PROFESSOR: We had a staff meeting yesterday, and we decided that what we're going to do is, we'll start with defects and solids. We didn't examine you on it with the last celebration. So we'll pick it up with defects, and we'll go through to the end of solutions, acid-bases. So the stuff that we covered on Monday, the nomenclature of organics, we're going to leave out. Because you don't have enough time with the recitations to really dig into that, and I think it's-- with the test being on a Monday this time, and not on a Wednesday, the schedule is little bit of out of balance from the way I'd like it to be. But I thought having the third celebration the Wednesday before Thanksgiving was not wise. I know that a number of you are going to be in transit that on Wednesday.

But let me remind you that Wednesday, we will have a full-blown lecture. I'm going without any slow down. So next Wednesday, we will start biochemistry. So those of you who are not here, please make sure that you have viewed the lecture. Because when you return on Monday, you will have no idea what's going on. And it'd be a good idea not to blow biochemistry, because on the final exam-- if you fail the final, it's not good. It's really not good.

So just to be clear, we're going to start with defects and solids, and go through, and end with acids, bases, and solution chemistry.

OK. So today I want to start to get some mileage out of what we learned on Monday. I want to talk today about one of the applications of organic chemistry, and that's polymers. So we're going to take two lectures on polymers, and then we'll feed into biochemistry, and you'll see a very natural progression from what we're doing now into the biochemistry.

So let's begin with a little bit of reflection on what we've done so far. Up until now, we've looked at various solid structures. We've started with single atoms. We looked at crystals, disordered crystals, and so on. We've looked at compounds, and we've even looked at small change. We looked at alkanes, straight chain alkanes, branched alkanes. And we've looked at network solids.

Here is a regular network. This is the structure of graphite, for example. Nice, ordered crystalline structure. Diamond grows in three dimensions without abatement. We've looked at disordered networks, such as silicate glasses.

So that's what we've looked at up until now. What I want to talk about today is polymers. Polymers are macromolecules. These are long chain molecules. By long, we're talking about thousands and thousands of

repeat units. And this is the distinguishing feature between macromolecules that are found in the body, versus macromolecules that are man-made.

Mother Nature is a polymer engineer. We are a macromolecular organism. This is all polymer. It's all polymer. The changes in shape is all elasticity in a polymer. And inside, of course, I've got a ceramic skeleton, which keeps the frame in place. But this is all polymers. But the difference here is, this is not a repeat unit. Whereas when we have a man-made structure, it's the same repeating chemical structure.

And the other thing I want to say at the beginning is their importance in commerce. Polymers are found everywhere today. Trash bags, auto parts. And in culture, they're absolutely essential to culture. Let's think about it. When you play that DVD, that DVD is information embedded in a polymer. The magnetic drags. What are magnetic drags? These are polymers that have been coated with gammaferic oxide or some other magnetic material. Without polymers we couldn't have the modern era.

And if you go back before the DVD, with the CD, before that was magnetic tape and cassette, and before that was this. You might see some of these around. This is an old way of presenting musical information. This is the phonograph record, photograph recording. And this is information that is scribed into a platter, and it's made of polyvinyl chloride. That's why you hear the term vinyl. Why is Virgin, the big Virgin enterprise, called Virgin? Because Virgin Records, when they made their platters, they started with virgin vinyl, not recycled polymer. And so their platters would lie flat on the turntable. Whereas some of them you buy, you put them down, and they warp. It's OK, because the needle would still track, but it looked kind of-- playing like this.

And it's too bad that we've lost this. Because this gives rise to the real estate possibility for artwork, and liner notes, and so on, that you don't get when you download something for $0.99. OK? So an electromechanical device moves along here, and jiggles in the grooves, and those mechanical wigglings get converted into energy that ultimately gets fed through the loudspeakers.

And now let's talk about visual information. Daguerre invented halide photography in the early 1800s, but we didn't get motion pictures. Cinematography had to wait for the advent of polymers, because only when we could make material that would come out miles long on which we could coat with halide photosensitive emulsion, could we imagine images flashing past us faster than the persistence of vision. You need-- what's the persistence of vision? Around a twentieth of a second. Motion pictures are 24 frames a second. So you couldn't have glass plates on which you've got halide film zipping past at 24 frames a second for 90 minutes. So only with the advent of polymers did we have the birth of cinematography.

