is an essential property of any molecular compound. In polymers, molecular weight takes on added significance. That's because a polymer is a large molecule made up of repeating units, but how many repeating units? Thirty? A thousand? A million? Any of those possibilities might still be considered a representative of the same material, but their molecular weights would be very different, and so would their properties.

That variation introduces some unique aspects of polymer molecular weight. Because polymers are assembled from smaller molecules, the length (and consequently the molecular weight) of a polymer chain depends on the number of monomers that have been enchained into the polymer. The number of enchained monomers in an average polymer chain in a material is called the *degree of polymerization* (DP).



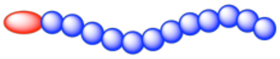
Notice that key point: it is just an average. In any given material, there will be some chains that have added more monomers and some chains that have added fewer. Why the difference? First of all, polymer growth is a dynamic process. It requires monomers to come together and react. What if one monomer starts reacting, forming a growing chain, before any of the others get started? With its head start, this chain will become longer than the rest. What if something goes wrong with one of the growing chains, and it can no longer add new monomers? That chain experienced an early death, and it will never grow as long as the others.

As a result, when we are speaking about the molecular weight of a polymer, we are always talking about an average value. Some chains in the material will be longer (and heavier) and some chains in the material will be shorter (and lighter). As with any group of measurements, it's helpful to know how widely distributed the individual values really are. In polymer chemistry, the width of the distribution of molecular weights is described by the *dispersity* (Đ, also called, in older texts, the polydispersity or the polydispersity index, PDI). The dispersity of a polymer sample if often between 1 and 2 (although it can be even higher than 2). The closer it is to 1, the narrower the distribution. That is, a dispersity of 1.0 would mean that all of the chains in a sample are exactly the same length, with the same molecular weight.



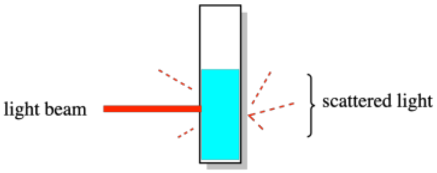
The original idea of dispersity was based on alternative methods of measuring the molecular weight (or the chain length) of a polymer sample. One set of methods gave something called the *number average molecular weight* (symbol M_n). These methods essentially took the weight of a sample, counted the molecules in a sample, and therefore found the average weight of each molecule in that sample. A classic example of this approach is a colligative properties experiment, such as a freezing point depression. You know that impurities in a liquid tend to disrupt intermolecular interactions and lower the freezing point of the liquid. You may also know that the amount by which the freezing gets lowered depends on the number of molecules or ions that get dissolved. Hence, if you weigh a sample of polymer, dissolve it in a solvent, and measure the freezing point, you could figure out the number of molecules dissolved and consequently arrive at M_n.

That's not so easy in practice; freezing point depressions are very small. They're not used very often anymore. A very common example of the kind of measurement widely used to determine M_n today is end group analysis. In end group analysis, we use ^{1}H NMR measurements to determine the ratio of a specific proton in the repeat units to a specific proton in the end group. Remember, the end group might be something like the initiator, which only added onto the first monomer to get the polymerization going. By the end of the polymerization, it is still found at the end of the polymer chain, so it is an end group. There is only one of them per chain, whereas there are lots of monomers enchained in the polymer, so the ratio of those enchained monomers to the end group tells us how long the chain is.



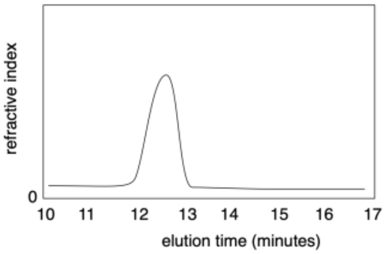
DP = ratio of repeat units to end group

The other set of methods upon which dispersity was based gave something called the *weight average molecular weight* (symbol M_w). The classic example was a light-scattering experiment. In this experiment, a solution of polymer was exposed to a beam of light and the resulting scattered light -- coming from the sample in different directions -- was analyzed to determine the size of the polymer chains in the solution. The results were more heavily influenced by the larger molecules in solution. As a result, this measurement of molecular weight was always higher than measurements based on counting every single molecule.

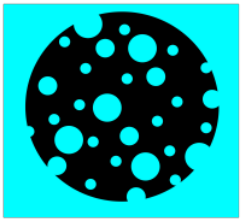


The resulting ratio, Đ = M_w / M_n, became known as the polydispersity index or, more recently, the dispersity. Because M_w was always more strongly influenced by longer chains, it was a little bigger than M_n and therefore the dispersity was always bigger than 1.0.

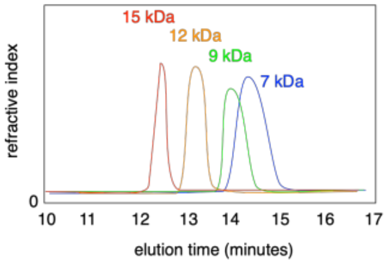
Nowadays, both molecular weight and dispersity are most commonly measured using gel permeation chromatography (GPC), synonymous with size-exclusion chromatography (SEC). This method is a high-performance liquid chromatography (HPLC) technique. Solvent containing a sample of polymer is pumped through a specialized chromatography column capable of separating molecules based on their size differences. As sample emerges from the column, it is detected and recorded. Most commonly, the presence of sample in the solvent emerging from the column causes a slight change in the refractive index. A graph of refractive index versus time presents a record of the amount of sample emerging from the column at a given time. Because the column separated molecules based on size, the time axis corresponds indirectly with chain length of molecular weight.



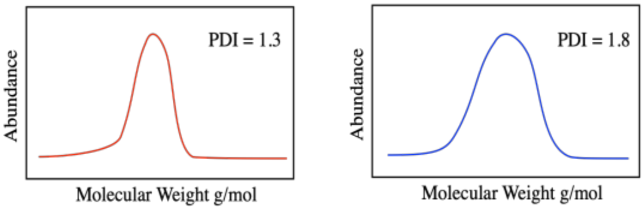
How can the column separate molecules based on size? The column is packed with a porous material, usually insoluble polymer beads. The pore sizes vary. These pores a crucial to separation because molecules flowing through the column may tarry in the pores. Smaller molecules could become delayed in any of the pores in the material, whereas larger molecules will only be delayed in the very largest pores. Consequently, a longer elution time corresponds to a lower molecular weight.



If you injected a series of different polymers into a GPC, each having a different molecular weight distribution, you would observe each one eluting at a different time. What's more, each peak may be broader or narrower, depending on the dispersity of that particular sample.



The wider the peak in GPC, the broader the distribution of molecular weights; the narrower the peaks, the more uniform are the chains. Normally a software package analyzes the curve to determine the dispersity.



Note that the x axis on a GPC trace is most commonly labeled as "elution time" and it normally runs left to right. However, often the x axis is labeled "molecular wright" because that is really the quantity we are interested in. In fact, sometimes the axis is reversed, so that peaks with higher molecular weights appear to the right, because it can feel more natural to look at it that way. You need to look carefully at the data to see how it is displayed.

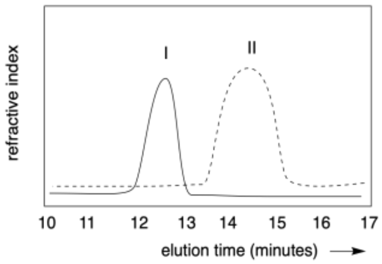
There are some problems with relying on GPC for molecular weight measurements. The main difficulty is that polymers in solution tend to coil into balls, and those coils will contain greater or lesser amounts of solvent, depending on how strongly the polymer and solvent interact with each other. If it interacts more strongly with the solvent, it will pull lots more solvent molecules inside its coils. The coil has to get bigger to make room for those internal solvent molecules. If it doesn't interact strongly with the solvent, it will mostly just stick to itself, blocking the solvent molecules out. There is a broad range of behaviors in between.

As a result, different polymers may swell to different extents in different solvents. That matters because GPC is really using size of the polymer coil as an index of its molecular weight, so comparing GPC traces of two different kinds of polymers has to be done with caution.

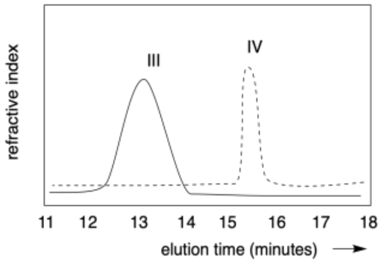
Problem CP1.1.

In each of the following cases, state which polymer has the higher molecular weight, and which one has a narrower dispersity

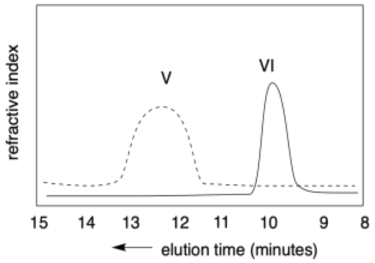
a)



b)



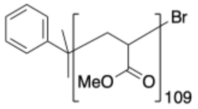
c)



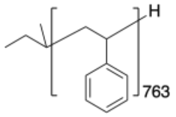
Problem CP1.2.

Calculate the molecular weight of the following samples.

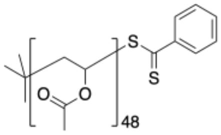
a)



b)



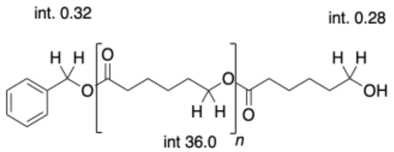
c)



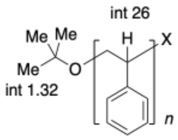
Problem CP1.3.

Use NMR end group analysis to determine the degrees of polymerization in the following samples.

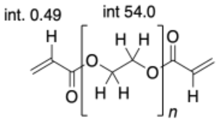
a)


int. 0.32
int. 0.28
H H
O
O
O
H H
OH
H H
O
int 36.0
n

b)


int 26
Me Me
H
X
Me
O
int 1.32
n

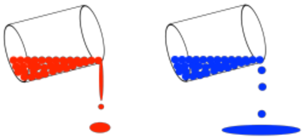
c)


int. 0.49
int 54.0
H
H H
O
O
O
O
H H
H
n

4.2: Viscosity of Polymers

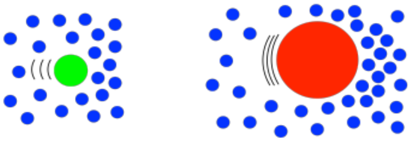
Polymers have come to occupy a very important niche in the materials we use every day. What makes them unique? Why do they have properties that aren't easily replicated by other materials?

Let's start with a property that you are probably familiar with. *Viscosity* is a term we use to describe the "thickness" of different liquids. For example, we say that honey is more viscous than water. Motor oil is more viscous than gasoline. When we say that, we mean that water is much easier to stir or to pour than honey. The honey moves more slowly. It resists the movement of the spoon when we stir it. Viscosity is often described in very general terms as "resistance to flow". The honey doesn't flow very easily, especially compared to something like water.

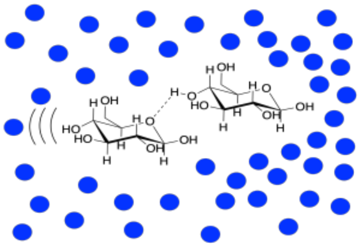


Now, honey isn't a polymer. It's a very concentrated solution. It contains a little bit of water and a whole lot of sugars, plus other small molecules produced by the plants from which the bees gathered the nectar to make the honey. The sugars aren't polymers, either; they are simple monosaccharides such as glucose and fructose. Nevertheless, this high viscosity is something honey has in common with polymer solutions, as well as with some *oligomers*, which are short-chain polymers that can be liquids instead of solids.

Why is honey so viscous? Partly it's just that the sugar molecules in the water are much larger than the water molecules, so they experience a lot more drag as they move through the solution compared to just plain water.



