



# 8. If Plastics are Polymers, Are All Polymers Plastic?

## Learning Objectives

1. Represent the structure of a polymer using the model of a collection of strings
2. Apply the string model of polymer structure to explain strengthening of polymers via chain orientation
3. Define the yield strength and tensile strength on the tensile stress-strain curve of a typical polymer
4. Explain the mer unit as the logical building block for understanding polymer structure
5. Recognize and draw, and rationalize the relative mechanical behaviour, resistance to chemical dissolution, and softening behaviour upon heating of the following mer units:
  1. Polyethylene
  2. Polypropylene
  3. Polyvinylchloride
  4. Polytetrafluoroethylene
  5. Polymethylmethacrylate
6. Use molecular weight as a means of describing the average length of polymer molecules
7. Compare the number average molecular weight to the weight average molecular weight and explain the importance of each
8. Determine both the number average molecular weight and the weight average molecular weight of a polymer sample, provided with the molecular weight distribution data
9. Recognize the mechanistic similarities between melting, plastic deformation, and chemical dissolution of polymers
10. Predict the changes to the mechanical properties, softening temperature, and resistance to dissolution resulting from changes to the molecular weight, extent of cross-linking, and the strength of secondary bonds
11. Differentiate between and infer the property implications of the following microstructural features of polymers: crystallinity, chain length, branching, and extent of cross-linking
12. Show how differences in electronegativity between atoms in a molecule can create electric dipoles, which in turn can allow secondary bonding
13. Describe the changes in elastic constant and strength for polymers accompanying changes in temperature close to room temperature
14. Explain the changes in mechanical behaviour of polymers with small changes in temperature close to room temperature in terms of the relative magnitudes of the thermal energy and the



- bond energies
15. Differentiate between the glass transition temperature and the melting temperature of a polymer using an explanation based on microstructure
  16. Explain the viscoelastic behaviour of a polymer
  17. Criticize the shortcomings of the string model of polymer structure as applied to the optical properties of polymers

## What's a Polymer Anyway?

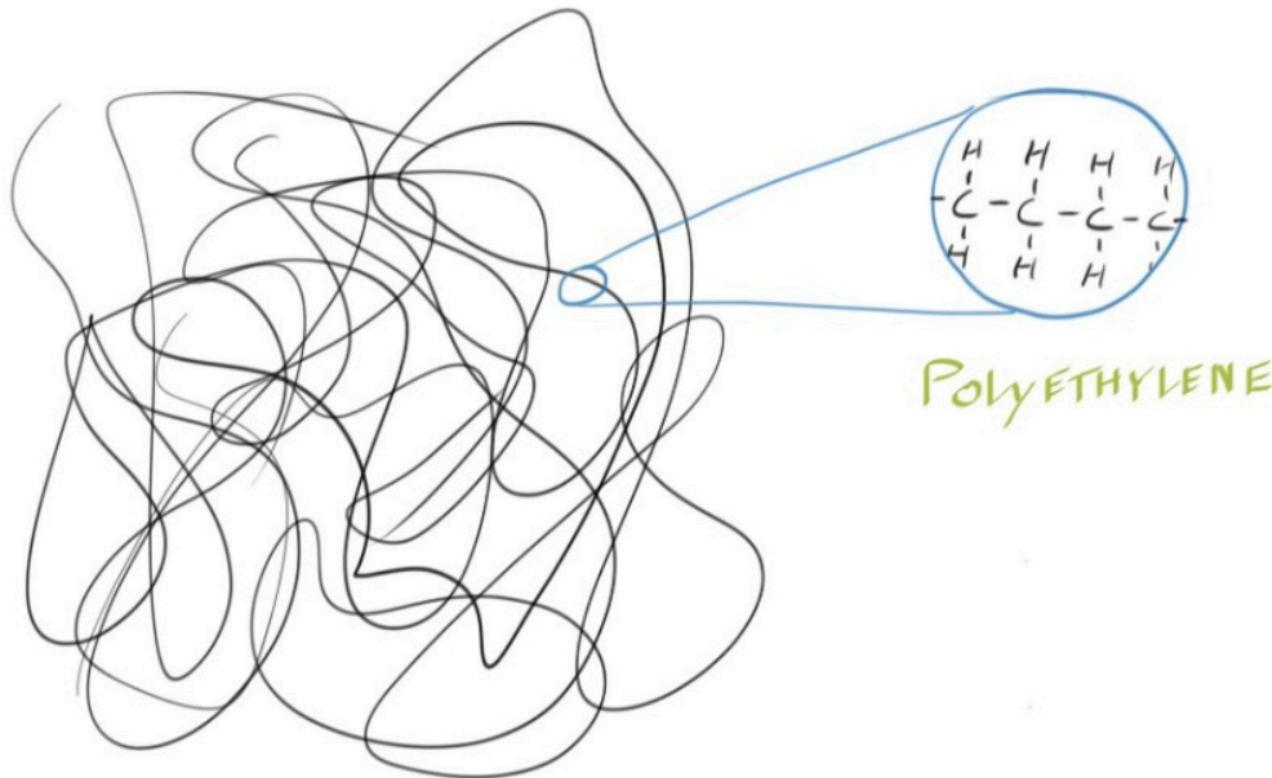


[Link to this video on U of T servers.](#)

So, what's the big deal with polymers? Aren't they just plastics? Why do we need a whole section on them? Okay, these are fair questions, and perhaps saying, "polymer," rather than "plastic" in everyday conversation would be a little [pretentious<sup>①</sup>](#). So, to get started, it will be okay, in fact useful, to think of polymers using the common word, "plastic." This brings to mind so many common everyday items: plastic bags, cases for cell phones, styrofoam cups, many toys, yogurt containers, bicycle helmets, children's drinking cups, yoga mats, buckets, etc. As you consider these items, you may begin to think of some of the properties that they all share. They are all relatively light weight, say compared to the same item made from a metal. They are not too strong, that is, you could scratch any of them with a knife. With the exception of perhaps the yoga mat, you could probably melt any of these items. You could likely also dissolve, or at least significantly damage these items, if you submerged them in a solvent, say acetone.

I think a good place to start will be to quickly dissect the name: *polymer*. The first bit, "poly" means that there are lots and lots of things that repeat. When I say lots, I really mean a lot. One thousand to ten thousand repeats is common. So, then what is this repeat? That's what we call the mer unit, and, of course that's where the mer in polymer comes from. With crystalline metals and ceramics we had the unit cell as the building block that we could repeat in all three dimension to build the larger solid.

With polymers, the mer unit is the building block, but it is typically only repeated in one dimension (with a few notable exceptions that we'll get to later). Yes, this means that polymers, in their simplest form, have linear things (curvilinear would be a better description) making up their structure. Imagine a string. A long string. Now imagine a lot of them. Now imagine crumpling those long strings up into a loose ball. That is a fairly good picture of the structure of a polymer.



**Figure 1.** A schematic sketch of part of the microstructure within a sample of polyethylene, a polymer.

Figure 1 also shows what the structure of the string within the polymer may be. Probably the simplest polymer is *polyethylene* and so the "string" would consist of thousands or tens of thousands of carbon atoms all connected to each other and surrounded by hydrogen atoms. Each of these great long strings of atoms is actually a very large molecule. Therefore, the bonds that hold these atoms together *within* the molecule or string would be called *intramolecular* bonds, since the prefix *intra* means within. Because these intramolecular bonds are so much stronger than any of the other bonds present we often call them strong *intramolecular* bonds, although you'll probably agree that it is redundant to say both strong and intramolecular. I mean, if they weren't strong they wouldn't be able to hold the molecule together would *they?*<sup>①</sup> This simple model of a polymer as a bunch of long strings is surprisingly good at explaining and predicting polymer behaviour. And not just mechanical behaviour either. We can use the *string model* to explain softening and melting at elevated temperatures as well as chemical dissolution (dissolving in a solvent).



## EXERCISE YOUR KNOWLEDGE



8.1.1

Mark as: None ▾

The microstructure of a polymer is generally best visualized in which of the following ways?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a As a highly ordered solid
- b Using a unit cell that describes the entire structure
- c As a collection of small molecules, roughly 10-20 atoms each
- d As a collection of very long molecules intertwined with one another

## Stretching a Plastic Bag Has Never Been This Exciting



[Link to this video on U of T servers.](#)

You may have had this happen at one point or another. You go to the market/supermarket to buy some groceries. Being the healthy person you are, you buy some bananas, apples and milk. Well, it doesn't really matter exactly what you buy as long as it's quite heavy and you put it all into one plastic bag. You notice that the handle of the plastic bag starts to stretch. It gets uncomfortable as the handle begins to press into your hand a little. Is the handle going to tear? You're worried. The handle slowly stretches a little more, but then, as if by magic (but really by science), the handle stops stretching. If

you look carefully at the handle (and this depends a bit on the type of bag) you may even be lucky enough to see a colour change in the handle where it has stretched. So, how can we use our *string model* of a polymer to explain this amazing plastic bag? Well, when we first get the bag and it hasn't yet been stretched, all of the strings, or molecules, are pretty much randomly oriented in the plane of the bag. It's a little like taking a pot of spaghetti, or udon, or ramen, or vermicelli, or pho and dumping it onto a table (anyone else hungry and sad about the wasted food?) You can imagine that all of the noodles are laying out on the table, somewhat flat against the table, but completely disorganized along the surface of the table. Now, all that healthy food in that plastic bag of yours is stretching the handle of the bag. What happens to the strings/molecules/noodles? Imagine if you stuck your fingers into the noodles on the table and separated them. You'd likely get some strange looks from other people in the restaurant, but you'd also see the noodles begin to line up with each other along the direction between your fingers. This is what is happening to the molecules in the plastic bag as it stretches and is illustrated in Figure 2.

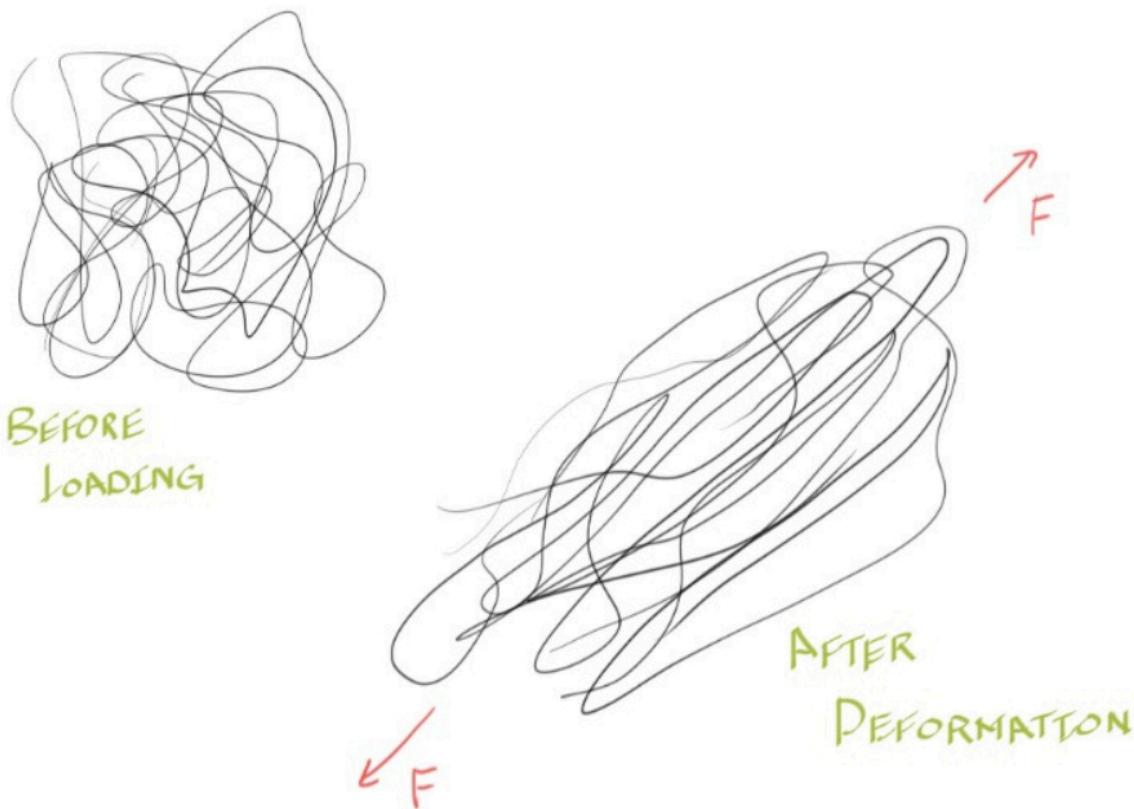


Figure 2. Sketch of strings getting stretched out and aligned with the loading axis.