So what I'm talking about here changed the world. It changed the world, and gives birth to the fantastic access

that we have to information. And now, of course, as things move digitally, and they dematerialize, you're going to see a shift away. But all this stuff was enabled by the advent of polymer chemistry.

So with that as a motivator, let's dive in. This is good stuff. It's really, really good. So now the payback comes. You know, all those little lessons about, where's the electron, where's the orbital, you know, who wants to learn that stuff. You have to learn it! If you're going to write the great novel, you've got to learn how to spell.

All right. So let's go. So the polymer, it comes from the Greek poly, meaning may, right? Poly is many And the mer, the mer is this repeat unit, if you like. Many units, many units.

So let's take a simple example. Last day we studied polyethylene. So polyethylene looks like this. Double bond, one, two, three, four, four hydrogens. So this is just ethylene. And what I can do with ethylene, is I can react it. Ethylene's a gas, room temperature. Put it into a reactor and expose it to an initiator. And the initiator is a radical. You know what the radical. It's something that's got this unpaired electron. It's very active. And the radical sees a unit of ethylene, which I'm going to write like this. We don't need to put the 120 degrees now. And what the ethylene does, is this radical attacks this double bond and figures, well, it's better to have two single bonds than one double bond. Reacts the double bond, breaks it, and then forms the following. The radical now bonds to the ethylene, breaks that double bond, and transfers the unpaired electron to the end.

But now this thing is itself a radical, and it's swimming in a gas of ethylene. So now a second C_2H_4 comes up against this, and it's turned into the following, are now C C C C C, one, two, three, four, one, two, three, four. And so on. And this can go without limit, until we shut down the reactor, or we introduce something that terminates, that will cap this. All right?

So this is the beginning of it. And what you see is attachment, attachment, attachment, breaking of double bonds. And so we have a repeat unit here. This repeat unit, the mer unit, is this ethylene unit, and it can go to a value of n that is very, very high. What kind of numbers can we expect to get? We can have numbers here where n takes values-- and these aren't hard and fast, but just to give you some idea-- you could have a, you know the oxymoron jumbo shrimp. You could have a short chain polymer. A short chain, long chain. You know?

Boy, you're really dead today. What's the matter with you? Sleep deprived? You've--

All right. So n can go up to about 10,000. Now what's the atomic mass of this, just as representative? This is 2 times 12 is 24, 25, or 26, 27, 28. 28's roughly 30, so 30 times 10,000, you've got 300,000. That's 300,000 grams per mole. This means you can have molecular weights on the order of a million grams per mole for one molecule.

And by the way, the polymer people, they come from a different branch of science. So they don't use this grams per mole. Instead of grams per mole, they like to use the word, the dalton, as a unit of measure. So you might see

in the pollymer literature, you'll see the polymer with so many kDa, kilodaltons, thousands of grams per mole. That's the nomenclature you will see. OK.

Now, what are the properties of these things going to be? Oh wait, I'm going to show you something. To give you a sense. You need to be awakened. So let me give you a sense of just how long these molecules are. So I'm going to give you a little mechanical model here. I'm going to put up here so we get some--

So what I've got here is just a pull chain. If you go in the basement, you might see these pull chains. They're just made of brass, little brass balls, and then they've got links between them. And when you cut them-- you buy them by the foot at the hardware store. You put it on a light, you can turn the light on and off by toggling up and down.

So I'm going to say, let's say this distance here represents the distance between mer units. This distance could be between 2 mer units. And I figured, let's see, I've got 40 feet here, and I did the math. So this thing here, with the 40 foot pull chain, has a polymerization index-- let's call this the polymerization index. So my polymerization index, I calculated it for this thing. It's on the order of about 3,000. So that's pretty good. It's right in the middle of this. It's actually-- this qualifies as a bona fide polymer.

So let's take a look at what happens here. This is one molecule. So what do you know about interactions between molecules? Now, in the liquid state, what's this going to be? Is it going to be fluid, or is it going to be viscous? It's going to be viscous. Look, this is one molecule, and it entangles with itself.