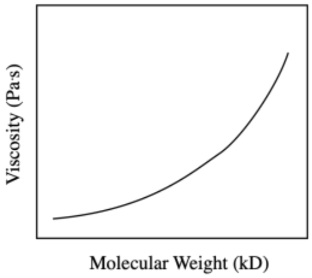
The strong intermolecular attractions between the individual sugar molecules are also a major factor. Sugars are covered in OH or hydroxyl groups that are capable of strong hydrogen bonds. As these molecules move past each other in the very concentrated solution, they cling to each other, slowing down the flow of the liquid.



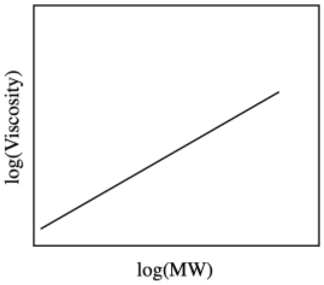
The motor oil example works in a similar way. Motor oil and gasoline are composed of the same class of compounds, hydrocarbons, composed of carbon chains covered in hydrogen atoms. They're very similar to each other. The intermolecular attractions between the molecules are much weaker than those between sugar molecules; they're just London dispersion forces. The major difference between motor oil and gasoline is that the motor oil contains much longer hydrocarbon chains. The molecules are bigger, and so they experience more drag as they move through the liquid. The amount of intermolecular interactions is also crucial in determining how tightly two molecules hold onto each other, and this factor is especially important in very weak London dispersion forces, where a small advantage goes a long way. Those longer hydrocarbon chains in the motor oil cling to each other much more strongly than the shorter ones in the gasoline, so gasoline flows much more easily than motor oil.

For similar reasons, oligomers and polymers, if they are liquids, also display high viscosity. The extended contact between their long molecular chains leads to enhanced intermolecular attractions that contribute to a resistance to flow. Increased drag is also a factor; even in solution, these very large molecules encounter more resistance as they move past solvent molecules compared to the resistance smaller molecules would experience.

In fact, viscosity measurements of polymer solutions are another way to determine the size of the polymer -- leading to the chain length and the molecular weight. The larger the polymer, the more drag and also the more intermolecular attraction, and so the higher the viscosity.



So, the viscosity increases with the molecular weight, but not necessarily in a linear way. That can make it more difficult to use a graph like this to predict molecular weight from a viscosity measurement. One common thing to do in this situation is to take the log of the values. That approach will often give a straight line when two things are related.



Often in nature one physical property that depends on another will follow a "power law". That means that one quantity depends on the other raised to some exponent. In this case, the relationship is described by the **Mark-Houwink equation**:

$$[\eta] = KM^{\alpha} \tag{4.2.1}$$

In this equation, [η] is the intrinsic viscosity; that's the viscosity attributed to the solute, rather than the viscosity of the solvent itself. *M* is the molecular weight. *K* and α are constants for a particular polymer.

If you take the log of both sides of the equation -- that's OK to do mathematically, just like you could multiply both sides of an equation by four or subtract three from both sides and still have an equivalent expression -- you get:

$$\log[\eta] = log(KM^{a}) \tag{4.2.2}$$

If you take the log of two things multiplied together, it's the same as adding the individual logs of both things.

$$\log[\eta] = \log K + \log(M^{a}) \tag{4.2.3}$$

And if you take the log of something raised to an exponent, the exponent just comes down to become a coefficient.

$$\log[\eta] = \log K + \alpha \log M \tag{4.2.4}$$

or

$$\log[\eta] = \alpha \log M + \log K \tag{4.2.5}$$

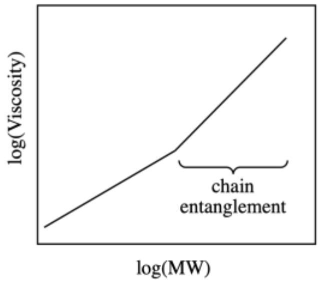
That looks like an equation for a straight line:

$$y = mx + b. \tag{4.2.6}$$

Here, you plot $\log[\eta]$ on the y axis, $\log M$ on the x axis, and you get a straight line with those constants, α and K, as the slope and y-intercept, respectively.

This approach does not yield an absolute measurement. You couldn't take two completely different polymers, take viscosity measurements, and make conclusions about which one had a higher average molecular weight. However, if you took a series of polymers of the same kind and measured their viscosities in solution, you would be able to deduce which ones were longer and which ones were shorter.

In fact, the dependence of viscosity on the molecular weight of polymers is more complicated than this graph suggests. If you deal with large enough polymers, the graph starts to look like this one:

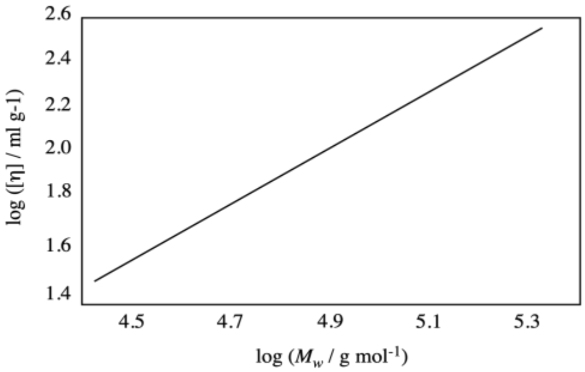


Why does it bend? Remember, polymers in solution are coiled up into balls. A longer chain just corresponds to a bigger coil. At some point, these chains become big enough that they aren't likely to stay coiled independently of each other. They become more and more likely to interact with each other. They become entangled with each other.

There are plenty of other factors you would have to take into account in using viscosity to assess molecular weight. One of them is concentration, for example. The more concentrated a polymer solution, the more large molecules you have exerting drag and interacting with each other. Higher concentration leads to a higher viscosity measurement. Consequently, you would have to make sure you accounted for the polymer concentrations if you used this method.

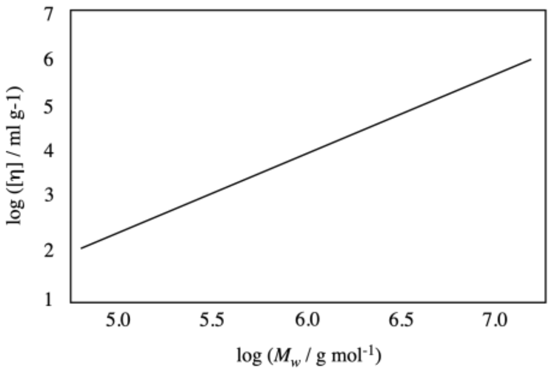
Problem PP2.1.

Estimate the values of α and *K* for the polymer that provided the plot below.



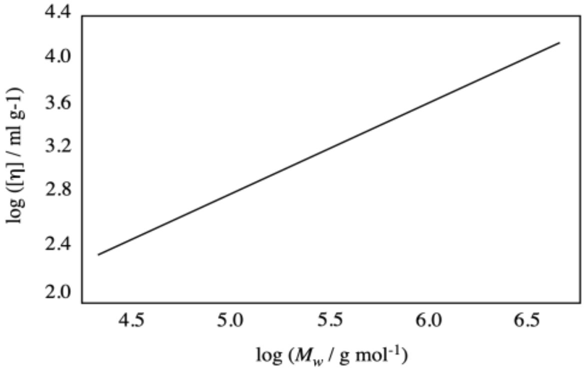
Problem PP2.2.

Suppose you have a polymer described by the plot below. If your sample has a molecular weight of 1 million g/mol, what would you expect for intrinsic viscosity under the conditions of this experiment?



Problem PP2.3.

Suppose you have a calibration plot, below, for a particular polymer. If you measure the intrinsic viscosity of a sample and find that the value is 800 ml / g, what is the molecular weight of the sample?



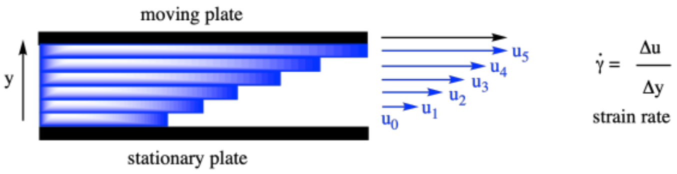
Problem PP2.4.

Ethanol (CH_3CH_2OH) has an "absolute viscosity" of 1.095 centipoise, whereas ethylene glycol ($HOCH_2CH_2OH$) has an absolute viscosity of 16.2 centipoise. Explain why the two values are so different.

4.3: Rheology

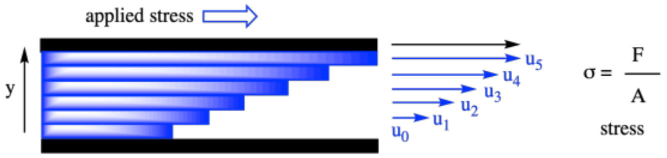
Viscosity measurements are the realm of a field of science called *rheology*. Rheology is, literally, the study of flow. Another very simple definition, attributed to chemical engineer Chris Macosko at University of Minnesota, is the study of "what happens when you squish stuff". There's an element of force or pressure that comes into play here, too.

One of the common ways of assessing properties in rheology is to place a sample between two parallel plates and move one plate with respect to the other. One plate says still and the other one moves. What happens to the liquid between the plates? There ought to be some friction between the stationary plate and the liquid that will keep the liquid still. There also ought to be some friction between the moving plate and the liquid that will make the liquid move along at the same speed as that plate. So at one extreme, the liquid is moving along with the sliding plate and at the other extreme the liquid is perfectly still. If we imagine that the liquid in between these two extremes is divided into very thin layers, then each layer must be moving at a slightly different speed than the next.

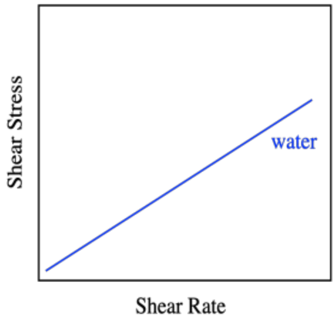


In the diagram, the symbol, *u*, stands for the speed of the layer of liquid. The arrow beside the layer is meant to convey its relative speed: the top layer is moving the fastest, the next layer is a little slower, and so on; the bottom layer isn't moving at all. There is an important quantity, called the strain rate or shear rate (given as a symbol the Greek letter gamma, γ, with a dot on top) that describes how the speed of the liquid moving along the x-axis (left to right) changes, layer by layer, in the y-direction.

What does this picture have to do with viscosity? Well, in order to get that top plate to move, we have to apply some sort of force to it. In rheology the force is given per unit area (like pressure); this force per unit area is described as the stress (given as a symbol the Greek letter sigma, σ).

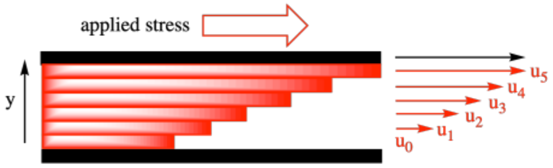


What if we wanted to slide the plate even faster? What would happen to the liquid? Well, the shear rate would go up. The top layer would be moving even faster, and the bottom layer would still be stationary. And what would we have to do to get that faster shear rate? We would have to push the top plate a little harder. The result is a graph that looks like this:

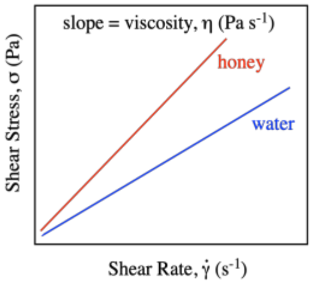


The graph says that shear stress and shear rate are directly related. The stress is called "shear stress" because of the direction of the force parallel to the liquid, causing shear strain. When we increase the shear rate, the shear stress also increases proportionally. So, if we did this experiment using water as the liquid between the plates, we would get a linear relationship between shear stress and shear rate. That's how Sir Isaac Newton described the behavior of liquids, so when we see that linear relationship between stress and strain, we describe the liquid as a *Newtonian liquid*.