So, how does this explain the bag suddenly stopping stretching? Well, remember how the bonds between the atoms were *strong* bonds? Now these strong intramolecular bonds are becoming aligned along the loading axis and so the polymer is actually getting stronger.

This is probably also a good time for us to discuss the weaker bonds in a polymer. When a polymer is plastically deformed, one of the things that occurs within the microstructure is that molecules slide

past one another. You may be able to imagine this by thinking about yourself in that restaurant with your fingers jabbed into the noodles spilled on the table. As you move your hands apart, noodles slide past each other and in the case of the noodles, there is a frictional force that is overcome between the noodles. In a polymer these "frictional" forces are forces that occur between molecules, so we could call them *intermolecular* forces, since the prefix *inter* tells us the force is between molecules. When atoms come together the first thing that happens is that they form primary bonds (which is why they are called primary) and next they can form secondary bonds. So, as we plastically deform a polymer and the molecules become aligned along the loading axis we get an increase in the amount of the load that is supported by primary bonds and less of the load supported by secondary bonds. More on these bonds later.



## EXERCISE YOUR KNOWLEDGE



8.2.1

Review

Mark as: None ▾

Polymers tend to be more ductile than metals for which of the following reasons?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a Polymers don't have dislocations, so plastic deformation is very difficult and polymers tend to deform elastically until fracture

b Plastic deformation occurs largely by the movement of long molecules past one another, overcoming weak forces between molecules as plastic deformation occurs

c Plastic deformation in polymers occurs mostly by the breaking apart of very long molecules into progressively smaller and smaller molecules

d Polymers have lower Elastic moduli than metals and so they must be more ductile

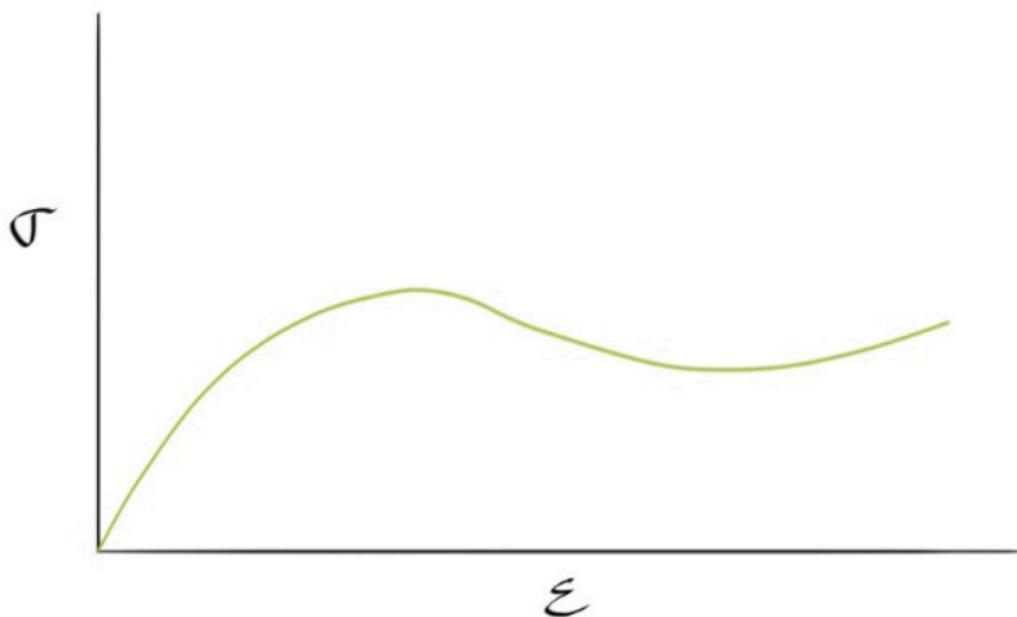
## The Stress-Strain Behaviour of a Typical Polymer





[Link to this video on U of T servers.](#)

Now that we've got a working knowledge of the relationship between the molecules in a polymer and the mechanical behaviour, let's dive into a stress-strain curve. I'll bet you never thought you'd read a sentence telling you to dive into a stress-strain curve. Well, maybe you did and that's why you're studying this. Figure 3 shows the generalized stress-strain behaviour for the type of polymer that we'd commonly call a plastic.



**Figure 3.** The generalized stress-strain curve for a plastic polymer.

Take a moment to really let Figure 3 soak in. Is there anything about this curve that is surprising? How does it compare to the stress-strain curve for a metal? How is it similar? You've probably noticed that there is an initial portion of the curve that is approximately linear. This region is followed by a curved region and a peak stress. After that, the stress decreases, but the unique feature of the polymer curve is that the polymer is somehow able to continue load bearing after the peak. Recall that metals will

that the polymer is somehow able to continue load bearing after the peak. Recall that metals will

always break after the peak, or ultimate tensile strength, because this is where necking occurs and the metal can't strengthen fast enough to overcome the rapidly decreasing cross-sectional area in the neck. This means that some polymers must have a microstructural mechanism that allows them to strengthen in the neck very significantly. Something significant like, say, a change in the proportion of primary bonds to secondary bonds supporting the load. That's right, the mechanism that we discussed earlier with the plastic shopping bag handle getting stronger is exactly what allows many polymers to continue load bearing after the onset of necking, which still corresponds to the peak of the curve. The alignment of polymer molecules with the loading axis in this manner is frequently called *chain orientation*.



## EXERCISE YOUR KNOWLEDGE



8.2.2

Review

Mark as: [None ▾](#)

Polymers are sometimes able to continue supporting load well beyond the ultimate tensile strength (onset of necking) for which of the following reasons?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a The surface of polymers is much smoother than that of metals and so there are no cracks to cause failure after necking
- b The molecules within a polymer can become elongated and oriented with the loading axis allowing the stronger intramolecular bonds to support the load
- c Polymers have high molecular weight and so are heavy and difficult to move
- d Polymers generally have low strength and so their ultimate tensile strength is low

## Defining Yield Strength and Tensile Strength

You'll recall from our discussion of the behaviour of metals that it was difficult for us to accurately and unambiguously determine the point on the stress-strain curve for a metal where plastic deformation begins. This led us to establishing a convention, the 0.2% offset yield strength. Now, with a polymer like the one shown in Figure 3, since the polymer continues to support load after necking, we can safely use the peak of the curve itself as an unambiguous point to define the yield strength. This is shown in Figure 4. By convention, the point where the polymer fractures is called the tensile strength.

SHOWING FIGURE 4. By convention, the point where the polymer fractures is called the tensile strength.

Note that these definitions are different from our definitions for metallic samples.

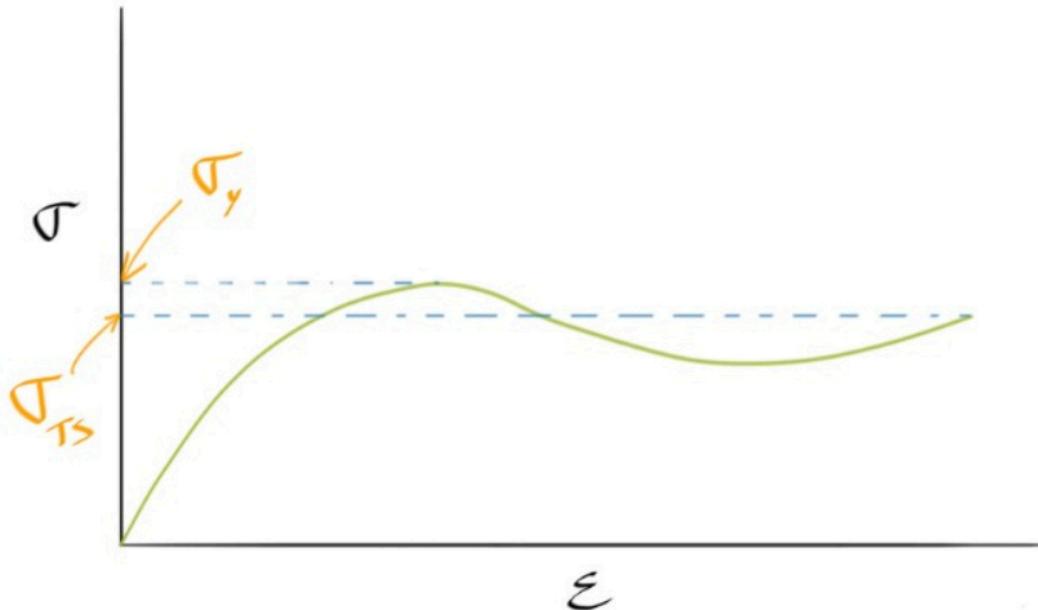


Figure 4. The generalized stress-strain curve for a plastic polymer, showing the yield strength and the tensile strength.

This is quite exciting, really. What is so exciting, you ask? Well, we've just started looking at polymers and already we've learned a strengthening mechanism - *chain orientation*. This principle is actually used industrially to make high strength polymers like Spectra® and Dyneema®, remember kite-board control lines in Chapter 2?