Now, to make a liquid, I have thousands of these things swimming around, above their crystallization-- oh, crystallization temperature. Freudian slip. Above their solidification temperature. When they solidify, are they going to form an ordered solid? One of these at each lattice site? Probably not. They're probably going to form disordered solids. So most of the polymers that we encounter are probably going to be disordered.

How is this held together when it forms a solid? It's polyethylene. Well, what's your menu? Is it ionic bonding? Is it metallic bonding? Is it hydrogen bonding? How is it held together? Weak van der Waals. Weak van der Waals bonds. But look at the surface area. So this is what it looks like. See, and it entangles, is even entangles with my clothing. It just grabs onto everything.

All right. Actually, why don't we-- David, let's cut to the screen.

So here we are. This is it. This is the polymer. And every once in a while, a polymer will do something like this. It'll say, you know, I still, even though I'm in this big long chain molecule I still want to try to order. Because I read in 3091 that ordering lowers the free energy of the system... So what it does, it starts doing this.

And can you see when it starts doing this, that it starts to take on-- if you walked into the room just now, and this

were blowing up really high, you might see just this little snippet and say, wow. This thing is starting to look like a cubic array isn't it?

This is a really good model. It's a really good model, because this is what really happens. And so that decreases the energy of the system. The bonds are greater there. So what's that going to do to the mechanical properties? Going to strengthen it, yeah. It's going to make things stiffer. Instead of being this soft, squishy polymer, it's going to have some stiffness to it.

And you've come up across that stuff. The most notable one being the CD case. The people that make those, I'd like to bring them here and sit them down and teach them some polymer science. Those things are so brittle. They crack, right? There's only two classes of jewel cases. Those that are cracked, and those that will crack. Because these people don't know what they're doing.

OK. So now let's have some time here to codify what we've just see. So first of all, we suspect that they're going to be solid at room temperature. Dominantly. We can engineer them to be liquid, but dominantly solid at room temperature. And van der Waals bonds abundant. OK. And the liquid, as a liquid, we expect viscous liquid. Good. Got that down. What else to have to know?

Let's do calculation here. So I did one here where I said, what's this distance? We saw last day that this distance, carbon-carbon, remember, we're looking at single bond, double bond. A single bond carbon-carbon is about 1.5 angstroms. So this is 1.5 angstroms. The distance between successive mer units is about 3 angstroms. And so if you take something 3 angstroms, and you make it this number of mer units, I came up with a polymerization index of 3571 when this thing weighs 10,010 kilodaltons. And so then that means that you'd end up with a length, molecular length is on the order of 10,714 angstroms, which is on the order of 1 micrometer, which then makes it greater than the wavelength of visible light. So this is really a different type of matter.

And we can go there. We've talked about viscous, so I'm going to remind you of two observations here. Viscous liquids, amorphous solids. If you put those two ideas together, what else can we call upon? We can go back to this. Yeah. Remember this? What's this? This is super-cool liquid, super-cool viscous liquid. This is the solidification temperature, which in the case of liquid to amorphous solid is the glass transition temperature. And here we have the excess volume, right? This is the volume, and then there's some crystalline volume, and so on. Right? I can cool at a second rate, and I get this. So this is slow cool, this is fast cool. We have a Tg up here. Tgf I'll call Tg fast, and Tgs, Tg slow. So that'll give me a different volume. So this is volume fast and volume slow. All right? And since I know that density is equal to mass over volume, so therefore v fast is greater than-- I observe v fast is greater than v slow, so therefore density of the fast cool must be less than the density of the slow cool.

Now I'm going to put some names on here. I'm going to call this the cooling curves for polyethylene. These are the cooling curves for polyethylene. So this, down here, gives me-- this is now high-density polyethylene, and up here is low-density polyethylene. Same thing, just different processing.

So faster cooling quenches in more free volume. And since volume is a measure of disorder, right? What's the difference between great disorder and not-so-great disorder? David, again cut to the projector, please? Forgive me, the document camera?