What happens if we do the experiment with honey instead of water? What would happen, for example, if we exerted a certain stress to get a certain shear rate with the water, and we wanted to get the same shear rate using honey? Well, the honey is thicker than the water. It's not going to move as easily. We will have to apply a greater stress in order to achieve the same shear rate that we measured with water.



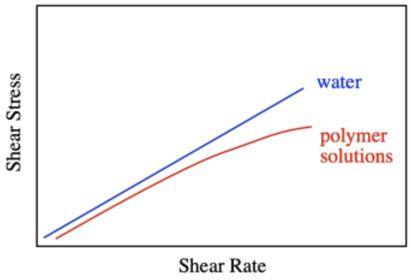
That would be true for every possible shear rate. If we were to graph shear stress vs. shear strain with honey, we would get a linear relationship, just like we did with water, but the value of shear stress would always be higher than for water. The slope of the line for honey would be greater than the slope of the line for water.



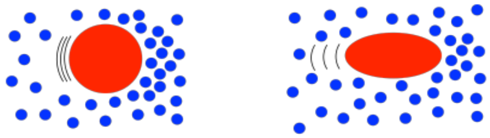
$$\eta = \frac{\sigma}{\dot{\gamma}}$$

Viscosity is formally defined as the slope of that line. Honey, being thicker than water, requires higher and higher stresses to achieve the same strain rates that you would get using lower stresses with water. In the simple kitchen analog of the experiment, you have to push the spoon harder to stir the honey than you do if you are just stirring water.

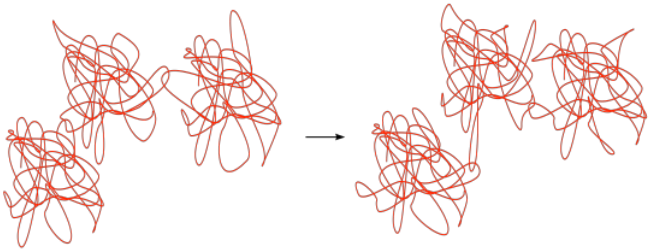
Honey and water are Newtonian liquids. The relationship is simple: increase the shear stress and you increase the shear rate. Not all liquids behave that way. Polymer solutions don't, for example. They display a non-linear relationship, in which the shear stresses needed to get higher shear rates are just not as high as you would expect.



That behavior is described as **shear thinning**. What makes polymer solutions do that? Remember that, in solution, an individual polymer molecule tends to coil up into a ball. Normally, those balls are spherical. At high shear rates, they distort into ellipses. That reduces the amount of drag, making the solution a little less viscous than you would expect. The shear stress still increases with higher shear rates, but not as much as if it were a Newtonian fluid.

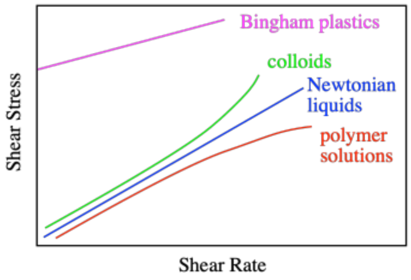


That's not all. Remember, polymers display chain entanglement, especially when they are very large. Chain entanglement increases the viscosity of the solution. These chains are mobile because the polymer is constantly undergoing conformational changes. As the solution gets sheared, some of the polymer chains may wiggle loose from their neighbors, but random conformational changes will always result in new entanglements right away.



But what happens at a very high rate of shear strain? The polymer chains still become untangled, but they don't have time to form new entanglements, because everything is whizzing by too quickly. Without those entanglements, viscosity doesn't increase as sharply as you would expect.

Some liquids behave just like water, but polymer solutions do not. That's a consequence of the enormously long chain structures of the polymers. It's worth pointing out that there are other things that don't behave in the "normal" way. Colloids often display shear thickening. You can see examples of this in videos of people running across wading pools filled with corn starch and water, a colloidal mixture in which the solid cornstarch particles are just suspended in the water, not dissolved. If you walk across the pool, you sink. If you run, you stay on top. That's shear thickening, and it has to do with how those solid particles move during shearing. When you walk, they just slide past each other, but when you run, they all collide, and come to a stop.



A Bingham plastic, on the other hand, actually appears to be a solid until you give it a good shove; then it flows like a liquid. Peanut butter behaves sort of like that.

Exercise 4.3.1

Honey is a Newtonian fluid, but molasses undergoes shear thinning. What might you deduce about the composition of molasses and honey?

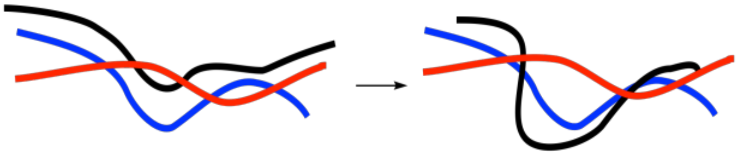
4.4: Glass Transition

The glass transition is probably the most commonly-cited characteristic of a polymeric material. At the glass transition temperature, the physical nature of the material changes subtly. It goes from being a rubbery, flexible material at higher temperature, above the glass transition, to a glassy, harder material at a lower temperature. The material is still a solid either way, but there is a definite change in how it responds to stimuli.

A material could certainly be useful in either state. We might want a plastic to be more rigid, like a water bottle or a rod for a shower curtain. Alternatively, we might want it to be softer, like a seat cushion. Either way, it might be helpful to know the temperature at which the material will change from one type to the other.

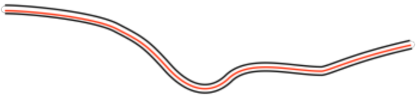
The glass transition is a little like what happens to gummy bears when you put them in ice cream. Straight from the bag, gummy bears are chewy, but they don't feel like they will break your teeth. Put them on ice cream and that changes. They become much harder to chew.

The classic explanation for the glass transition is based on the idea of **chain flow**. Polymers are long-chain molecules and, given a little energy, the chains move around. They wiggle. They undergo bond rotations, switching from one conformation to another. A block of material contains piles of chains, like a nest of snakes. Chain ends and loops squirm past each other continuously.

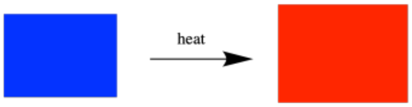


Chain flow allows a material to adapt when forces are exerted on it. We can bend an eraser because the chains in the rubber slide over each other and adopt a new shape. At least, that's what happens at room temperature. It might not work if the eraser were accidentally dropped in some liquid nitrogen, which is very, very cold.

As a block of material cools down, it contracts. The molecules become packed more closely together. At some point, the free volume -- that's the amount of volume in the material that is not actually taken up by the molecules -- becomes too small to allow chains to move past each other. All of those chains need a little room around them if they are going to undergo conformational changes, and conformational changes are how polymer chains move. Without that extra room, the material suddenly becomes less flexible.



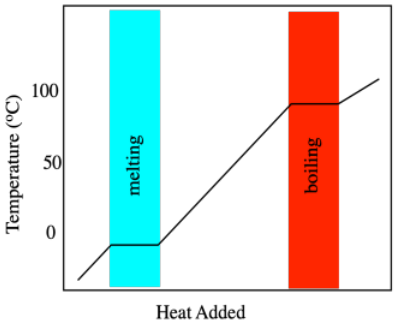
If we start in the glassy state and increase the temperature, the volume of the material is expanding, and the free volume is increasing, too. At some point, the free volume becomes great enough that chains can slip past each other. The material becomes more flexible. It becomes rubbery.



Now, this transition is not the same thing as melting. The chains are not completely overcoming their interactions with each other and gaining freedom of movement in any direction. The chains are still highly entangled. Portions of the chain are sliding past each other but overall things have not changed that drastically. The block of polymer does not turn into a gooey puddle of liquid.

Well, if a material can change from glassy to rubbery at a certain temperature, there will be consequences in how the material behaves. For example, the tires on your car are meant to be rubbery and flexible; that factor helps them grip the road. If the weather gets too cold and your tires become glassy, the tires no longer have the same amount of flexibility, and you don't have as much traction. "All-weather tires" are composed of a rubber that has a very low glass transition temperature, helping to avoid this problem. ("Snow tires" are a different thing; they have patterns in the treads that help channel away the snow in order to improve traction.) Knowing when this change will occur would be very useful. So, how do we determine the glass transition?

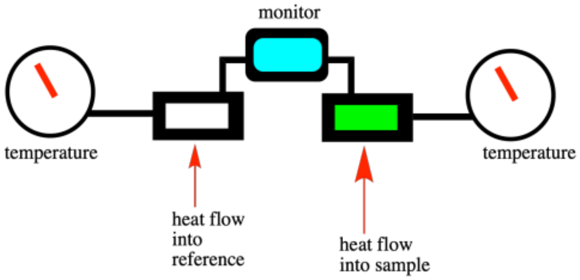
Phase changes, such as melting points, are measured using **calorimetry**, so let's start there. When a solid is heated, its temperature increases. That seems simple enough. Temperature is basically a measure of heat content, so as heat flows in, the measured temperature rises. This simple relationship breaks down at the melting point. At that point, heat flowing into the material is consumed by the breaking of intermolecular forces. Overcoming these attractions costs extra energy. Consequently, there is a point at which the temperature rise in the material stalls out temporarily while it melts.



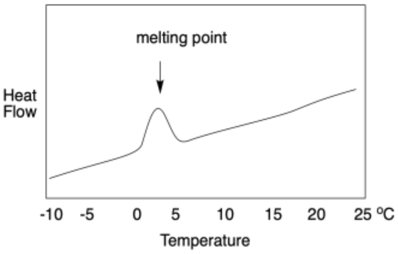
This extra heat needed to melt the material is called the heat of melting or, more commonly, the heat of fusion. Heat of fusion actually refers to the opposite process as the material is cooled and frozen. As heat is carried away from a cooling material, it cools down gradually, but there comes a point at which those strong intermolecular interactions form, giving off some extra heat. The fusion temperature is the same as the melting temperature, and the heat of fusion is the same as the heat of melting, but in one case the heat is added and in another case the heat is given off. In principle, if we just heat something up and look for that stalling point in the temperature, we can find the temperature of the phase transition.

Differential scanning calorimetry

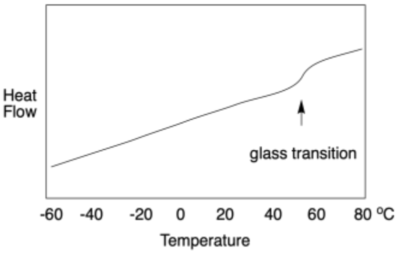
Differential scanning calorimetry (DSC) is a technique that is commonly used to measure phase transitions, including the glass transition temperature. It is based on the same ideas but the experiment is run in a slightly different way. In DSC, we have two tiny sample chambers side by side. One contains the material we are interested in and the other (empty) one is used as a reference. The instrument heats both samples at a constant rate, all the while maintaining both of them at the same temperature. Consequently, it may actually add more heat to one chamber than the other, so that they both reach 30.5 °C at the same time, then 30.6 °C, and so on. Once we reach the melting point of the sample of interest, heat flow into that sample must be increased so that it can keep up with the reference. Past that point, the heat flow drops back to a more normal level.



If we look at a DSC scan, we see a graph of heat flow on the y-axis and temperature on the x-axis. The heat flow usually stays pretty constant as the temperature increases. At the melting point, heat flow increases, but then it drops back down once the melting point has been overcome. It may not drop back to the same level as before, however, because the heat flow that is recorded is related to the heat capacity of the material. The solid and the liquid usually respond differently to heat. In general, because the molecules in a liquid can freely rotate, they have something else to do with added heat. Liquids thus have a slightly higher heat capacity than their corresponding solids.