### EXERCISE YOUR KNOWLEDGE



8.3.1  
Review

Mark as: None ▾

The yield strength of a polymer is generally defined in which of the following ways?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a At the 0.2% offset yield strength

b The initial peak of the curve, where localized plastic deformation begins

c At the point where fracture occurs

d Polymers don't display a yield strength



8.3.2

Review

Mark as: [None](#) ▾

The tensile strength of a polymer is generally defined in which of the following ways?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a At the 0.2% offset yield strength

b The initial peak of the curve, where localized plastic deformation begins

c At the point where fracture occurs

d Polymers don't display a yield strength

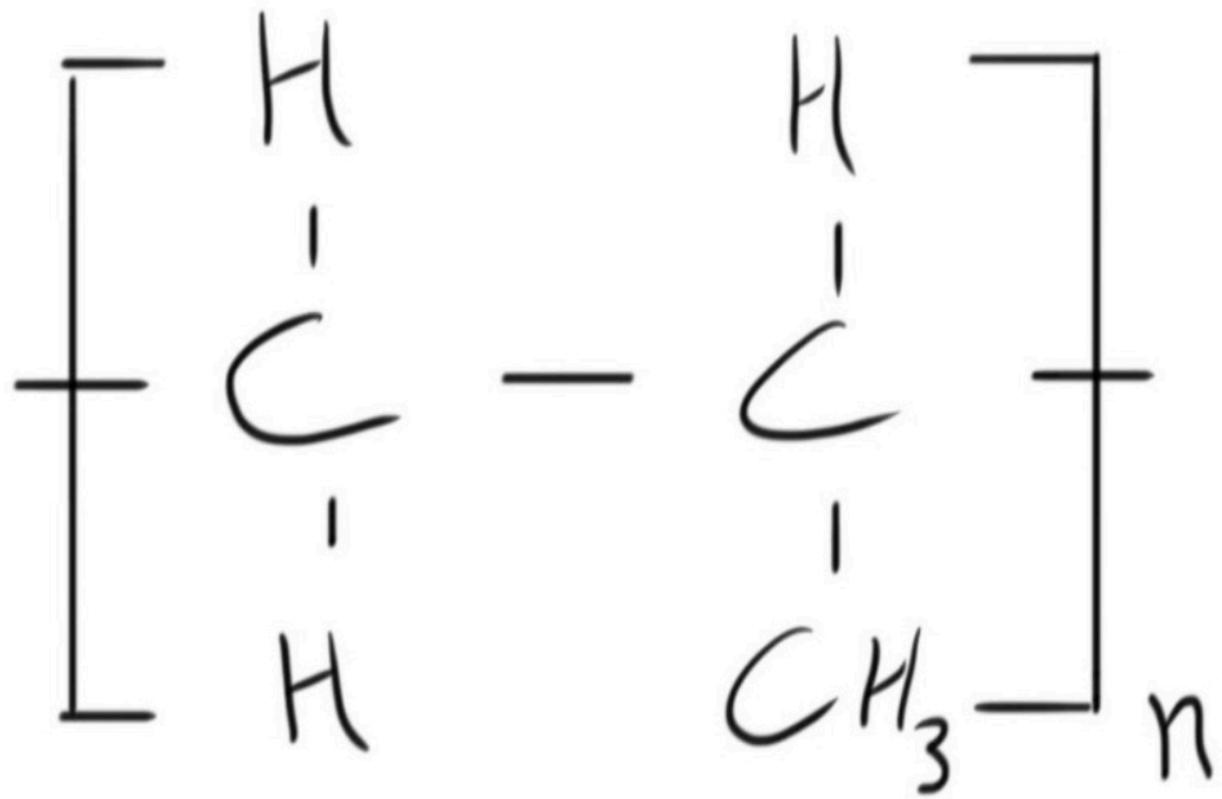


## Changing Those Mer Units

So, we've learned one way to strengthen a polymer. Surely there are other ways? You bet. What if we actually used a different mer unit to form our polymer? So far, we've looked at polyethylene, but there's a good chance you've heard of some other polymers.

### Polypropylene

Polypropylene (PP) is a very common and useful polymer. Those nifty reusable cups from Starbucks® are made from PP. If you look on the underside of plastic containers you'll frequently see the recycling code that identifies what mer unit is used. The recycling code for PP is 5.



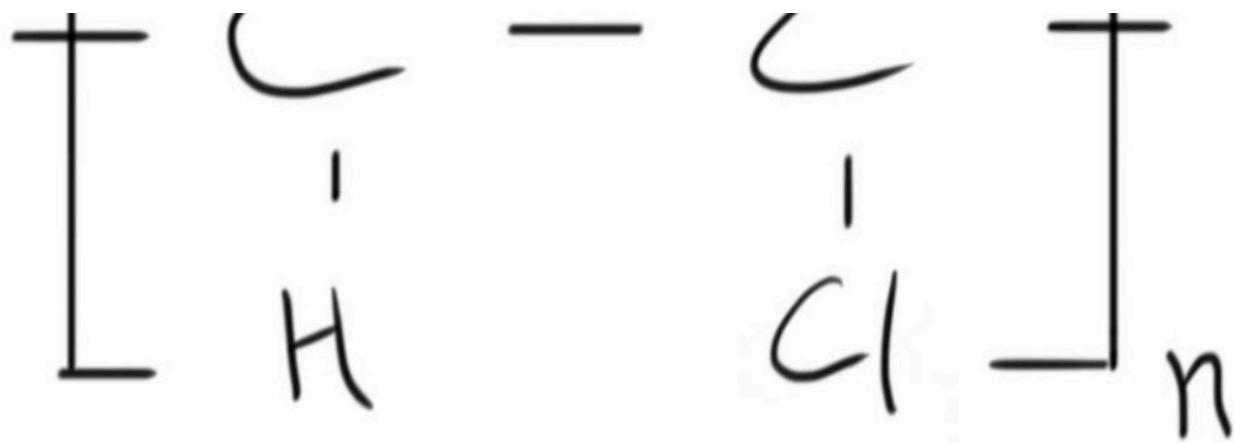
**Figure 5.** The mer unit for polypropylene. The methyl ( $\text{CH}_3$ ) group makes it slightly harder for chains to slide past one another, increasing the strength.

Often the abbreviation (PP) is also embossed on the plastic. I'm writing this in my kitchen, at the moment and on the counter in front of me I've got a plastic 2 litre jug for water or juice. It's made from PP. Generally, PP is a little stronger and has a higher elastic modulus than polyethylene. This increase in mechanical properties comes from the extra  $\text{CH}_3$  (methyl) group on the mer unit, as shown in Figure 5.

## Polyvinylchloride

The next polymer you should really know about is polyvinylchloride (PVC). Did I mention that PE, PP, and PVC are the three polymers produced the largest amount in the world, respectively?



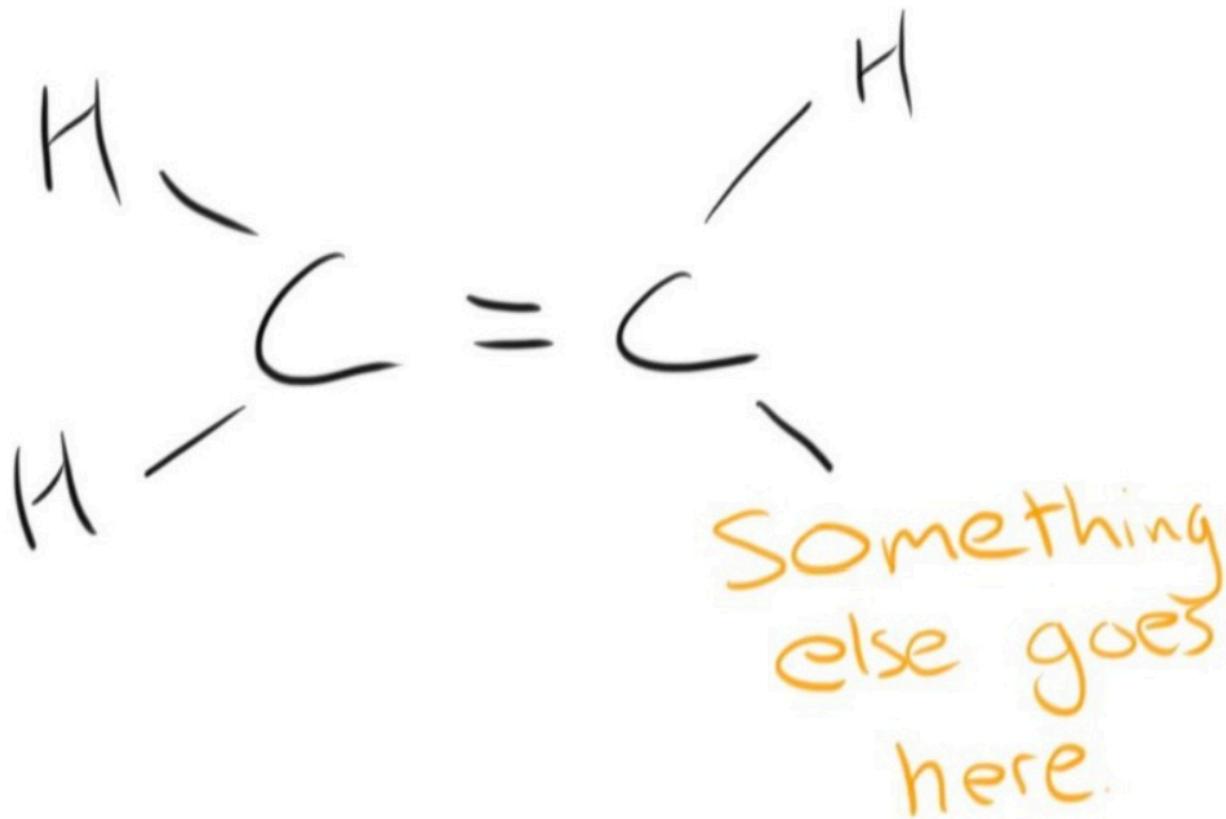


**Figure 6.** The mer unit for polyvinylchloride. The chlorine group creates a stronger attractive force between makes it slightly harder for chains to slide past one another, increasing the strength.

PVC's name tells us that there must be a chlorine atom in the mer unit. That is absolutely correct.

Figure 6 shows the mer unit for PVC.

In case you are like me and get hung up a little on why things have the names they do, and in this case, what the *vinyl* part of PVC means, let me quickly explain. The vinyl group is just two carbons bonded with a double bond and one hydrogen missing, as shown in Figure 7.



**Figure 7.** The vinyl group. I hope that by seeing this, the name polyvinylchloride makes more sense.

PVC is a very versatile polymer and can have a wide range of properties. In its simplest form, it is quite strong, with a relatively high elastic modulus. This has to do with the chlorine atom bonded onto each mer unit. To better understand this effect we need to take a look at the periodic table.



## EXERCISE YOUR KNOWLEDGE



8.4.1  
Review

Mark as: [None ▾](#)

The most convenient building block for describing polymer molecular structure is which of the following?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a An individual atom

b An individual molecule

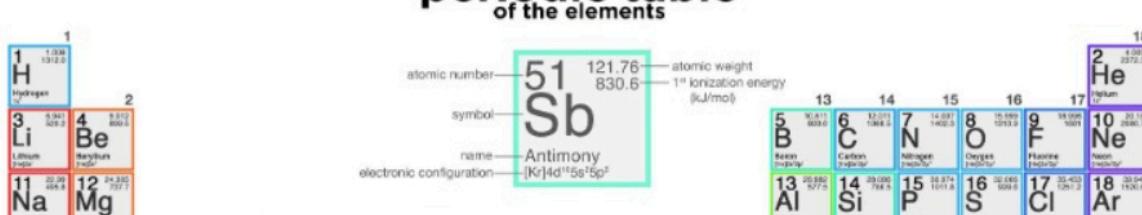
c A unit cell

d The mer unit



## The Periodic Table and Electronegativity

Thankfully, Dayna Lau, a summer student of mine created a beautiful periodic table, so I have included it in Figure 8.