So the difference between high disorder and low disorder is this. This is the order, here. So what that tells me is that in high-density polyethylene, there is a greater percentage of zones like this. And we just reasoned that this is going to give stiffness and so on, and sure enough, for the low-density polyethylene, low-density polyethylene is used in things like food wrap, things like stretch and seal, where you can pull because you can move those macromolecules relative to one another without fracturing the material to stretch it over. Whereas the high-density polyethylene is used in such things as milk jugs, where you want a little bit of stiffness. Polyethylene milk jugs are still kind of floppy, but there's a little bit of stiffness to it.

The other thing is, because the low-density polyethylene is dominantly amorphous, with almost none of this second zone here, it's transparent to visible light. But now, let's think about what's going on here. Where I've got this chain, and then all of a sudden I get to this. All right? So this is clear and colorless. Right? It's a high band gap material. There's no free electrons. It's going to be transparent to invisible light. So this is transparent to visible light all along. But can you see that because I have this zone of ordering, the density of matter here is different, and so therefore, when a photon comes in, the index of refraction-- now, you know, this is one of those days where n is going to come up. So here n is the polymerization index. Here it's index of refraction. So maybe we'll use a different color. How about that. All right? So the green n is index of refraction.

So the index of refraction in the amorphous zone, is different from the index of refraction in the partially crystalline zone. So index of refraction varies from zone to zone. Even though each zone is clear and colorless, can you see that this boundary between the ordered and in the disordered zone acts like an interface? And what happens when you have an interface with a different index of refraction?

It scatters light. And as a result, the milk jugs, they appear white. You can't see through them, even though they're constituted of the same continuous material. But there's these density fluctuations, because this is a higher density than this. So you can rationalize all of this stuff. OK. So this is what we would call partial crystallization in this zone. And that gives rise to the changes.

Now, how would we distinguish these? What technique would I use to see if I've got order in this polymer, that I don't know anything about? How do I interrogate atomic order? What technique would I use? X-ray defraction.

Thank you.

Back to the slides, please, David. I'll find you the piece.

This is called polyethylene, but remember last day, the IUPAC notation for this is ethyne, so this becomes polythene. And in the UK, it's known as polythene, and there's a Beatles song, Polythene Pam. The only reason-- I put up here for two reasons. One is, it has something to do with polymers. At least they knew something about polymers. It's apparently, they must have been in a drug haze at this period in their careers. This is absolutely terrible. Some of your parents probably adore the Beatles. If you want to provoke a conversation at Thanksgiving, pull out this one and ask them to talk about the lyrics here. But this is just garbage. This is garbage! This should be trash bag, is what it should be.

But evidently, this woman used to show up at parties dressed only in a polythene bag, a see-through polythene bag, I might add. So this is a paean to her. Anyways, it's bad. Yeah, yeah, yeah.

Anyway. So here we are. This indicates chrystalline polyethylene. Here you can see the C2H4 unit. And it's attempting to try to occupy, as these beads line up here, they're trying to set up a faux lattice. And this is what you might see. And towards the end of the lecture, I'll show you a transmission electron micrograph where you can see this by dying it with different colors. OK.

So now here's some x-ray defraction. So this is crystalline, where they zoomed in on one of these zones, and they've just gotten the defraction pattern from that zone. And you see Bragg peaks. And then this is in the amorphous region. it's not featureless. There's one broad peak. Why one broad peak? Because even though there's no long-range order, you have short-range order. You know that you've got a carbon on either side, you've got hydrogens and so on. So that short range order gives you the broad peak.

But look at C here. Isn't this interesting? That if you have a polymer that has both some order and a lot of disorder, if you take the x-ray defraction pattern more broadly, more globally, you get the additive spectrum. So you can see that this is amorphous, but there are some zones of crystallinity. And that's the additivity power of x-ray defraction that allows us to interrogate.

So now let's talk in a little more fine structure about molecular architecture. So tailoring molecular architecture. And why are we doing this? Because we want to engineer these materials for desirable properties. Like CD cases that break after about one or two uses, OK? Of polymers.

Actually, there's probably a business opportunity there. You start a company where you make jewel cases that actually work. People might be willing to pay, you know, a penny more for something that works.