All of that explanation hopefully prepares us for a DSC study of the glass transition temperature. It works the same way, but only up to a point. If we look at a DSC scan, we still see heat flow on the y-axis and temperature on the x-axis. At the glass transition, heat flow bumps up slightly -- and remains there. It looks very different from a melting point. A DSC scan of a melting point shows a "peak" at the transition temperature. A DSC scan of a glass transition point shows only a little step, like a riverbank



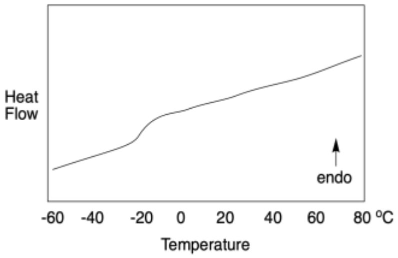
Why is it different? Well, the glass transition is not really a phase change like the melting point or boiling point. It does not involve a physical change of state. It was a solid before and it is a solid afterward. No intermolecular interactions must suddenly be overcome to free the molecules from each other. Instead, it's just a volume change. The free volume became great enough that the chains can slip past each other, but the chains are still clinging together in a solid-state. Now, that additional movement does have consequences. The material becomes more flexible. If heat flows in, there is more freedom of motion into which the heat can be distributed. In other words, there is a slight increase in heat capacity, and that's what we observe in DSC.

> One practical note: DSC scans can actually be displayed in two different ways. The y-axis can either display heat flowing in or heat flowing out. That means melting points can look like peaks or like valleys, depending on how the data is displayed. Often the data are labeled with an arrow that says "endo" to tell you which direction along the y-axis means more heat is flowing in (or possibly "exo", meaning which direction means heat is flowing out). You need to look carefully if things seem backward.

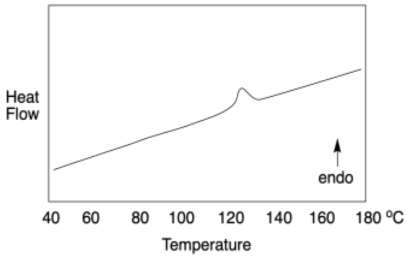
Problem CP4.1.

For each DSC trace, state what sort of transition is occurring at what temperature.

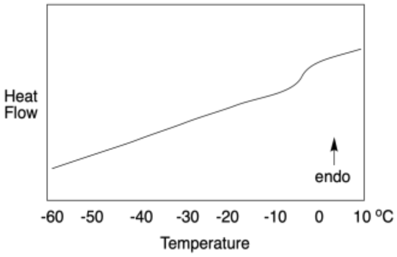
a)



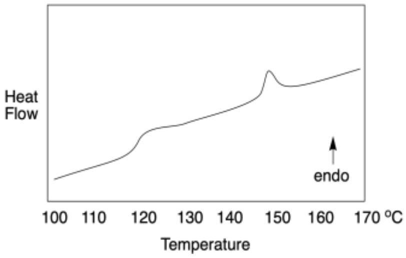
b)



c)



d)



Why does the glass transition temperature vary from one kind of polymer to another? What structural factors influence the glass transition temperature? This structure-property relationship isn't a straightforward one, as there seem to be a number of different variables involved. However, the simplest of these factors is just molecular weight. The higher the molecular weight of a polymer, the higher its glass transition temperature. This relationship is true only up to a certain point, however. The non-linear dependence of the glass transition temperature of molecular weight is described by the **Flory-Fox equation**:

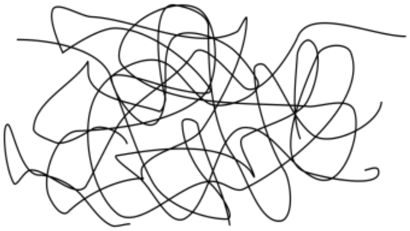
$$T_g = T_{g(\infty)} - \frac{K}{M_n} \tag{4.4.1}$$

Here, $T_{g(\infty)}$ refers to the glass transition temperature of an infinitely long chain of the polymer. K is a constant for a particular polymer, such as polystyrene or polyethylene.

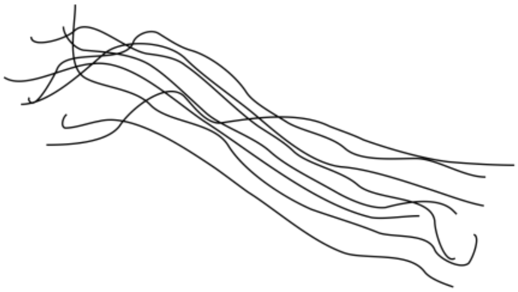
A plot of T_g *vs.* M_n resembles a saturation curve; the line rises sharply, gradually stalling out and continuing parallel to the x-axis. In other words, although this relationship of increasing glass transition temperature with increasing molecular weight holds true at relatively low molecular weights, the glass transition temperature remains constant once a threshold molecular weight has been reached.

4.5: Crystallinity in Polymers

We often think of polymers in the form of plastics: solid materials that serve some structural function, like a water bottle or some Venetian blinds. Polymers are different from many other such solids. Metals, for instance, have crystalline structures, in which atoms form a regularly repeating pattern, row upon row. Polymers, in contrast, are generally somewhat *amorphous*. Think of a strainer filled with cooked spaghetti, the long chains of pasta looping over each other randomly. That's how the molecules of amorphous or "shapeless" polymers tend to distribute themselves.



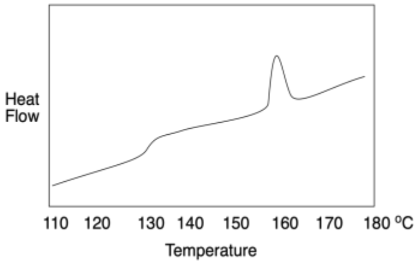
Polymers are capable of forming more ordered structures. If they aligned instead with their long chains parallel to each other, they would be able to get much closer together, and intermolecular attractions between the chains would be much stronger. The energy of the system would decrease, so this more crystalline structure should be inherently favored.



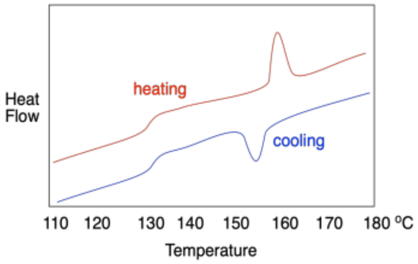
So why doesn't that always happen? Think about a polymer cooling from a completely melted state, in which case the structure is certainly amorphous. As it cools, the material becomes less like a liquid, and then less soft. With small molecules, that transition is relatively abrupt, as the molecules slide into place, guided by their strengthening intermolecular attractions. The molecules just have to rotate a little to face the correct direction, or maybe budge a little to the side. With polymers, the transition is much more gradual, because those great, long chains have to slide over each other and uncoil in order to lie parallel. At some point, there just isn't enough energy for them to keep working their way into the optimal alignment. As a result, many polymers are semi-crystalline, with regions called *lamellae* where portions of chains have aligned parallel to each other, but also with large amorphous areas that are much more randomly oriented.

As a result, a polymer sample might be 80% amorphous with only 20% of its chain lengths aligned in crystalline lamellae. Even so, those crystalline domains exert a strong influence on the properties of the polymer. Because of the stronger intermolecular attractions between these closer chains, the chains are much less able to slide past each other. The result is a material that is stronger and more rigid, and that can be very important for reliable structural materials.

How do we know whether a polymer sample contains crystalline domains? We can use differential scanning calorimetry to observe the transition between an ordered crystalline phase and a disordered melt phase with added heat. As we saw when we were looking at glass transition, a melting point shows up as a peak on a DSC trace. You can look for it at a temperature above T_g, which you will recall looks more like a step in the baseline. Below T_g, the chains are not mobile enough to move out of alignment with each other. In the example below, you can see T_g at about 128 °C as well as a melting point, T_m, when attractions between chains in the lamellae are overcome, at 155-160 °C.



If this were a regular molecular or elemental solid, the melting point would be the same as the fusion point; the material would melt at the same temperature during warming as it froze during cooling. In polymers, it usually doesn't work out that way, and a *hysteresis* is observed. In hysteresis, a sample has changed because of previous events, leading to results that don't seem to be reproducible in the way that we would normally expect. In general, the crystallization temperature, T_c, is lower than the melting temperature, T_m. That's because, as the material melts, the chains move out of alignment with each other and, because of chain entanglement, they are hindered from getting back into alignment with each other again, leading to a delay in crystallization.



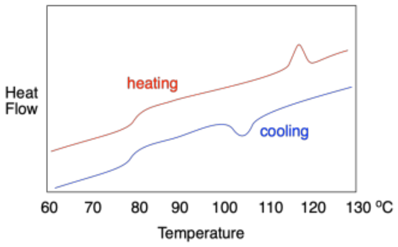
✓ Example 4.5.1

Dec 31, 2019, 7:15 PM

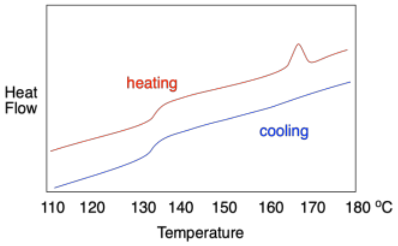
Problem PP5.1.

Describe what is observed in each of the following DSC traces.

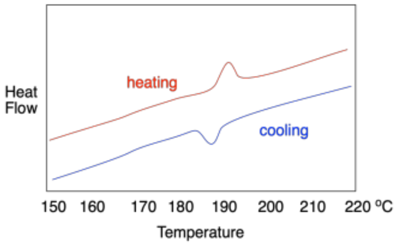
a)



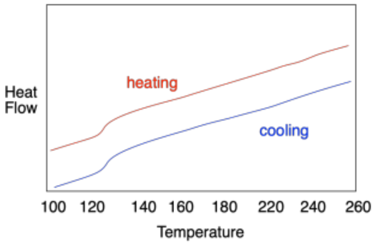
b)



c)

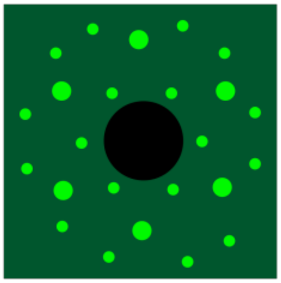


d)



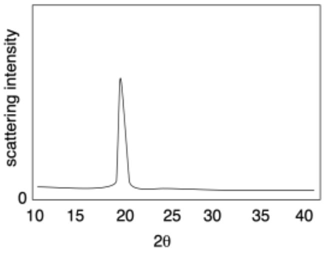
Crystallinity can also be probed in other ways. The classic approach is through X-ray diffraction. When X-rays pass through ordered materials, they give rise to diffraction patterns, bright spots in space where ricocheting X-rays have constructively interfered with each other, shining starkly amid the blackness where the X-rays have undergone destructive interference.

The drawing below is a cartoon of an X-ray diffraction pattern. It might be captured by a digital camera or, in earlier days, a sheet of photographic film. The bright spots result from X-rays scattering out from the middle, where they have encountered the sample. In the middle, the black circle blocks the original X-ray beam, which would otherwise be too bright to allow observation of those spots around it.



The data from an X-ray diffraction experiment is fed into a program that can mathematically deconvolute why the spots showed up where they did. The process has been compared to throwing a stone over your shoulder into a pond, then watching the ripples to decide where the stone must be. With one stone, that should be pretty easy. You would find the stone at the center of a circle of ripples. With two or more stones, interference patterns make the ripples more complex, and so it may take more work to determine where each stone lies in the pond.

The picture below illustrates the results of a relatively simple X-ray diffraction experiment commonly used with crystalline polymer samples. The technique is called wide-angle X-ray scattering, or WAXS. It simply reports the angle at which scattering intensity is observed relative to the initial X-ray beam. That angle corresponds to a distance between atoms in the sample, which in this case usually corresponds to a distance between parallel polymer chains. Sometimes there can be more than one peak, but this example is a simple one to start with.