Period	Period	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Group	Group	Alkali metals	Alkaline earth metals	Post transition metals	Metalloids	Other non-metals	Halogens	Noble gases	Lanthanoids	Actinoids						
1	1	Li	B	C	N	O	F	Ne								
2	2	Be	Mg	Al	Si	P	S	Cl	Ar							
3	3	Na	Mg	Al	Si	P	S	Cl	Ar	K	Rb	Fr				
4	4	Mg	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se
5	5	Al	Si	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	Br	Kr
6	6	Si	P	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br
7	7	P	S	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Kr
8	8	S	Cl	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Xe	
9	9	Cl	Ar	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
10	10	Ar		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
11	11			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
12	12			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
13	13			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
14	14			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
15	15			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
16	16			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
17	17			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
18	18			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
19	19			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
20	20			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
21	21			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
22	22			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
23	23			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
24	24			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
25	25			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
26	26			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
27	27			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
28	28			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
29	29			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
30	30			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
31	31			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
32	32			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
33	33			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
34	34			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
35	35			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
36	36			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
37	37			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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39	39			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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41	41			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
42	42			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
43	43			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
44	44			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
45	45			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
46	46			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
47	47			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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51	51			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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60	60			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
61	61			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
62	62			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
63	63			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
64	64			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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71	71			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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81	81			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
82	82			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
83	83			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
84	84			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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90	90			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
91	91			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
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94	94			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
95	95			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
96	96			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
97	97			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
98	98			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
99	99			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			
100	100			Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn</td			



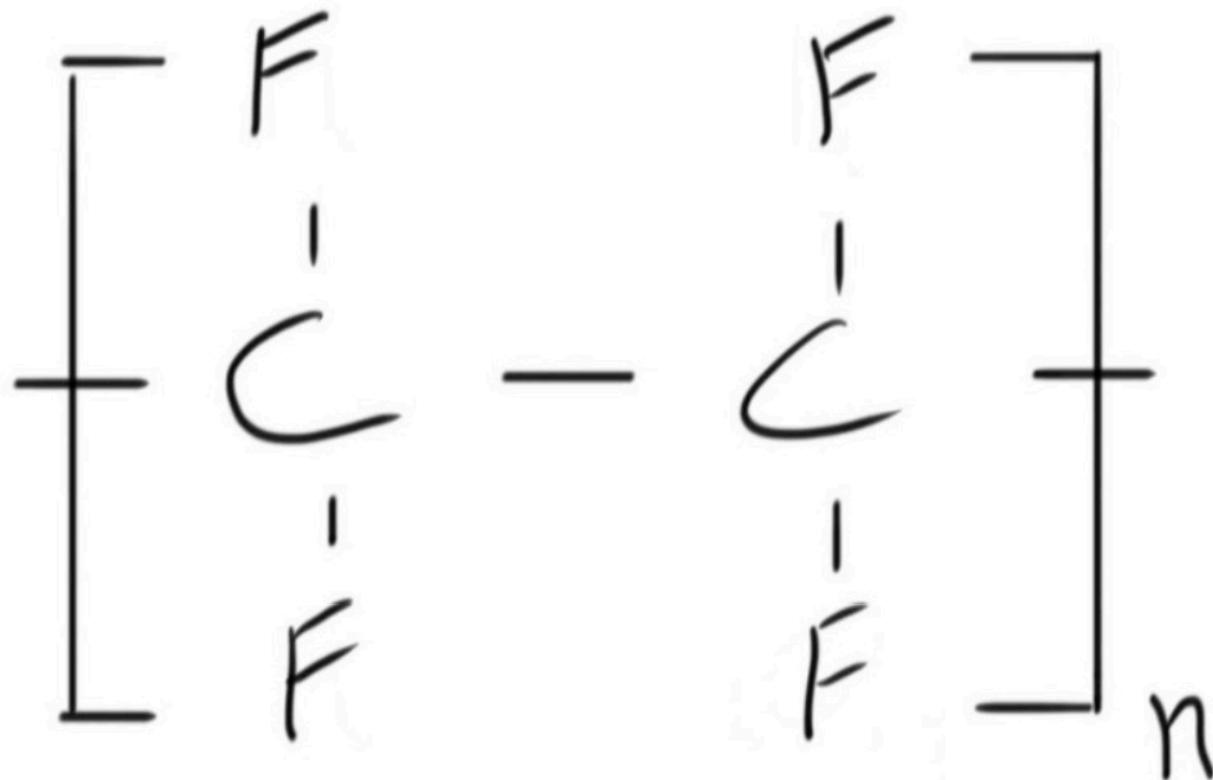
for dipole

**Figure 9.** An example of a polar molecule. HCl is an electric dipole due to the electronegativity difference between hydrogen (H) and chlorine (Cl). Sometimes dipoles are sketched schematically using a shorthand notation using an arrow with the tail made into a "plus" sign and the head pointing towards the negative end. Since the charge is less than the full charge on an electron or proton, the lower case Greek delta is used to indicate a partial charge.

Because the electron carries a negative charge, this imbalance in the electron cloud can create charged regions of the molecule. When a molecule has a negative and positively charged ends, or *poles* we say that it is a *two-poler*. Okay, I just made that up. That's not what we call it. There is a better term, and that term is *dipole*. Figure 9 shows the HCl molecule as an example of a dipole.

## Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) might be my favourite polymer. It might be. There are lots of excellent polymers to choose from, so don't quote me on that. The name is quite a mouthful, but there's a good chance that you've heard of one of the trade names for PTFE: Teflon® or Gore-Tex®. The mer unit for PTFE is shown in Figure 10.



**Figure 10.** The mer unit for PTFE. The large fluorine atoms protect the intramolecular bonds in PTFE so that it is a very nonreactive polymer.

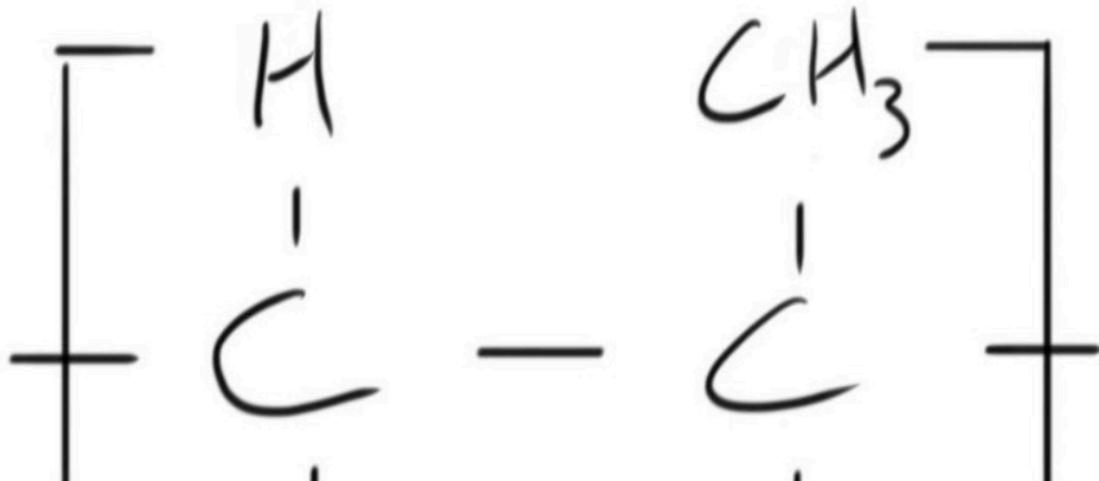
PTFE is used in non-stick surfaces. Other forms of fluorinated polymers are used in non-stick

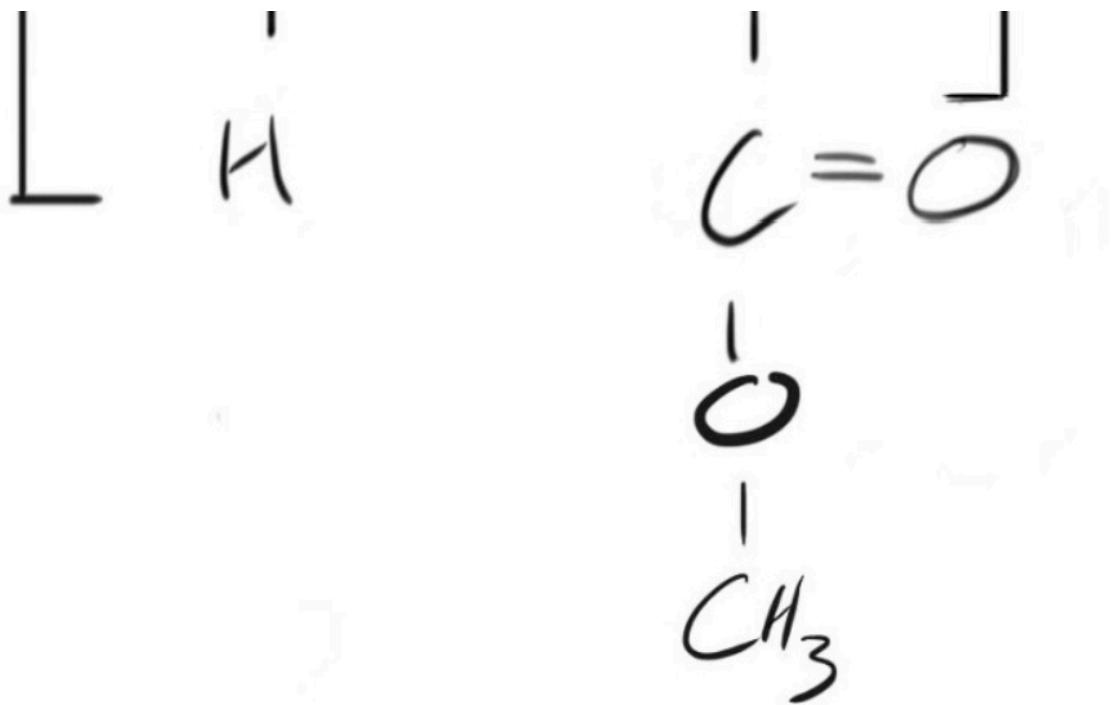
cookware and release films for prevent epoxy from sticking to surfaces during composite manufacturing. The key to PTFE's success as an nonreactive polymer lies in the large fluorine atoms bonded to each carbon. These fluorine atoms are quite large and protect the intramolecular bonds within PTFE from being broken easily. Note, that although fluorine is highly electronegative, the PTFE molecule is non-polar since the fluorine atoms are geometrically symmetrical about the molecule and so the centre of positive charge lies at the same point as the centre of negative charge.

Gore-Tex® is a form of PTFE that has been formed into thin films and stretched. The stretching introduces fine holes, or pores, in the film. PTFE, is a polymer that repels water (it is *hydrophobic*) so this means that water tends to form beads on the surface of PTFE. This prevents liquid water from passing through the pores in GoreTex®, however, individual molecules of water, as in the vapour phase, can freely diffuse through these pores. This is how GoreTex® used in outdoor clothing is able to keep the user dry in the rain while also allowing sweat to evaporate and diffuse out of the clothing. The marketing types like to call this "breathing." I suppose you're more likely to buy an expensive jacket that breathes than one that allows gas phase diffusion of water whilst preventing migration of liquid phase water.

## Polymethylmethacrylate

Oh, maybe this is my favourite polymer. Polymethylmethacrylate (PMMA) has several very interesting uses. The name is another big one, but in the name you may recognize the term *acrylate* telling us that this is an acrylic. You may know that some acrylics are used for windows because they can be made beautifully optically transparent. In fact, you may know one of the trade names of PMMA, Plexiglas®. What's more, if you are wearing glasses while you read this, there is a good chance that you are learning about PMMA while looking through PMMA. How meta. The reason that we are able to make PMMA optically transparent is very interesting and starts from the mer unit, which I've sketched in Figure 11.