All right. So how do we change this? What I'm going to show is a whole bunch of cartoons of architecture. But how do we control this? It's processing. It's processing. Processing and in the synthesis algorithm. I'm assuming I already have polyethylene, so how am I going to tailor it? It's in the processing. And so what I can do, is I've got a number of levers I can move. One is the composition of the polymer, and the second one is, I can use catalysis. I already hinted at that last day in talking about gasoline. How do you start with petroleum and get octane and not heptane and so on? By playing with cataylsis, we can direct certain forms. You can actually preferably synthesize a certain architecture by using catalysts.

So let's look at these variables. First one is composition, obviously. If you change the composition of something, you can very much expect to change its properties.

So what do we have here? We can-- here's a simple example I can start here with. This is ethylene. Or I can put a chlorine here, so this now becomes chloride, right? This will become, what's the radical, is vinyl, so this is vinyl chloride. So if I polymerize this, this becomes polyethylene. If I polymerize this, this becomes polyvinyl chloride, PVC. Which is why you heard the fellows from Blue Man Group at the beginning banging on PVC tubing to make their music.

All right. So I use a pure, in other words, only one mer. It's pure polyethylene. This it's called a homopolymer. Only one mer type in use.

If I want to make the polymer analogy of an alloy-- in ally metals, alloy has more than one metal mixed in, or a metal can even have nonmetals mixed in. Then the polymer term is called copolymer. I'll call this a copolymer. And a copolymer has greater than one mer type.

So for example here, this could just be polyethylene. Whereas here, an example would be polyethylene, and then the notation is hyphen lowercase c hyphen, which is an indication of the fact that you're making a copolymer. And this copolymer has mer units of ethylene, and mer units of vinyl chloride. So this is a copolymer of polyethylene and polyvinyl chloride.

And then we can start looking at the various ways of arranging these. So we can start with, for example, we can have a sequence of random mer types. So as you're going down the chain, you get either an ethylene, or a vinyl chloride. So this is called a random copolymer, and it's designated polyethylene-r-polyvinyl chloride. And actually, I think I've got a cartoon showing this. Yeah.

So A and B are different mer types. And so a random copolymer just has A, B, B, A, A, A, B, A, whatever. And this is controlled in the synthesis process. So I can take the same mix of A and B, in other words, the same two mer types, but mix them in an alternating sequence. So they're very regular. It's 1 mer of ethylene, and then one mer

of vinyl chloride, alternating all the way down the backbone. So this gives you a regular copolymer, and it's designated A for alternating, because we've already used R for random. So instead of a sequence of random, we have a sequence of alternating mer types. So that would be, in this case, polyethylene alternating PVC. So that's two of them.

And then you see the block copolymer shown. And in that case, the mers grouped into-- they call them blocks, even though it's a line. You know, maybe it's like walking down the street. I've walked down one block. So this is one block, and then there's the next block. They're grouped into blocks. So in that case, we have the block copolymer, lowercase b, and then PVC. And what you see there is a run. A run of--

So all of the A's are grouped, and then we have all of the B's. And this is actually an artist's misconception. In point of fact, most block copolymers that you find, this is the stuff they use for the soles of your sneakers and so on. They're block copolymers. They're usually just a diblock. There's usually just two different mer types. One half of the macromolecule is one mer type, the other half of the macromolecule is the other mer type. Sometimes you might find a triblock, where you might find block A, block B, and then another block A. But this is a pentablock and he's even got ellipses here as though this thing keeps going. There's no commercial product that looks like that. It's usually a diblock, occasionally a triblock. OK?

And then the last thing you can do, as is shown up here, is what is known as the graft. And in the graft, the thing that distinguishes the graft is mers grouped into blocks. In this case, a long side chain of other mer. So that's different from side group that we saw last day. These are long macromolecular chains. So you see here the primary backbone is A, and then you have this very, very long macromolecular chain of B. And this is called the graft copolymer. So that would be polyethylene, could be the backbone, and then long side chains of polyvinyl chloride. And all of these have their different architectures.

And I think I have an example here of one. This one, I think I mentioned last day, when we were looking at the butadiene. So this is hard-sided luggage. And if you go to grandma's house, and she hasn't gotten into the digital age, and isn't an old hipster with a cell phone, she's still got the old hard plastic telephone, it's made of this stuff. ABS, which is acrylonitrile butadiene styrene. And the backbone is butadiene, and then you have-- OK, so here's the backbone. It's long butadiene, which we saw last day. And then you've got side chains of two types. And this is just indicating A, A, but this is a macromolecule. This might be 3,000 units long, whereas this is 10,000 units long. And this might be 2,000 units long. So you have side chains of acrylonitrile and side chains of polystyrene. And that's the hard plastic.