The relationship between this scattering angle and an interatomic distance is given by Bragg's Law, a fundamental starting point in X-ray crystallography first expressed by Sir William Bragg and his son, Sir Lawrence Bragg. The law states that:

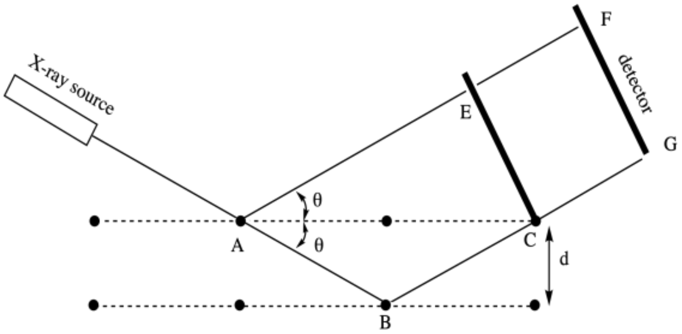
$$n\lambda = 2d\sin\theta \tag{4.5.1}$$

in which *n* is an integer (typically assumed to be 1), lambda is the wavelength of the X-ray used (commonly 1.541 Å, although others are possible), *d* is the distance between regularly repeating atoms and θ is the scattering angle.

Rearranging Equation 4.5.1, we find:

$$d = \frac{1.541}{2\sin\theta} \tag{4.5.2}$$

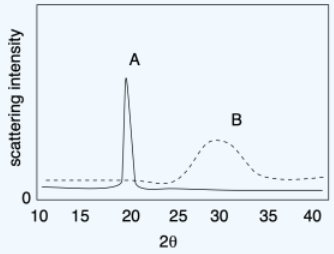
In other words, the distance between atoms is inversely proportional to the scattering angle. The greater the angle, the smaller the distance.



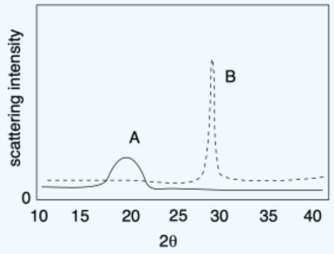
✓ Example 4.5.1

In each of the following cases, determine which sample (A or B) has a higher crystalline content.

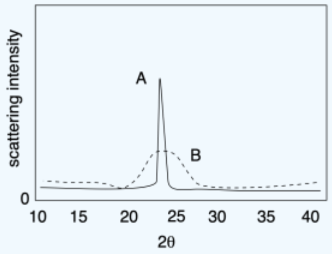
a)


scattering intensity
A
B
0
10
15
20
25
30
35
40
2θ

b)


scattering intensity
B
A
0
10
15
20
25
30
35
40
2θ

c)

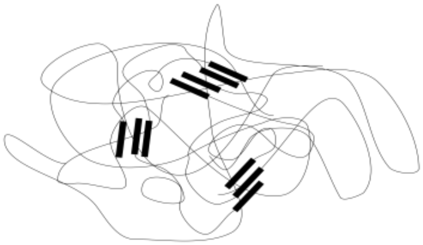

scattering intensity
A
B
0
10
15
20
25
30
35
40
2θ

4.6: Microphase Separation

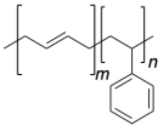
Crystalline domains provide additional strength to polymer materials. The strong attraction possible between closely-aligned chains results in long segments of the polymer being held more firmly in position. Consequently, chain flow is more limited, and the material becomes more rigid.

Sometimes, more rigid segments of a polymer are deliberately built into the structure. For example, in block co-polymers, softer, more flexible blocks are often paired with harder, more rigid blocks. The *soft segments* may have greater conformational flexibility, or weaker intermolecular attractions between themselves, or both. The *hard segments* may be more conformationally rigid or they may have stronger intermolecular attractions, such as strong dipoles or hydrogen bonds.

If the block lengths are the right size, the two segments are able to separate into two phases. As a result of stronger intermolecular attractions, lengths of chains containing hard segments cluster together, pushing out the soft segments that would otherwise get in the way of these intermolecular attractions. This phenomenon is called *microphase separation*. The result is that the material contains islands of strength and rigidity in a matrix of flexible polymer chains. That can be a very useful combination. The flexible chains of the soft segments allow the polymer to be distorted, bent or compressed, but the hard segments put limits on that flexibility, keeping the material firmly together.



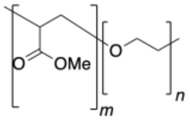
Because we are usually dealing with very large numbers of enchained monomers, the difference between the two kinds of segments need not even be dramatic. A copolymer of butadiene and styrene, both hydrocarbons, can form microphase separated materials. In this case, intermolecular attractions are dominated by weak London dispersion forces, but the aromatic groups of the styrene, with their delocalized pi systems, have London dispersion forces that are slightly stronger. As a result, the polystyrene blocks can cluster together, surrounded by the softer polybutadiene blocks.



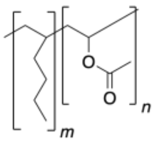
Problem PP6.1.

Identify the hard segment and the soft segment in each of the following block-co-polymers.

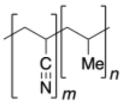
a)



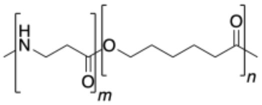
b)



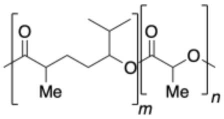
c)



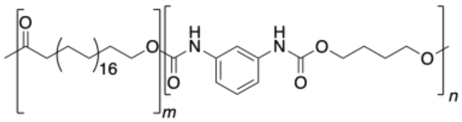
d)



e)

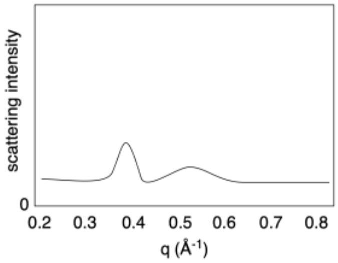


f)



Sometimes, the separation between these phases can be directly observed via microscopy. Tunneling electron microscopy (TEM) is a technique that can generate images of a cross-sectional slice of the material. The material is generally stained with a heavy metal, such as osmium, that binds preferentially to one phase or the other. The stained phase shows up darker under TEM than the phase that isn't stained.

X-ray diffraction techniques can often be used to measure distances between hard segments. Small-angle X-ray scattering (SAXS) is very similar to wide-angle X-ray scattering (WAXS). Because of the inverse relationship between scattering angle and distance, SAXS is used to probe regularly repeating structures at greater distances than those seen in WAXS. That makes it possible to see peaks if the hard segments are distributed regularly enough within the soft matrix.



Note that, in SAXS, the x-axis is usually labeled as q, the scattering vector:

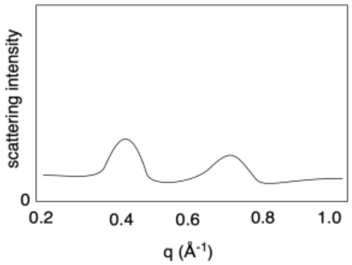
$$q = 4\pi\sin\theta / \lambda$$

But since $d = 2\sin\theta/\lambda$ then $q = 2\pi/d$ or $d = 2\pi/q$. That gives us a pretty straightforward way of calculating distances between regularly-spaced hard segments (or any other regularly-spaced objects). Once again, just as in WAXS, there is an inverse relationship between the quantity shown on the x-axis and distances through space.

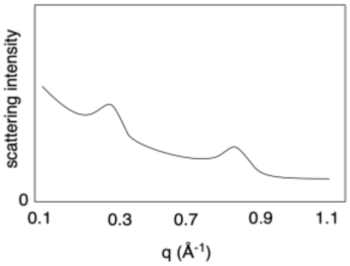
Problem PP6.2.

Calculate the approximate distances revealed in the following SAXS results.

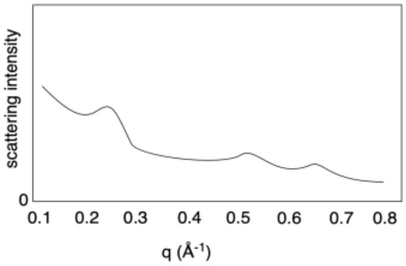
a)



b)



c)



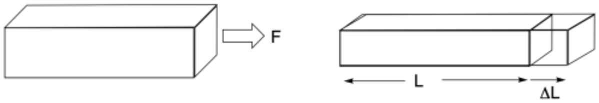
4.7: Stress-Strain Relationships

If you think about materials made from polymers, a couple of things might readily come to mind. You might think about the ubiquitous use of plastics in structures around us, such as automobile bumpers. You might think about a rubber band that you use to fasten something more firmly, either at home or in the lab. In either case, the function of the material relies on its response to stimuli. Do we want it to be flexible, to change shape, but then snap back to where it came from? Exactly how much flexibility do we need? Where is the trade-off between flexibility and strength?

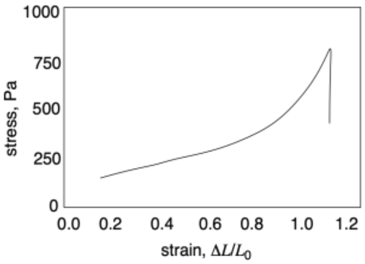
These questions are important in polymer chemistry. Consequently, we often need to probe how materials behave under different conditions so that we know how they can be employed most effectively.

Tensile testing is one of the simplest ways to probe how a material responds to stress. Remember, the stress in this context means the force exerted on the material per unit of cross-sectional area. As such, it has units of pressure, such as Pascals (Pa). To do the experiment, the two ends of a sample are attached to two clamps, one of which is movable. The movable clamp is then pulled so that the sample becomes stretched. The force required to pull the sample is recorded and, given the cross-sectional area of the sample perpendicular to the force, the force is converted into units of strain.

The experiment also measures the distance that the sample is stretched (the strain). That distance is usually expressed as a ratio, comparing the change in length to the original length of the sample. It can be written either as a fraction or as a percent.



In the rough sketch below, we can see what typically happens in such an experiment. The sample stretches (the strain increases), and it gets harder to stretch as seen by the increasing force (and therefore increasing stress) that is needed to keep stretching it. Eventually, the stress plummets, because of the sample breaks.



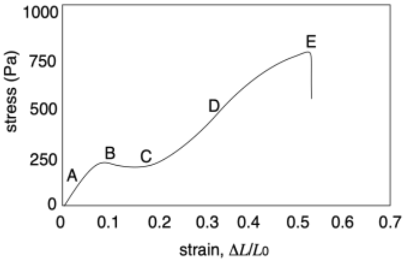
Already in this graph, we can see a couple of important pieces of information we can learn from tensile testing. Number one, how far can we stretch this material before it breaks? That quantity is called "strain at break". In this sample the strain at break looks like about 1.1 or 110%; that means the sample was stretched to twice its original length, and then some. Number two, how much stress can the sample support without breaking? That quantity is called "ultimate tensile strength". In this sample, the ultimate tensile strength is just over 750 Pa.

If we look more closely at the graph from another sample, we will get a third important quantity, and see some additional features. The important quantity can be derived from the first part of the curve (A), in which stress increases linearly with strain. In this linear region, the material is behaving as a "Hookean solid", meaning it obeys Hooke's Law. Hooke's Law says that stress and strain should be directly proportional. In his original words, the extension is proportional to the force:

$F = kx$

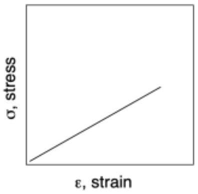
in which F is the force, x is the extension of the solid, and k is the proportionality constant.

Hooke's Law is commonly applied to the behavior of mechanical springs, but it also holds for other solid materials. The slope in the linear region of the graph (A) would equal that proportionality constant, k, because the graph shows the ratio of F/x. In materials science, this slope is more commonly called "Young's modulus". It is a measure of the inherent stiffness of the material.



Young's modulus: E = σ/ε

in which σ = stress and ε = extensional strain.