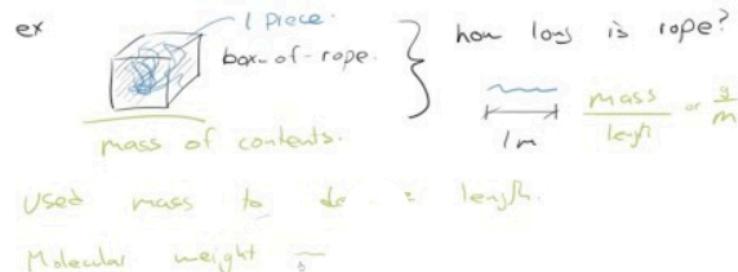
**Figure 11.** The mer unit for polymethylmethacrylate. Note the large side group that is present off each mer unit.

The large (often called "bulky" side group that is present on each mer unit prevents the molecules from organizing close to one another. This ensures the polymer is completely disorganized, or *amorphous*.

You see, polymer molecules can become aligned with one another and highly organized, which we call *crystalline*. When a polymer crystallizes, the index of refraction is different from when it is amorphous.

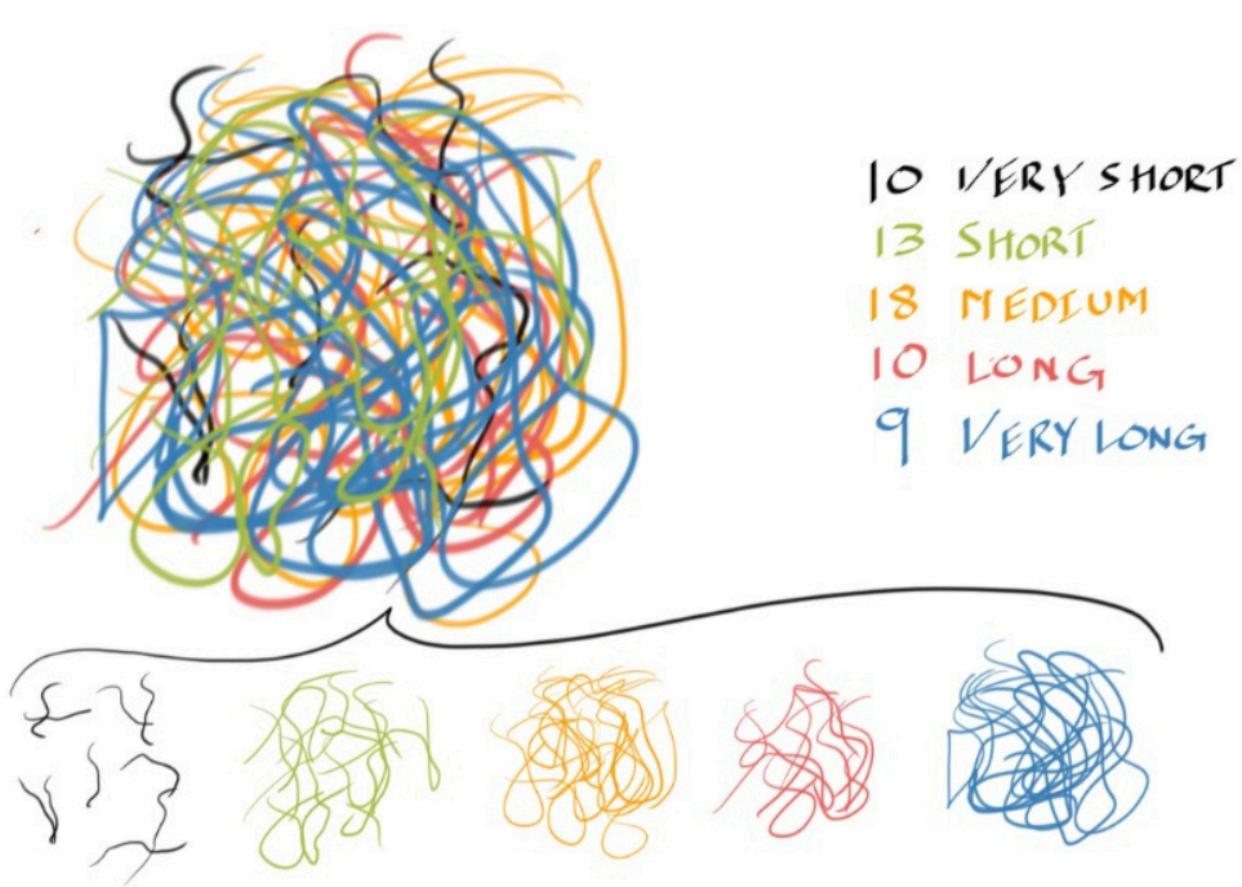
If the polymer contains parts that are amorphous as well as parts that are crystalline (so-called *semicrystalline*) then light passing through the polymer will not follow a direct path and the polymer will be translucent or opaque. So, part of the reason that PMMA is transparent is because the mer unit ensures that it stays 100% transparent. Don't worry if this is still a little unclear. We just covered an awful lot of ground in a very short amount of space. This will all make more sense once we've covered more detail on polymer structure.

## How Long Are These Molecules, Really?



[Link to this video on U of T servers.](#)

I told you earlier that polymer molecules are long, in fact, I recall mentioning thousands or tens of thousands of carbons, or even more. But, how are we to quantify the length of a specific batch of polymer? You may well wonder if there is any need to do so. Well, let me tell you, there is a very good reason to be able to describe the length of polymer molecules. "Fine," you say, "lets just say they are so-many millimeters and be done with it." Whoa there! It's a little more involved than that. First, we need to understand that when polymers are synthesized, it is somewhat difficult to control the length of the molecules that result, and so we end up with a few molecules that are really short, a few that are very long, and a bunch in between. Well, this was a bit of a crude description, as you might guess, we are left with a *distribution* of molecule lengths.



**Figure 12.** A hypothetical polymer sample consisting of some "very short" molecules, some "short" molecules, some "medium" molecules, some "long" molecules, and some "very long" molecules.

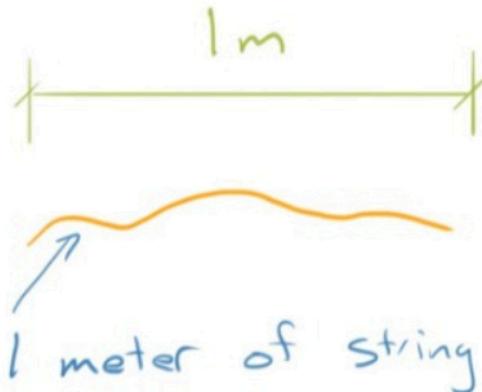
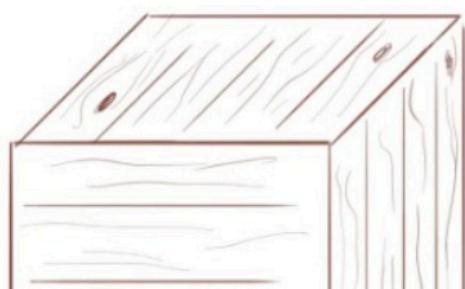
Figure 12 shows a hypothetical polymer sample that has been broken down into five ranges of molecule length: very short, short, medium, long, and very long. Hopefully, while looking at Figure 12 you'll realize that there is not one single length that describes the length of every molecule in the sample. Just like grades in a class will follow a distribution, so are the molecule weights in a polymer spread over a range. The distribution for our hypothetical polymer in Figure 12 is shown in Figure 13.

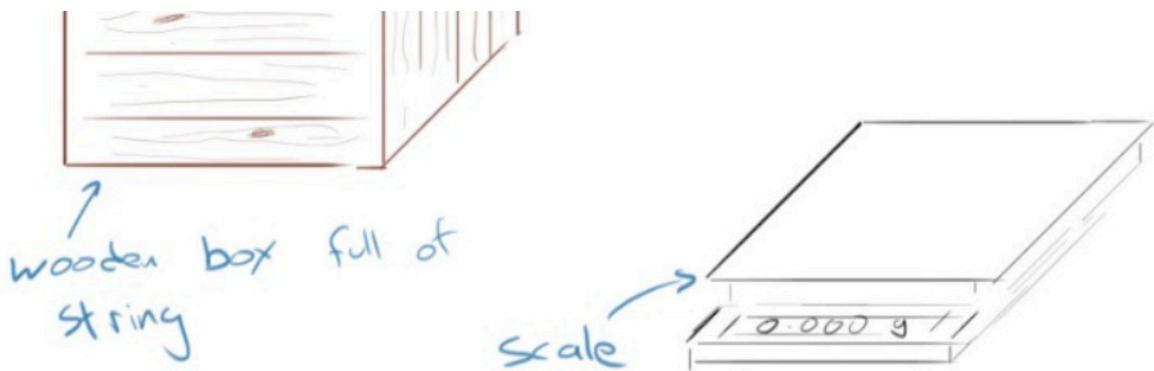


**Figure 13.** The molecular weight distribution for the hypothetical polymer sample in Figure 12. Our grouping into only five length groupings is very coarse and the actual distribution would be smooth, as shown by the nice smooth curve.

Looking at the distribution now, and perhaps considering the distribution of grades in a class as an example, you may have come up with one way to attempt to describe the length of the molecules in this sample. We could use an average. Simply sum up all of the molecule lengths and then divide by the total number of molecules. But what units do we use? While we could use length units, it is customary to use molar mass, or commonly (and rather dimensionally inconsistent, but that is another discussion) *molecular weight*.

I find that students often get a little stuck on using units of mass (but often calling it weight) to describe a length. This may help; please bear with me. Imagine that I showed you a wooden box about large enough to hold a watermelon, as shown in Figure 14.





**Figure 14.** A hypothetical problem, as an analogy for polymer molecular weight. You are presented with a wooden box containing a length of string. You are not allowed to open the box, and you need to determine the length of string in the box. You are given the mass of the empty box and a one meter length of the string, along with a balance. You can use mass to determine the length of the string in the box.

I told you that the box contained a single length of string. I told you the mass of the empty box, and I gave you a one meter length of string and a balance to check the mass of anything you like. After pondering this problem briefly, you can likely see that you could check the mass of the one meter length of string to calculate the mass per unit length of the string. You can then use this mass per unit length along with the mass of the empty box and the box plus string to calculate the length of the string in the box.

So, my hope is that you see how we can use mass to describe length. In fact, you can imagine if you were buying and selling large crates of this string, mass would be the obvious measure for quantity of the string, even though the end user is concerned with length.