It's coming back, because people want luggage that doesn't destroy their contents anymore. So that's coming back.

OK. So this is what we can do in terms of composition. Let's look at, also, the side group arrangement. And this is called tacticity. Tacticity, which is the equivalent of what we saw last day as stereo isomerism. Remember, I showed you the cis and trans on the butadiene. On the cis, you've got, in one case, you've got whatever the functional group is. I'm going to put A, A, B, B. And then so this is the cis version, or I can do a trans version, which is instead, I'll put in A up here and an A down here. I'll put a B up here and a B down here. So this is a trans version.

So imagine the analogy for polymers. So let's look at that. It's easier to see it, and then we can just document it. So here's three different polymers, all right? So I'm going to start with the lowest one. This is called isotactic, because this is vinylchloride. There's vinyl chloride by itself. There's the vinyl radical from ethylene. And then we tack on chlorine. And now when we polymerize, we're going to break this double bond in order to link this carbon to the neighbor. So now the backbone only has single bonds, right? You start with the double bonded precursor, and now you've got this chain of single bonds. Right? But look at the chlorine. The chlorine could either be below, or it could be above. Well, in this case, the chlorine is always below the chain. So this is called isotactic polyvinyl chloride.

Now this one, you know, they're trying to mix two things at once. I would have shown this with vinyl chloride in all three, but OK. So imagine now, in this case it's syndiotactic. This happens to be polystyrene, because this is vinyl benzine, or what's the other way to call it, phenyl ethylene. You can have either way. All right? So you can say you're putting a phenyl group onto vinyl, or you're putting onto the ethylene, or vice versa. But the radical, this thing here is called styrene, and we're going to break that double bond and away we go.

So this is the benzine ring, and it alternates from above the chain to below the chain. Above the chain to below the chain. So in this, this is called syndiotactic. And the top one is a polypropylene, so you start with propylene, that has the double bond here. It's got three carbons and the methyl group coming out, and so you break that double bond and make the chain. And it seems to be on a random basis where that methyl group appears. Sometimes above the chain, sometimes below the chain.

So those are three different ways of arranging, so three different tacticities. So we've got isotactic, we've got syndiotactic, and we've got atactic. So the way to remember them, isotactic obviously means, everything's on the same side. And when I'm talking about the same side, what is it? Same side of the backbone. And we're talking about the position of functional groups, right? That's what this is all about. The positioning of functional groups. In other words, a methyl, or a benzine, or what have you. So same side of backbone. Atactic is random, and then by elimination, this one must mean alternating, above and below. On opposite sides of the chain.

And these have different propensities for crystallization. Which of these three-- imagine that all three of them were

polyvinyl chloride. Which of the three, atactic, syndiotactic, isotactic, would be most favorable from the standpoint of partial crystallization, to loop back and forth? The one that's most regular, so the isotactic one has. OK.

Third one. Third one is the backbone configuration. This is the configuration of the main chain, all right? And this is called conformality. You see, they have different words for everything that came from a different heritage.

So to me, it answers the question, how distended is the chain? And we saw this last day, when we looked at what happens when we start with something like this, where we have staggered or eclipsed, remember, orientation of the hydrogens here. In the case of staggered, we get the lower. Both of these are straight chains, because if you start at one end, you move monotonically all the way down the chain to the other end. There's no branching here. But one of them, the lower one, has staggering of that carbon-carbon bond, with the result, things form this giant loop. So in polymers, imagine this, instead of being 36 units long, imagine it being 3,600 units long. So now you can have things to do this. You can even take a little break here and crystallize and so on.

So how do I distinguish that from something that does this? So how distended is the chain? This one here is as distended as it can be, and others can be much more coiled. So this one is called linear chain. This is branch chain. Now, this is not graft. Don't confuse this with the graft copolymer. Graft copolymer means, I have one mer down the backbone, and a second mer off to the side. That's a graft copolymer. This is a homopolymer. A homopolymer that has different branches. So all of these, let's put this here to remind us. These are homopolymer cartoons. Homopolymers that haven't changed anything. So this is something that actually has different branches. So this is branched chain, branch chain architecture. Good.