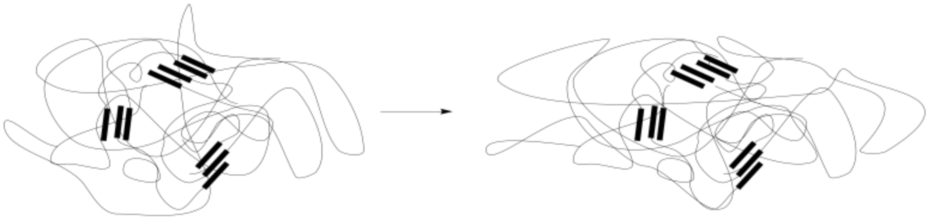
The extensional strain is just the strain observed by stretching the material. In the graph shown above, Young's modulus is around:

250 Pa / 0.1 = 2,500 Pa.

This initial region of the curve, in which Hooke's Law is obeyed, is sometimes called the "linear elastic region". The word "elastic" does have an immediate connotation in everyday English, bringing to mind a rubber band that can be stretched, so we think of the stretching part when we hear the word "elastic". However, the returning motion is an essential feature of elastic behavior. The rubber band always comes back to its original shape. Likewise, within the linear elastic region, any solid material returns to its original shape after it is deformed under stress.

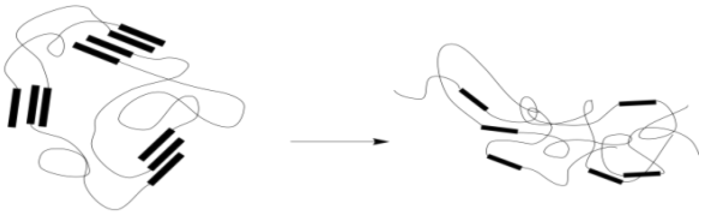
With most solids, such as aluminum or concrete, the linear elastic region spans a very narrow range of strains. Just by looking, we wouldn't notice these materials being deformed. However, this linear stress-strain relationship is typical of solids. In rheology, that behavior is described as elastic. Of course, with many polymers, a sample can be stretched so far that you can see the change with the naked eye, and it still returns to that original shape.

What makes polymers different? The long-chain structure of polymers does make them behave differently from other materials. These chains can undergo conformational change: each bond along the chain can rotate, converting the polymer chain into a slightly different shape. That ability gives a "soft material" a great deal of flexibility. The conformations of chains can adapt to accommodate stress, moving the chains into new shapes that offer lower-energy packing between each other. When the stress is removed, the chains eventually slide back into their original conformations. They return to their equilibrium shapes.



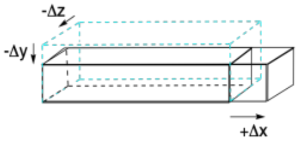
The presence of physical or chemical crosslinks help the material return to its original shape, functioning as anchor points so that the chains don't stray too far. Those interactions might be found in hard-phase interactions in a microphase separated material, as illustrated here, although they could also be found in a homogeneous material.

The linear elastic region isn't all we see in the stress-strain curve above. At point (B), the linear relationship is suddenly lost. The stress might even drop, as seen in this particular case. This feature on the graph is called the "yield point". The stress being experienced by the material, and the resulting strain, has become sufficient to overcome the natural elastic behavior of the solid. As noted previously, physical crosslinks such as hydrogen bonds help to reinforce the elastic behavior of a polymer sample. If, at some point, those interactions are overcome, the chains will start to slide more readily past each other.



As a result, the material loses its elasticity. When the stress is released, the material will still spring back as the chains settle into a new conformational equilibrium. However, that equilibrium will not be the same as the one before. New physical crosslinks will form as groups form intermolecular interactions with the nearest neighbors they encounter. It isn't likely that these will always be the same groups that they were interacting with before. As a result, the material will settle into a slightly different shape. You have probably seen this happen before when a rubber band has been stretched too far, too often, or for too long. Chains have dropped their old interactions and picked up new ones that formed more easily in the extended shape.

At point (C) of the example graph, the slope of the curve starts to increase. The same change in stress results in smaller and smaller changes in strain; the material is getting stiffer. This phenomenon is called "strain hardening". This feature would not always be observed, but if it did happen, what would explain it? In polymers, one explanation may lay in the fact that the volume of the material should remain constant as it is stretched. If the sample is getting longer, that means it is also getting narrower.



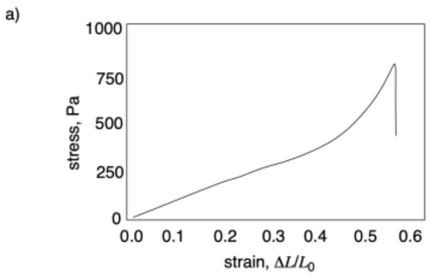
As a consequence of that narrowing cross-section, chains become compressed together. At some point, physical crosslinks begin occurring between neighboring chains. These crosslinks don't occur in equilibrium positions, with polymer chains coiled around each other like they were in the original sample. These crosslinks occur when chains are extended, lying parallel to each other, at closer contact distances than normal.

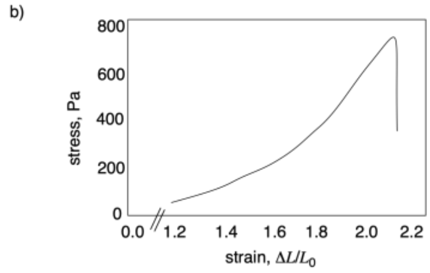
We can see the opposite sort of thing happening at (D), when the slope of the curve is decreasing instead of increasing. This phenomenon is called "strain-softening". Again, it might not be observed in all samples. When it does happen, what causes it? In this case, the answer is simpler. Having overcome the interactions that held the chains together, there is nothing left to resist further deformation. As the chains begin to disentangle from each other, it becomes even easier to pull them apart, facilitating the extension or stretching of the sample.

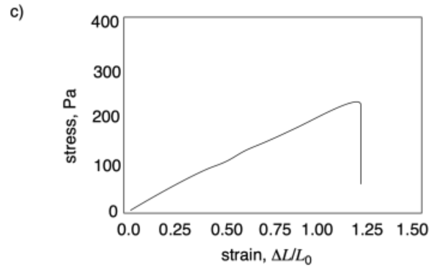
Eventually, at the breaking point (E), the chains start to lose contact with each other at some location in the sample, resulting in a catastrophic rupture of the sample.

Problem PP7.1.

In each of the following curves, estimate ultimate tensile strength and strain at break.

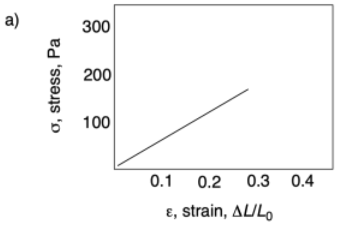


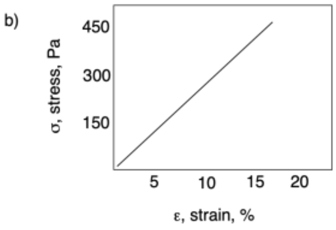


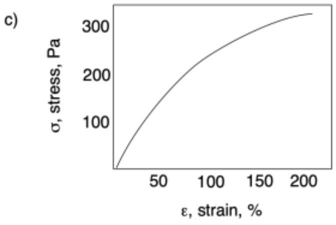


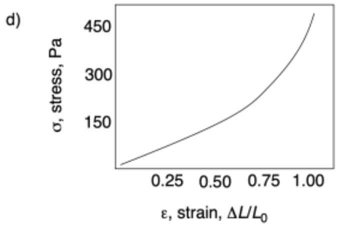
Problem PP7.2.

In each of the following curves, calculate Young's modulus.





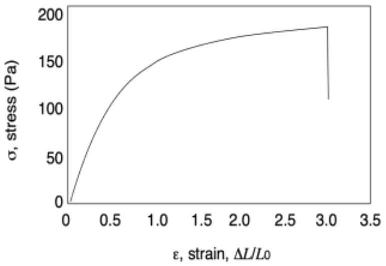




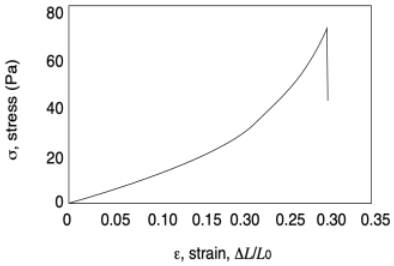
Problem PP7.3.

In each of the following curves, identify any diagnostic features.

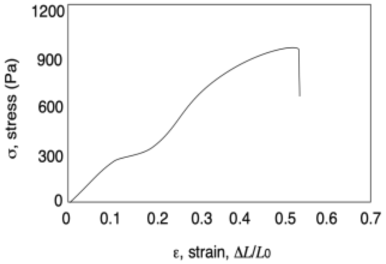
a)


σ, stress (Pa)
200
150
100
50
0
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
ε, strain, ΔL/L0

b)

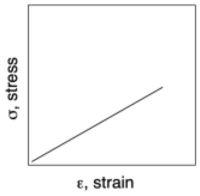

σ, stress (Pa)
80
60
40
20
0
0
0.05
0.10
0.15
0.30
0.25
0.30
0.35
ε, strain, ΔL/L0

c)


σ, stress (Pa)
1200
900
600
300
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
ε, strain, ΔL/L0

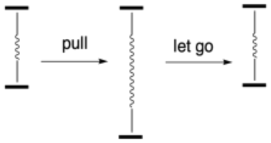
4.8: Storage and Loss Modulus

We saw earlier that the inherent stiffness of a material can be assessed by its Young's modulus. The Young's modulus is the ratio of the stress-induced in a material under an applied strain. The strain is the amount of deformation in the material, such as the change in length in an extensional experiment, expressed as a fraction of the beginning length. The stress is the force exerted on the sample divided by the cross-sectional area of the sample. If the strain is limited to a very small deformation, then it varies linearly with stress. If we graph the relationship, then the slope of the line gives us Young's modulus, *E*. That's the proportionality constant between stress and strain in Hooke's Law.

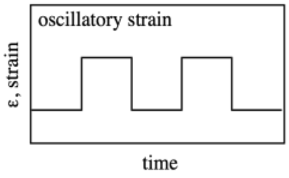


$$E = \sigma / \varepsilon$$

Hooke's Law is sometimes used to describe the behavior of mechanical springs. The modulus can be thought of the resistance to stretching a spring; the more resistance the spring offers, the greater the force needed to stretch it. The same force is what snaps the spring back into place once you let it go.



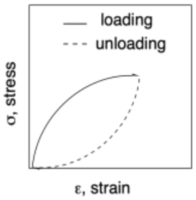
In the experiments we saw earlier, we didn't let go. We continued to stretch the material farther and farther, applying generally increasing stress until the material finally broke. Now we will look at a much more limited approach. Instead of stretching the material as far as we can, we will only stretch it a tiny bit, then release the stress so that it snaps back to its original length. We can then stress it again and release it again. We can keep repeating. Instead of a continuously increasing strain, this sample is subjected to an oscillatory strain, one that repeats in a cycle.



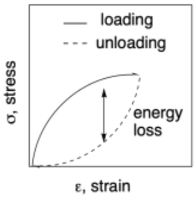
This approach is called dynamic mechanical analysis. We can use dynamic mechanical analysis to measure the modulus of the material. Instead of continuously moving all the way through the linear elastic region, beyond which Hooke's law breaks down, we carefully keep the sample in the Hookean region for the entire experiment. Now, one experiment should be good enough to extract the modulus, but we are letting go and doing it over again. Why?

The principle reason for running the experiment this way is to get some additional information. We can get this information because polymers don't quite follow Hooke's Law perfectly. In reality, even within the linear elastic region, the stress-strain curve is not quite linear. In the picture below, the curvature is exaggerated quite a bit, just for illustrative purposes.

Even if the relationship is not quite linear, then as we release the strain, the stress in the material should simply follow the curve back down to zero. It does not. Instead, there is a phenomenon called hysteresis at work. Hysteresis just means that a property of the material depends on how the material came to be in its current situation. In this case, Hooke's Law seems to imply that a specific sample subjected to a specific strain would experience a specific stress (or vice versa). However, it depends whether we are stretching the sample or letting it relax again. As we let the sample relax back to its initial length, the strain is different from what we saw when we were stretching it. Typically, it's lower. Again, we can see this in the curve below, where the curvature has been exaggerated.