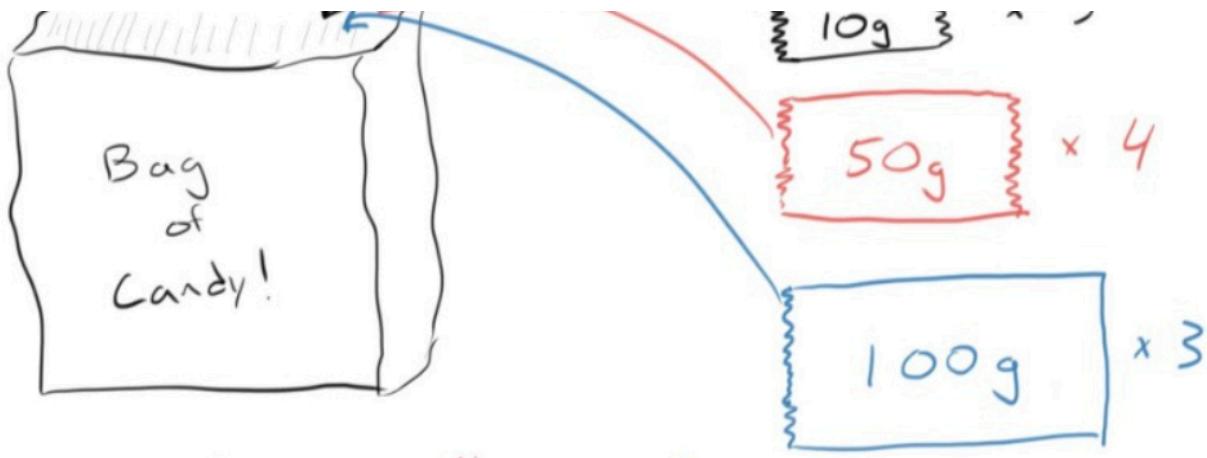
Wow, what a journey we've taken here just to get to molecular weight. A few paragraphs ago we were about to sum up all of the molecule lengths and divide by the number of molecules. Technically, this is known as the *number average molecular weight* and can be defined as

$$\overline{M}_{\text{number}} = \sum_{n=1}^i M_n x_n \quad (1)$$

for a sample containing  $i$  groups (in our previous example we had five groups), where  $M_n$  is the molecular weight of the  $n^{\text{th}}$  group, and  $x_n$  is the number fraction of the  $n^{\text{th}}$  group (or said another way, the number of molecules in that group, divided by the total number of molecules).

Equation 1 can be a little daunting to look at initially, but hopefully with a little time you'll see that it is exactly the way that you would calculate the average grade for a class on a test, for example. Figure 15 attempts to help clarify this by using an example of calculating the average weight of candy in a bag of candy.





$$\bar{M}_n = 10g \cdot \frac{5}{12} + 50g \cdot \frac{4}{12} + 100g \cdot \frac{3}{12}$$

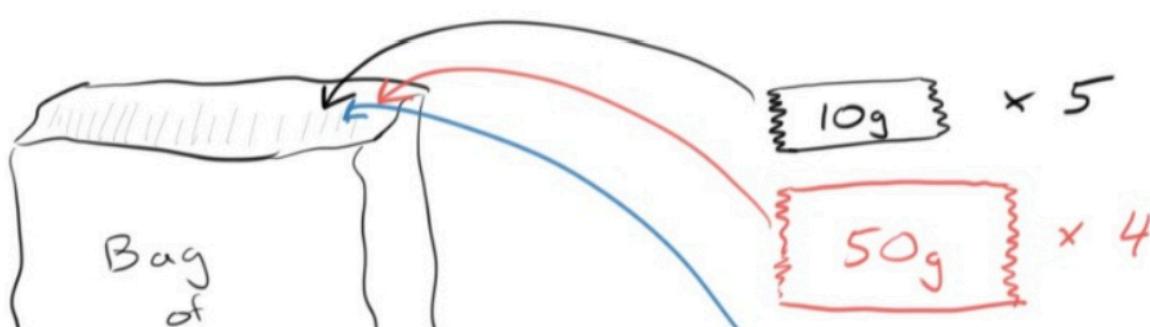
$$= 45.8 \text{ g}/\text{bar}$$

**Figure 15.** Calculating the average weight of candy bars in a bag of candy, using the *number average candy weight*.

After considering the example in Figure 15 I think you'll agree that the number average calculated does not match the mass of any individual candy bar in the bag. Also, on its own, this average tells us very little about the candy bars in the bag. Are almost all of them small? Are there any candy bars that are really big? Clearly, the most descriptive way of conveying the contents of the bag would be the distribution itself. So it is with polymers: the number average molecular weight is useful but not very descriptive on its own. Thankfully, there is another way that we can calculate the molecular weight that can provide a little more information. This molecular weight is another average, but it is not immediately very intuitive. It is called the *weight average molecular weight* and it can be defined as

$$\bar{M}_{\text{weight}} = \sum_{n=1}^i M_n w_n \quad (2)$$

for a sample again containing  $i$  groups, where  $M_n$  is the molecular weight of the  $n^{\text{th}}$  group, and  $w_n$  is the weight fraction of the  $n^{\text{th}}$  group (or, the combined mass of molecules in that group, divided by the total mass of all molecules). Returning to our candy bar analogy, you'll see that the weight average gives us a different value than the number average, as shown in Figure 16.





$$\bar{M}_w = 10 \text{ g} \cdot \frac{50}{550} + 50 \cdot \frac{200}{550} + 100 \cdot \frac{300}{550}$$

$$= 73.6 \text{ g}$$

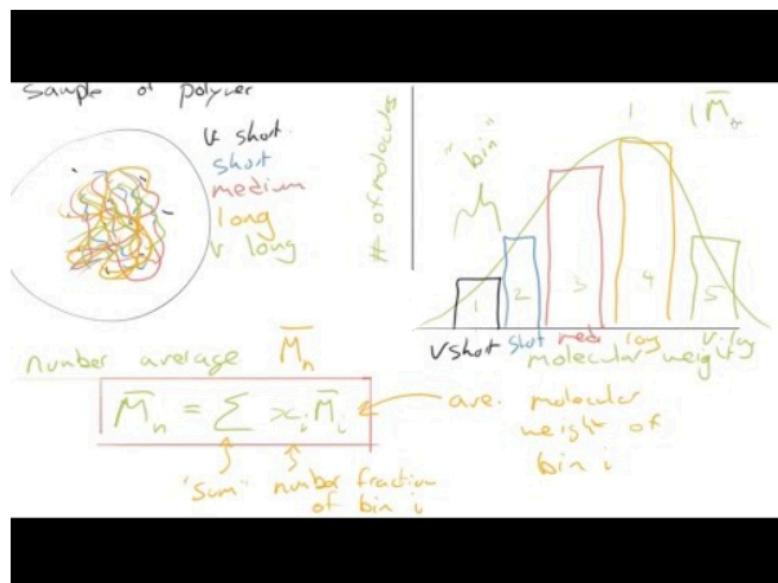
↓  
bar

**Figure 16.** Calculating the average weight of candy bars in a bag of candy, using the *number average candy weight*.

The weight average molecular weight is, in fact, always larger than the number average (except in the hypothetical case when all the molecules are exactly the same length). Finally, by comparing these two averages with a simple fraction we can give an indication of how broad the distribution is. This is called the dispersity (although it used to be, and is still frequently called the polydispersity index) and is defined as

$$D = \frac{M_{\text{weight}}}{M_{\text{number}}} \quad (3)$$

The symbol is pronounced "dee-stroke". If all the molecules were the same length, the dispersity would be one and the distribution would be a vertical line. As the distribution spreads out the dispersity increases from one.



[Link to this video on U of T servers.](#)

### hypothetical polymer



5 short 5000 nm  
6 medium 8000  
9 long 11000  
4 v. long 15000

$$\overline{M}_n = \frac{5 \cdot 5000 + 6 \cdot 8000 + 9 \cdot 11000 + 4 \cdot 15000}{24}$$

$$= 9666 \text{ g/mol}$$



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### EXERCISE YOUR KNOWLEDGE



8.5.1

Review

Mark as: [None ▾](#)

The average length of molecules in a polymer are typically described by which of the following quantities?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The average length of the molecules from one end to the other

b The average mass of the molecules in the sample

c The average linear dimension of the coiled molecule, measured in the x, y, and z directions



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### EXERCISE YOUR KNOWLEDGE



8.5.1

Review

Mark as: [None ▾](#)

The average length of molecules in a polymer are typically described by which of the following quantities?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The average length of the molecules from one end to the other

b The average mass of the molecules in the sample



b The average mass of the molecules in the sample

c The average linear dimension of the coiled molecule, measured in the x, y, and z directions



### 8.8.2

Review

Mark as: [None ▾](#)

Are the following statements true or false?

- (a) HDPE mostly contains linear polymer chains
- (b) Increasing chain length decreases the strength of a polymer
- (c) Poly(methyl methacrylate) (PMMA) can be made 100
- (d) Cross linked polymers have van der Waals bonds between the chains

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a True, True, False, True

b True, False, True, True

c True, False, False, False

d True, True, True, False



### 8.8.3

Review

Mark as: [None ▾](#)

Which of the following polymers would you expect to have the highest yield strength?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

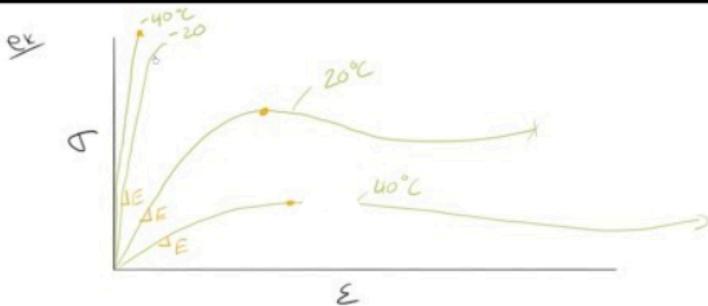
a Ultra high molecular weight chain oriented polyethylene

b Low molecular weight amorphous polyethylene

c Ultra high molecular weight amorphous polyethylene

d Low molecular weight chain oriented polyethylene

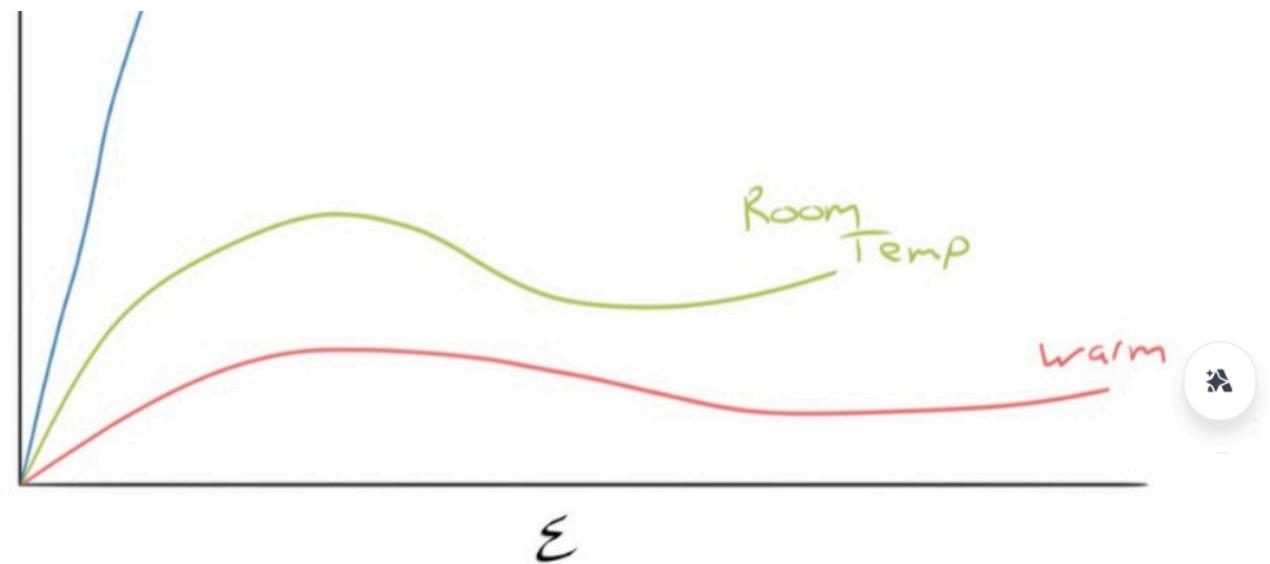
## Hey, Watch the Temperature Changes There!



[Link to this video on U of T servers.](#)

Yes, we need to talk about temperature changes. However, you may well wonder, if temperature changes are so important why did we not discuss them with metals or ceramics? Well, that's due to a bit of a recurring theme with polymers. Much of the behaviour of polymers is due to the weak, intermolecular, bonds. These bonds, or *interactions* as they are sometimes called, can be disrupted much more easily by the thermal energy, even when the temperature is relatively low: close to room temperature. In a metal or a ceramic, most of the properties are determined by the nature of the strong, primary, bonds holding them together (more on these later) and these bonds have bond energies significantly higher than the thermal energy close to room temperature.

Cold



**Figure 19.** A stress-strain curve for a hypothetical plastic polymer at three temperatures. It is not uncommon for polymers to experience significant changes in mechanical properties with relatively small changes in temperature.

Figure 19 shows the stress-strain behaviour for a typical plastic polymer around room temperature, as well as at the sorts of temperatures that you might expect in a structure on a hot sunny day, with a little solar heating, and also at a temperature as you might find on a cold winter day with snow falling.



## EXERCISE YOUR KNOWLEDGE



8.10.1

Review

Mark as: None ▾

Which of the following is the best explanation for the use of the term elastic modulus when referring to polymers, rather than using the term, Young's modulus?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a Polymer elastic behaviour is based on several types of interatomic interaction
- b Polymers are non-linear elastic
- c Polymers typically exhibit high strain to fracture
- d None of the above



8.10.2  
Review

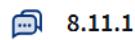
Mark as: None ▾

Which of the following would be expected to cause a change in the elastic modulus?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a An increase in the impurity concentration in a metal
- b An increase in the dislocation density of a metal
- c A reduction in the grain size of a metal
- d An increase in crystallinity of a polymer

Assigned as [Review](#) ⓘ



8.11.1

Explain why polymers are sensitive to small changes in temperature close to room temperature when metals and ceramics are not.

Responses

Reply

Showing All Responses ▾ Ordered by Newest Responses ▾

hidden,

5 months ago

Polymers have relatively weak intermolecular interactions compared to the ordered structures of metals and ceramics.  
Thus ch

Comments 0 2

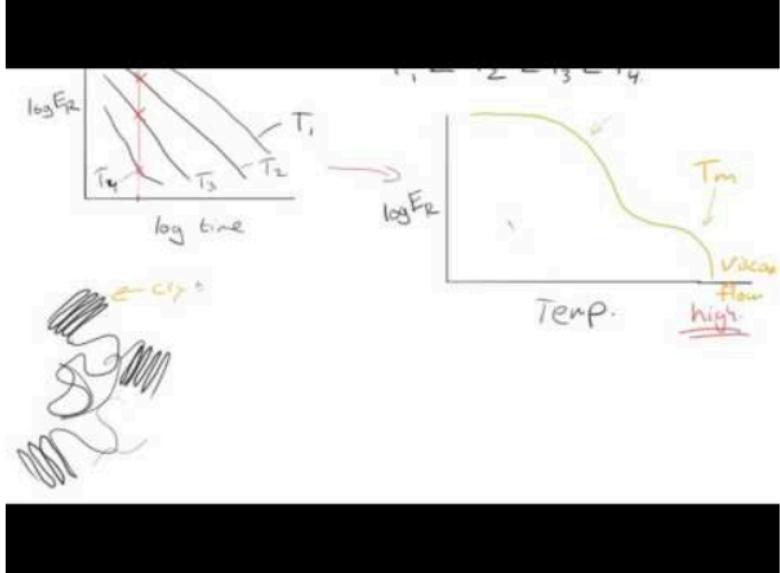
hidden,

5 months ago

Bonds of metals and ceramics have a higher bond energy

Comments 0 1

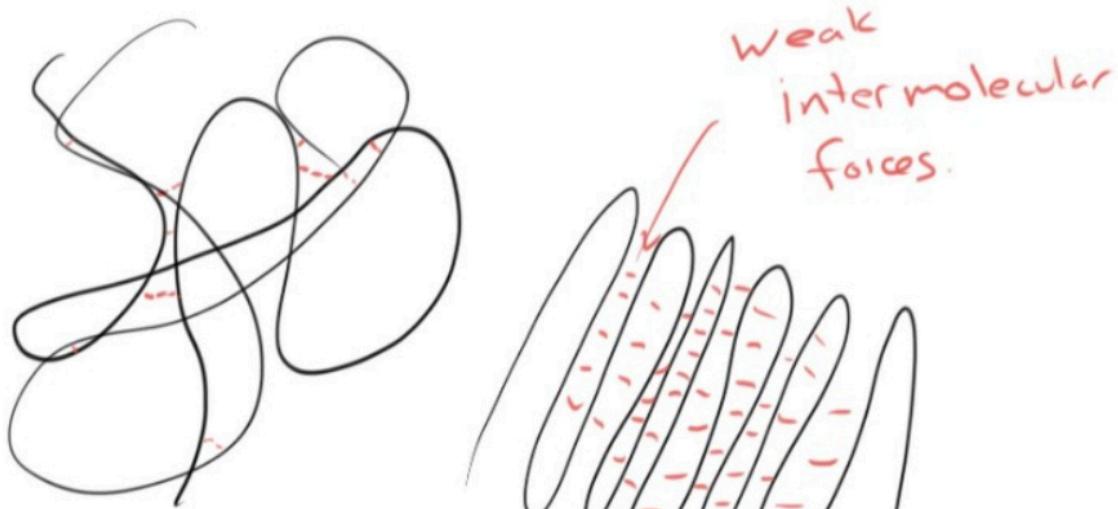
## When We Turn Up The Heat On Polymers

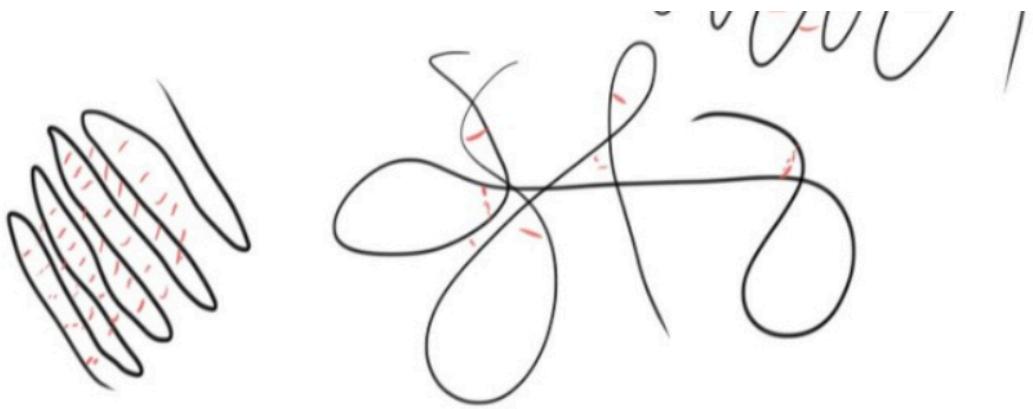


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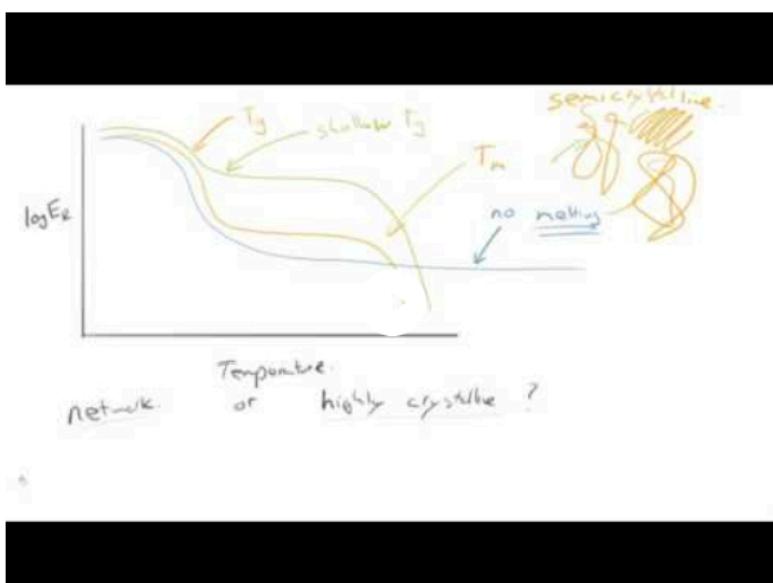
You may have noticed earlier that I was a little cagey about discussing what happens when a polymer is exposed to higher temperatures. I said, for example, that PVC can be used at a higher service temperature. The reason for this is that there are at least two important temperatures that you should be aware of when it comes to heating a polymer up. I think that the two most important temperatures to be familiar with are the *glass transition temperature*  $T_g$  and the *melting temperature*  $T_m$ . The melting temperature is likely the easiest of the two to understand since the picture you likely have in your mind currently is probably correct. Above the melting temperature the polymer will flow like a thick liquid because there is enough thermal energy to disrupt the weak intermolecular bonds and allow the molecules to flow freely past one another. This is generally true, in fact, the first bit about flowing like a thick liquid is correct. The second bit about the intermolecular bonds being overcome is true also, but it needs to be more specific. So, let's go back to the discussion of HDPE and LDPE and the idea of a semi-crystalline polymer. I've sketched the microstructure again in Figure 20, but this time I've added in little red dashes to illustrate the weak intermolecular bonds.





**Figure 20.** A cartoon sketch of the microstructure of a semi-crystalline polymer showing the weak, intermolecular bonds as red dashes. It will take a higher temperature to disrupt the weak intermolecular bonds in the crystalline domains versus the amorphous domains.

Upon heating, you may be able to imagine that the thermal energy will start to beat the intermolecular bond energy in the amorphous regions first, where the molecules are further apart. With continued heating the thermal energy will eventually be enough to disrupt the intermolecular bonds in the crystalline regions and all of the molecules will be free to flow past one another and the polymer will begin to flow like a thick liquid: melting. Therefore, the *lower* temperature, when the amorphous regions were disrupted is known as the glass transition temperature. It is worthwhile to note that the name for this temperature comes from the mechanical behaviour of a polymer at temperatures below the  $T_g$ , where it is hard and brittle, like common window glass.



[Link to this video on U of T servers.](#)

## 💡 EXERCISE YOUR KNOWLEDGE



8.12.1  
Review

Mark as: [None ▾](#)

Which of the following is the best description for the glass transition temperature?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a** The temperature upon heating, when molecules possess enough thermal energy to overcome the secondary, intermolecular interactions within the crystalline regions of the polymer
- b** The temperature upon heating, when molecules possess enough thermal energy to overcome the secondary, intermolecular interactions within the amorphous regions of the polymer
- c** The temperature upon heating, when molecules possess enough thermal energy to overcome the primary, intramolecular bonds within the amorphous regions of the polymer
- d** The temperature upon heating, when molecules possess enough thermal energy to overcome the primary, intramolecular bonds within the crystalline regions of the polymer

 **8.12.2**  
Review

Mark as: [None ▾](#)

A polymer that exhibits a very subtle (small) change in relaxation modulus around the glass-transition temperature would most likely have which of the following microstructures?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a** Fully amorphous
- b** Cross-linked
- c** Highly crystalline
- d** None of the above

 **8.6.1**  
Review

Mark as: [None ▾](#)

Please determine which of the following options will result in a polymer with a high melting point.