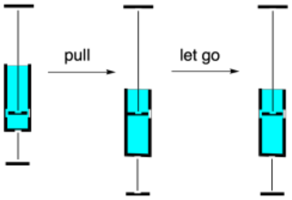
The difference between the loading curve (when the stress was first applied) and the unloading curve (when the stress was removed) represents an energy loss. A force was applied to move a sample or a portion of a sample, some distance. When the sample snapped back the same distance, the force was unequal to the one that was initially applied. Some energy was therefore lost.



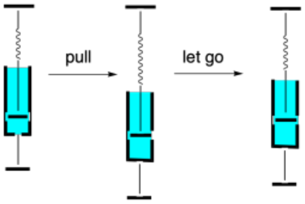
The slope of the loading curve, analogous to Young's modulus in a tensile testing experiment, is called the storage modulus, *E*'. The storage modulus is a measure of how much energy must be put into the sample in order to distort it. The difference between the loading and unloading curves is called the loss modulus, *E*". It measures energy lost during that cycling strain.

Why would energy be lost in this experiment? In a polymer, it has to do chiefly with chain flow. The resistance to deformation in a polymer comes from entanglement, including both physical crosslinks and more general occlusions as chains encounter each other while undergoing conformational changes to accommodate the new shape of the material. Once the stress is removed, the material springs back to its equilibrium shape, but there is no reason chains would have to follow the exact same conformational pathway to return to their equilibrium conformations. Because they have moved out of their original positions, they are able to follow a lower-energy pathway back to their starting point, a pathway in which there is less resistance between neighboring chains.

For that reason, stretching a polymer is not quite the same as stretching a mechanical spring. A "spring-and-dashpot" analogy is often invoked to describe soft materials. Whereas a spring simply bounces back to its original shape after being pulled, a dashpot does not. If you don't know what a dashpot is, picture the hydraulic arms that support the hatchback on a car when you open it upward. There is some resistance to opening the hatchback because a piston is being pulled through a hydraulic fluid as the arm stretches. When we stop lifting, the arms stay at that length, because the hydraulic fluid also resists the movement of the piston back to its original position. The dashpot has a tendency to stay put rather than spring back.

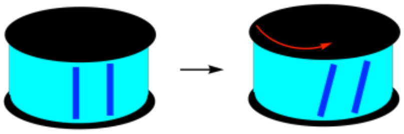


Polymers display a little of both properties. They have an elastic element, rooted in entanglement, that makes them resist deformation and return to their original shapes. They also have a viscous element, rooted in chain flow. That viscous element means that, when we distort polymeric materials, they might not return to exactly the same form as when they started out. Taken together, these behaviors are described as viscoelastic properties. Many materials have viscoelastic properties, meaning they display some aspects of elastic solids and some aspects of viscous liquids.

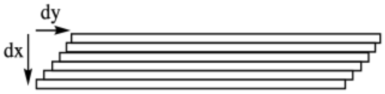


So far, we have concentrated on extensional deformations of materials: we have been looking at what happens when we stretch them. It's worth looking at another type of deformation because it is very commonly used in materials testing. This second approach uses shear instead of an extension to probe how the material will respond. A shear force is applied unevenly to a material so that it tilts or twists rather than stretching.

One of the reasons this approach is used so often is because it is very easy to do. A sample is sandwiched between two plates. The bottom plate is held in place while the top plate is twisted, shearing the material held in between.



If we take a closer look at a layer of the sample, maybe at the surface, along the edge of the sandwich, we can imagine breaking it down into individual layers. Under shear strain, those layers move different amounts. The top layer, right beneath that top plate moves the most. The bottom layer, sitting on the stationary lower plate, doesn't move at all. In between, each layer moves a little further than the one beneath it. This gradation of deformation across the sample is very much like what we saw in the analysis of the viscosity of liquids. The difference is that viscosity looks at the variation of strain with time. Nevertheless, modulus in solids is roughly analogous to viscosity in liquids.



We can use this parallel plate geometry to obtain values for storage modulus and loss modulus, just like we can via an extensional geometry. The values we get are not quite the same. For this reason, modulus obtained from shear experiments is given a different symbol than modulus obtained from extensional experiments. In a shear experiment,

$G = \sigma / \varepsilon$

That means storage modulus is given the symbol G' and loss modulus is given the symbol G''. Apart from providing a little more information about how the experiment was actually conducted, this distinction between shear modulus and extension modulus is important because the resulting values are quite different. In general, the value of the storage modulus obtained from an extensional experiment is about three times larger than the value of storage modulus obtained from a shear experiment.

$E' = 3\,G'$

The reason for the difference is that extension actually involves deformation of the material in three directions. As the material is stretched in one direction (let's say it's the y-direction), in order to preserve the constant volume of the material (there is still the same amount of stuff before and after stretching), the material compresses in both the other two directions (x and z).

Problem PP8.1.

Metric prefixes are frequently encountered when reading about modulus. Rank the following units of stress from smallest to largest, and in each case provide a conversion factor to Pa.

GPa kPa MPa Pa

4.9: Modulus, Temperature, Time

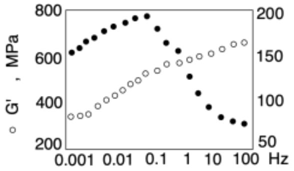
The storage modulus measures the resistance to deformation in an elastic solid. It's related to the proportionality constant between stress and strain in Hooke's Law, which states that extension increases with force. In the dynamic mechanical analysis, we look at the stress (σ), which is the force per cross-sectional unit area, needed to cause an extension in the sample, or the strain (ε).

$$E = \frac{\sigma}{\varepsilon} \tag{4.9.1}$$

Alternatively, in a shear experiment:

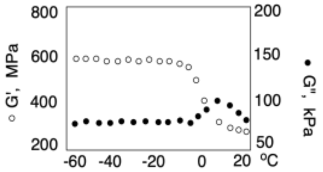
$$G = \frac{\sigma}{\varepsilon} \tag{4.9.2}$$

The dynamic mechanical analysis differs from simple tensile testing by performing the experiment cyclically. The sample is stretched and released (or sheared and released). It can then be subjected to additional stress and released again. There is an element of time involved here. Specifically, because the experiment is cyclic, it can be carried out at different frequencies. When you do that, and you plot the resulting modulus against frequency, you can get additional information about the sample. The results would typically be presented in a graph like this one:



What the graph tells us is that frequency clearly matters. When the experiment is run at higher frequencies, the storage modulus is higher. The material appears to be stiffer. In contrast, the loss modulus is lower at those high frequencies; the material behaves much less like a viscous liquid. In particular, the sharp drop in loss modulus is related to the relaxation time of the material. In this context, that's the time it takes the chains to flow into new conformations in response to the applied stress. If they don't have time to flow, then that viscous response of the material is lost. The material behaves much more like an elastic solid when subjected to high-frequency cyclic deformation. That's important to know, because a material might be subjected to vibrations or other stimuli during everyday use, and its properties might change accordingly.

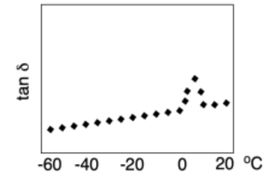
Another variation on this kind of experiment is called dynamic mechanical thermal analysis. Instead of changing the frequency of the stimulus throughout the experiment, the frequency is held constant and the temperature is changed instead. As a result, we can again see how the material responds under different conditions, which might tell us how it will behave in everyday applications. The result of the experiment might be a graph like the one below:



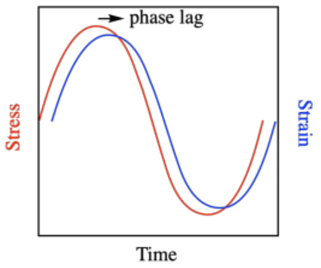
At this point, you are already familiar with the glass transition. It shouldn't be surprising that the properties are dependent on temperature. At the glass transition temperature, the expanding volume of the material with increasing temperature becomes sufficient to allow chain flow. As a result, the material suddenly behaves much more like a viscous liquid. Loss modulus increases. The stiffness of the material drops as the entangled chains not longer resist deformation as strongly. Storage modulus decreases.

The dynamic mechanical thermal analysis thus provides an alternative way to determine the glass transition temperature. Because it is actually measuring a different physical phenomenon than differential scanning calorimetry, the T_g obtained from a DMTA experiment may not agree exactly with one obtained from a DSC experiment. Nevertheless, it is often useful to have different ways of assessing properties.

In order to facilitate the analysis of the T_g in this experiment, a different quantity is usually displayed. Tan delta is just the ratio of the loss modulus to the storage modulus. It peaks at the glass transition temperature.



The term "tan delta" refers to a mathematical treatment of storage modulus; it's what happens in-phase with (or at the same time as) the application of stress, whereas loss modulus happens out-of-phase with the application of stress. Because it would take some time for the chains to move into new confirmation when they are subjected to stress, the strain actually lags behind the stress in these experiments.

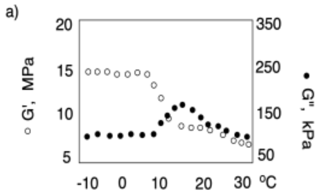


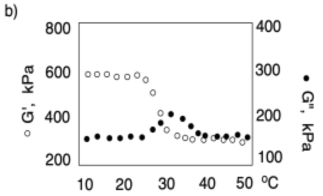
Delta refers to the phase lag, the amount of time between application of stress and the observation of maximum strain. You may remember that a sine curve and cosine curve are out of phase with each other. Storage modulus is described as being proportional to *cosδ* whereas loss modulus is proportional to *sinδ*. The ratio of *cosδ* to *sinδ* is just *tanδ*.

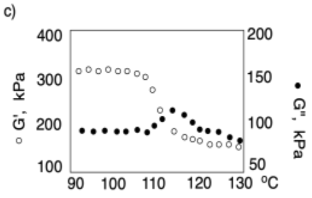
Why does *tanδ* peak at the glass transition temperature? Clearly, as chains begin to move more freely, loss modulus increases. Consequently, the material also becomes less stiff and more rubbery. The storage modulus drops. If tan delta is the ratio of loss modulus to storage modulus, it should increase at that point -- and it does. Why does it drop again? That's because loss modulus refers to an energy loss, but because the material has gotten softer, less stress (and less energy) is put into the sample in the first place, so the energy loss also gets smaller. As a result, tan delta goes up at the glass transition but drops again shortly beyond that point.

Problem PP9.1.

Estimate the storage and loss, modulus in the glassy phase and rubbery phase in each of the following cases.

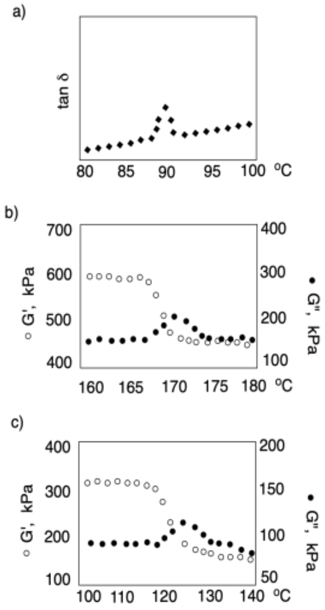






Problem PP9.2.

Estimate T_g in each of the following cases.


a)
tan δ
80
85
90
95
100
°C
b)
700
600
500
400
○ G', kPa
400
300
200
100
● G", kPa
160
165
170
175
180
°C
c)
400
300
200
100
○ G', kPa
200
150
100
50
● G", kPa
100
110
120
130
140
°C

4.10: Chapter Solutions

Problem PP1.1.

a) With a shorter elution time, **I** has a higher molecular weight than **II**. The narrower peak means that **I** has a narrower dispersity than **II**.

b) With a shorter elution time, **III** has a higher molecular weight than **IV**. The wider peak means that **III** has a broader dispersity than **IV**.

c) With a higher elution time, **V** has a lower molecular weight than **VI**. The wider peak means that **V** has a broader dispersity than **VI**.

Problem PP1.2.

a) repeat unit: 109 x ($C_4H_6O_2$) = 109 x 86.09 g/mol = 9,383.81 g/mol

end groups: C_9H_{11} + Br = 119.19 + 79.9 = 199.09 g/mol

total: 9,383.81 + 199.09 = 9,582.90 g/mol

b) repeat unit: 763 x (C_8H_8) = 763 x 104.15 g/mol = 79,466.45 g/mol

end groups: C_4H_9 + H = 57.12 + 1.008 = 58.13 g/mol

total: 79,466.45 + 58.13 = 79,524.58 g/mol

c) repeat unit: 48 x ($C_4H_6O_2$) = 48 x 86.09 g/mol = 4,132.32 g/mol

end groups: C_4H_9 + $C_7H_5S_2$ = 57.12 + 153.26 = 210.38 g/mol

total: 4,132.32 + 210.38 = 4,342.70 g/mol

Problem PP1.3.

The ratio of the repeat unit integral per proton to the end group proton per integral gives the degree of polymerization. We could take the entire integration of the end group and divide it by the entire number of protons in that group, or select one position to represent the end group. Similarly, we can select one position to represent the repeat unit.

a) repeat unit integral per proton = 36.0 / 2H = 18

end group integral per proton = 0.32 / 2H = 0.16

degree of polymerization = 18/0.16 = 112

b) repeat unit integral per proton = 26.0 / 1H = 26

end group integral per proton = 1.32 / 9H = 0.15

degree of polymerization = 26/0.15 = 173

c) repeat unit integral per proton = 54.0 / 4H = 13.5

end group integral per proton = 0.49 / 1H = 0.49

degree of polymerization = 13.5/0.49 = 28

Problem PP2.1.

α is the slope, which is [rise]/[run]. That's approximately [4.0-2.4]/[6.6-4.4] = 1.6/2.2 = 0.73.

K is the y-intercept. The equation for a straight line is y = mx +b; in this case, y = 0.73x + b. If we choose a point on the line, such as (x,y) = (4.9, 2.0), we can substitute those values on for x and y to get b.

So 2.0 = 0.73(4.9) + b, or b = 2.0 - 3.56 = -1.56.

Problem PP2.2.

If the molecular weight is a million g/mol, then log(M_w) = 6. Interpolating, log([η]) = 4, or [η] = 10,000 ml/g.

Problem PP2.3.

If the intrinsic viscosity, [η] = 800 ml/g, then log([η]) = 2.9. Interpolating, log(M_w) = 5.1, or M_w = 126,000 g/mol.

Problem PP2.4.

Ethylene glycol can form hydrogen bonds at either end of the molecule, forming a supramolecular assembly much like a polymer. As a result, it has a much greater drag in solution, higher viscosity.

Problem PP3.1.

Honey is a concentrated solution of simple sugars, which are small molecules. Molasses, although similar to honey in some ways, also contain starches, which are polymers. This polymeric content leads to shear-thinning behavior.

Problem PP4.1.

a) There is a glass transition at around -18°C.

b) There is a melting point at around 125°C.

c) There is a glass transition at around -4°C.

d) There is a glass transition at around 117°C and a melting point at around 146°C.

Problem PP5.1.

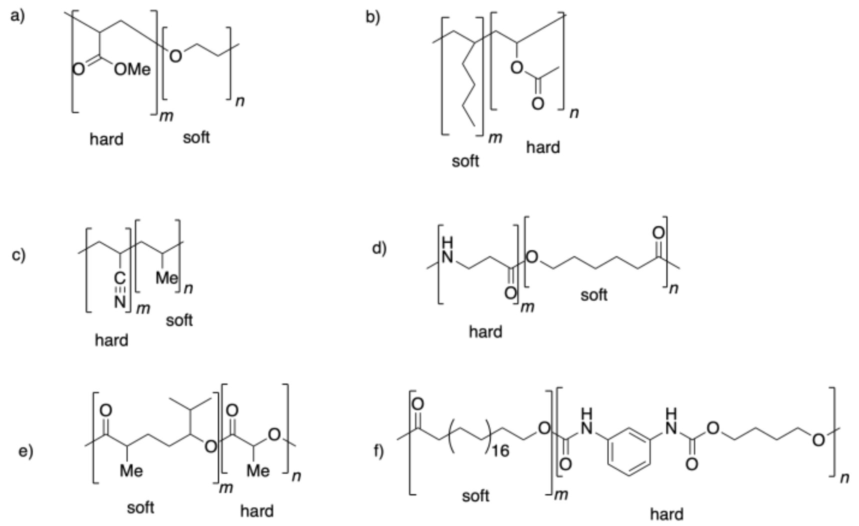
a) T_g is observed at around 78°C, T_m is observed at around 117°C and T_c is observed at around 104°C.

b) T_g is observed at around 134°C and T_m is observed at around 167°C, but T_c is not observed; the sample failed to crystallize, but remained an amorphous solid.

c) T_m is observed at around 194°C and T_c is observed at around 187°C. T_g is not observed, and probably occurs below 150°C

d) T_g is observed at around 123°C, but T_m is not observed. The experiment checked much higher than T_g (over a hundred degrees), so the material may be an amorphous solid.

Problem PP6.1.



Problem PP6.2.

a) d = (2 x 3.14) / 0.40 = 16 Å; d = (2 x 3.14) / 0.70 = 9.0 Å

b) d = (2 x 3.14) / 0.25 = 25 Å; d = (2 x 3.14) / 0.85 = 7.4 Å

c) d = (2 x 3.14) / 0.25 = 25 Å; d = (2 x 3.14) / 0.52 = 12 Å; d = (2 x 3.14) / 0.66 = 10 Å

Problem PP7.1.

a) ultimate tensile strength = 800 Pa; strain at break = 55%

b) ultimate tensile strength = 750 Pa; strain at break = 215%

c) ultimate tensile strength = 220 Pa; strain at break = 120%

Problem PP7.2.

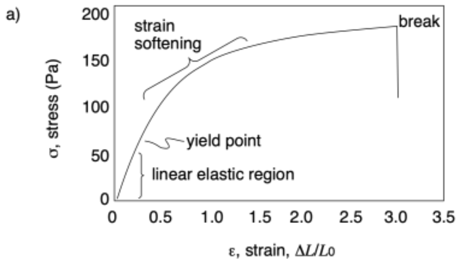
a) E = σ / ε = 180 Pa / 0.30 = 600 Pa

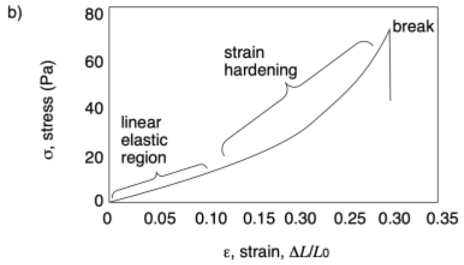
b) E = σ / ε = 450 Pa / 0.15 = 3,000 Pa

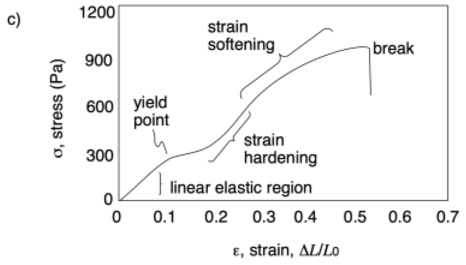
c) E = σ / ε = 50 Pa / 0.25 = 200 Pa

d) E = σ / ε = 75 Pa / 0.30 = 250 Pa

Problem PP7.3.







Problem PP8.1.

1 Pa = 1 Pa

1 kPa = 1,000 Pa

1 MPa = 1,000,000 Pa

1GPa = 1,000,000,000 Pa

Problem PP9.1.

a) glassy: storage modulus = 15 MPa; loss modulus = 70 kPa

rubbery: storage modulus = 7 MPa; loss modulus = 80 kPa

b) glassy: storage modulus = 600 kPa; loss modulus = 140 kPa

rubbery: storage modulus = 130 kPa; loss modulus = 150 kPa

c) glassy: storage modulus = 320 kPa; loss modulus = 80 kPa

rubbery: storage modulus = 70 kPa; loss modulus = 70 kPa

Problem PP9.2.

a) 89 °C

b) 170 °C

c) 124 °C

Index

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: Polymer Chemistry (Schaller)

Webpages: 49

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC 3.0: 81.6% (40 pages)
- CC BY-NC 4.0: 12.2% (6 pages)
- Undeclared: 6.1% (3 pages)

By Page

- Polymer Chemistry (Schaller) - *CC BY-NC 3.0*
    - Front Matter - *CC BY-NC 4.0*
        - TitlePage - *CC BY-NC 4.0*
        - InfoPage - *CC BY-NC 4.0*
        - Table of Contents - *Undeclared*
        - Licensing - *Undeclared*
    - 1: Monomers and Polymers - *CC BY-NC 3.0*
        - 1.1: Difunctional Carboxyloids - *CC BY-NC 3.0*
        - 1.2: Cyclic Carboxyloids - *CC BY-NC 3.0*
        - 1.3: Olefins - *CC BY-NC 3.0*
        - 1.4: Cyclic Olefins - *CC BY-NC 3.0*
        - 1.5: Coordination Polymers - *CC BY-NC 3.0*
        - 1.6: Supramolecular Assemblies - *CC BY-NC 3.0*
        - 1.7: Other Polymers - *CC BY-NC 3.0*
        - 1.8: Polymer Topology - *CC BY-NC 3.0*
        - 1.E: Solutions for Selected Problems - *CC BY-NC 3.0*
    - 2: Synthetic Methods in Polymer Chemistry - *CC BY-NC 3.0*
        - 2.1: Ziegler-Natta Polymerization - *CC BY-NC 3.0*
        - 2.2: Solutions to Selected Problems - *CC BY-NC 3.0*
        - 2.3: Step Growth and Chain Growth - *CC BY-NC 3.0*
        - 2.4: Cationic Polymerization - *CC BY-NC 3.0*
        - 2.5: Living Cationic Polymerization - *CC BY-NC 3.0*
        - 2.6: Anionic Polymerization - *CC BY-NC 3.0*
        - 2.7: Living Anionic Polymerization - *CC BY-NC 3.0*
        - 2.8: Ring-Opening Polymerization - *CC BY-NC 3.0*
        - 2.9: Radical Polymerization - *CC BY-NC 3.0*
        - 2.10: Living Radical Polymerization- RAFT - *CC BY-NC 3.0*
        - 2.11: Living Radical Polymerization- ATRP - *CC BY-NC 3.0*
    - 3: Kinetics and Thermodynamics of Polymerization - *CC BY-NC 3.0*
        - 3.1: Thermodynamics of Polymerization - *CC BY-NC 3.0*
        - 3.2: Kinetics of Step-Growth Polymerization - *CC BY-NC 3.0*
        - 3.3: Kinetics of Chain Polymerization - *CC BY-NC 3.0*
        - 3.4: Kinetics of Catalytic Polymerization - *CC BY-NC 3.0*
        - 3.5: Solutions to Selected Problems - *CC BY-NC 3.0*
    - 4: Polymer Properties - *CC BY-NC 3.0*
        - 4.1: Molecular Weight of Polymers - *CC BY-NC 3.0*
        - 4.2: Viscosity of Polymers - *CC BY-NC 3.0*
        - 4.3: Rheology - *CC BY-NC 3.0*
        - 4.4: Glass Transition - *CC BY-NC 3.0*
        - 4.5: Crystallinity in Polymers - *CC BY-NC 3.0*
        - 4.6: Microphase Separation - *CC BY-NC 3.0*
        - 4.7: Stress-Strain Relationships - *CC BY-NC 3.0*
        - 4.8: Storage and Loss Modulus - *CC BY-NC 3.0*
        - 4.9: Modulus, Temperature, Time - *CC BY-NC 3.0*
        - 4.10: Chapter Solutions - *CC BY-NC 3.0*
    - Back Matter - *CC BY-NC 4.0*
        - Index - *CC BY-NC 4.0*
        - Glossary - *CC BY-NC 4.0*
        - Detailed Licensing - *Undeclared*