- (a) Increasing molecular weight
- (b) Using branched mer units
- (c) Using a mer unit that will form a network polymer
- (d) Creating cross links between chains

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a a, b, c

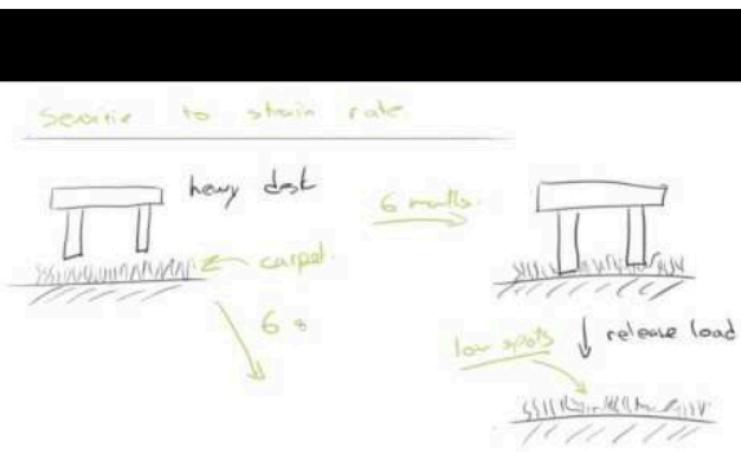
b b, c, d

c a, c, d

d b, d



## Why Does Temperature Have All The Fun? What About Time?



[Link to this video on U of T servers.](#)

We're approaching the end of our discussion of polymers now, and I know this has been a long chapter, so I appreciate you sticking with it. We've just finished talking about small changes in temperature in polymers, but there is another quantity that we need to discuss that was not an issue with metals or ceramics. Time. The great ruler of our universe. Okay, I'm being a bit dramatic here. You may be getting used to that! What I mean is that we need to understand that polymers can have

very different mechanical properties depending on how quickly we apply a load. That is, the time over which the load is applied. First off, polymers tend to behave in a more brittle fashion when loaded really quickly. A great example of this is the fantastic toy called Silly Putty®. This is a putty-like material made from a polydimethylsiloxane polymer. When left on a flat surface, for example, it will slowly flow like a very thick liquid. However, if you roll it into a ball between your hands to make a ball, a ball of Silly Putty® will bounce like a rubber ball and show no signs of any permanent deformation. Similarly, if you roll it into a cylinder between your hands and pull it apart very quickly it will snap like a brittle material. This fascinating behaviour is due to the relatively short molecules within Silly Putty® that must move past one another during deformation. When loaded quickly there is not enough time for them to move and instead the polymer fractures.

Another consideration of loading time on polymers that is equally, if not more, interesting is what happens when a load is applied for an extended time. This is perhaps best illustrated by considering a piece of heavy furniture placed onto a carpeted floor or a rug. First of all, the carpet is made from thousands of small polymer fibres that are oriented roughly vertically. When a heavy desk is placed on it, as shown in Figure 21 the carpet will become deformed different amounts depending on how long the desk is left on the carpet.

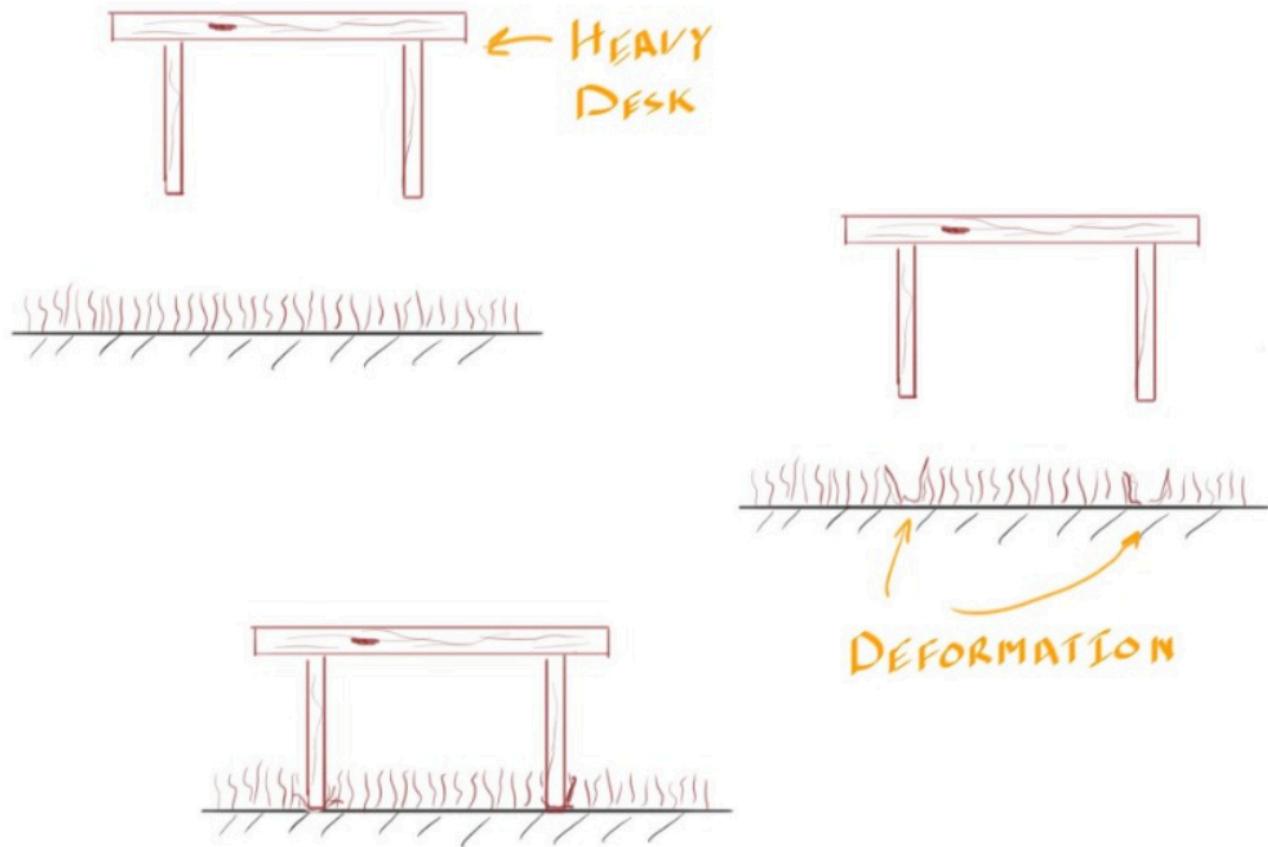


Figure 21. A heavy desk is placed on a carpeted floor. If the desk is removed immediately there is only a small amount of deformation in the carpet and this deformation typically disappears within a matter of seconds or minutes. However, if the desk is left for several months, the deformation is significant and it will take a very long time, with a lot of vacuuming to reverse the load, for the deformation to disappear, if it ever does completely.

When the desk is only left for a brief time, the strain is mostly elastic and the deformation will

WHICH THE DESK IS ONLY LEFT ON A SHORT TIME, THE STRAIN IS THINLY ELASTIC AND THE DEFORMATION WILL

disappear relatively quickly. However, when the desk is left on the carpet for a long time, say a year, the deformation will be significant and will take a long time to disappear when the desk is removed. The long time-scale deformation is known as *viscous deformation*, referring to the flow of a liquid. Over the long time period, the molecules will slowly move past one another leading to a slow, but permanent, deformation process. The deformation that occurs immediately when the desk is placed on the carpet and then disappears almost as quickly is essentially only *elastic deformation*. Putting these two types of deformation together gives a good description of the time-dependent nature of the deformation of all polymers and we call it *viscoelastic deformation*. Some polymers, like a high strength epoxy, will be closer to the elastic end, while a Silly Putty®, for example, is dominated almost entirely by viscous deformation.



## EXERCISE YOUR KNOWLEDGE



8.14.1

Review

Mark as: [None ▾](#)

Samples of linear polyethylene (PE), silica window glass (glass), and aluminum (Al) are prepared having identical dimensions. They are each loaded to 50% of their respective yield strength (fracture strength for the glass). The resulting strain is recorded immediately upon loading and then again after 300 days. Which of the following would you expect regarding the strain after 300 days compared to the strain immediately after loading?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a The PE strain will be higher, while the strain for the glass and Al will be unchanged

b The strains will be unchanged

c The PE and glass strain will be unchanged, while the strain for the Al will be higher

d The PE and Al strain will be higher, while the strain for the glass will be unchanged



8.14.2

Review

Mark as: [None ▾](#)

At higher temperatures, stress relaxation in a polymer would be expected to occur more rapidly.

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

a False

b True

## Tell Me Again Why Plexiglas® is Transparent?



[Link to this video on U of T servers.](#)

We've been quite successful thus far in understanding the behaviour of polymers by visualizing the molecules as a plate of noodles, so you may begin to wonder, "what are the limits to this model? Is there anything that our noodle model can't explain?" Well, as you recall from our discussion of scientific models earlier, there are almost always shortcomings to a model. If that wasn't the case we'd call it a law. As we approach the end of this chapter and segue into the next it is a perfect time to consider the optical transparency of Plexiglas® again. We said that some of the reason was due to the polymer being completely amorphous, and that is true. However, that doesn't explain why the amorphous polymer itself should be transparent. To add something interesting to this discussion, consider one of those little tags that are placed on some merchandise in a store to stop people from stealing. The ones that someone often forgets to demagnetize and then the alarm goes off at every store you walk into for the rest of the day while you are carrying the stuff you bought at that one shop. If you take one of those apart you'll likely see a small piece of metal foil and there is a good chance that it is an amorphous metal. The metal has a very complicated crystal structure so crystallization is a little slow. The metal is cooled quickly and there is not enough time for crystallization so the disorder

from the liquid state is frozen in. All very interesting, yes? Well, one of these so-called *glassy metals* will definitely be opaque. It will look pretty much like so many other pieces of metal: shiny and silver. So why is it that amorphous PMMA is optically transparent while amorphous metals will always be shiny and opaque? Well, to understand this we need to understand two more things. We need to understand what visible light is, and we need to understand how it interacts with the electrons in matter. Oh, this is going to be good.



## EXERCISE YOUR KNOWLEDGE



8.13.1  
Review

Mark as: [None ▾](#)



While useful for describing some mechanical behaviour, the string model of polymer structure fails to sufficiently describe the optical properties of polymers for which of the following reasons?

Select an answer and submit. For keyboard navigation, use the up/down arrow keys to select an answer.

- a Photons of visible light break polymers into small pieces so they can no longer be thought of as long strings
- b Photons of visible light cause new bonds to form between molecules creating a macro-molecular structure so they can no longer be thought of as strings
- c Photons of visible light interact with the electrons within a polymer, rather than by moving molecules relative to one another
- d Photons of visible light impart so much kinetic energy on a polymer that the molecules move sufficiently fast as to break all of the secondary bonds between chains

**All images and videos are created by the author.**