So which one of these is going to be harder to crystallize. Which one is-- well, obviously, I've given it away, I put that little piece of crystallinity in there. Can you see that when these two solidify, that the one on the right, because it's got these branched chains with the covalent bonds sticking out. It's not going to pack as well. And if it doesn't pack as well, it's going to have a higher free volume. If it's got a higher free volume, it's got a higher degree of disorder. So the branched chains have a greater propensity for disorder. So let's put that down. Branched chain, harder to crystallize. And crystallize, it's not a giant crystal or polycrystal. We're talking about the degree to which we can get that amount of ordering.

And then the last one I want to show you is, here's three different chains. 1, 2, and 3. And what we're going to do is we're going to cross-link. We're going to form bridges. These are covalent bridges. These are not hydrogen bonds. These are not weak van der Walls bonds. These are strong covalent bonds, all the way along here, linking backbone to backbone. So this is cross-linked.

And what do you think the mechanical properties of this are going to be? If I want extend this, like stretch and seal, I can pull chain number three relative to chain number one quite easily, until this covalent bond has bent

over as far as it can, and then what happens? I can't pull it anymore. And what happens when I let it go? It springs back. So this imparts elasticity. This makes the polymer rubbery. Cross-linked polymers are rubbery.

But you know, the polymer people, they want elevated words. If you say to a polymer person, oh, so you've made a rubber, they cringe. They want to have a fancy word. They call this an elastimer. It's got the word mer in it, so they're happy, and it's elastic, so it's an elastimer. Rubbery. So how are we going to make these cross-links? What are we going to have to look for as an architectural feature to make cross-links? We look at the backbone. If we've got a backbone going like this, all these carbon-carbon bonds, and down here I've got carbon-carbon bonds. If I break one of these bonds in order to go up in this direction, I've broken the chain.

So how am I going to have the bonding capability to form a covalent bridge between chains without breaking the very chain I'm trying to link? What feature am I going to have to have in the chain? I need, after polymerization, to still have some double bonds. And if I've got still double bonds in the backbone after polymerization-- and now would I do that? I have to have a double bond to break in the first place.

So what would happen if I started with a unit that had two double bonds in it? That way, I give up one double bond in order to make the chain, and I still have a second double bond. That's why the rubber has butadiene. The diene has two double bonds, after polymerization, still has one double bond, and now what I can do is break this double bond and this double bond, and link them.

But if I link them, they're going to be too close together. They're going to be scrunched in. I want to have some play, here. I want to make this rubbery. So what do I do? I put a spacer in here. What do I use as a spacer? An atom. And what kind of an atom do I need? I need an atom that's capable of making one, two covalent bonds. What am I going to choose? What atom do you know likes to make linkages?

How did we make silicate? What's the linker in silicate? Oxygen. You could use oxygen, but I want to make this thing even farther apart, and a little bit, you know, oxygen's small and it's got too much strength. If I want to make it weaker, but something that behaved like oxygen, sulfur, I'd go down one row in the periodic table. So I'd put a sulfur in here. And if I wanted to do a really good job, I'll put a sulfur here, since I got a double bond from both sides, I'll put two sulfurs, and make a disulfide linkage, and now I've got the making of rubber. Disulfide linkage. And again, the feature, I have to start with the backbone that has a covalent bond at the end. OK.

Well, let me tell you a little bit about the birth of rubber. It started here in Massachusetts. It started just across the river, in Roxbury. Nathaniel Hayward discovered that rubber treated with sulfur was not sticky. If you take natural rubber-- you ever work with natural rubber? It's very sticky. You can't do anything with it. And Hayward reasoned that by playing with the sulfur, he could-- he didn't understand the molecular architecture. But he learned that by playing with sulfur, and introducing sulfur to the rubber, he lost the stickiness and he got an enhanced elasticity.

So Charles Goodyear came to Boston from Ohio to meet with Hayward, and he learned about disulfide linkage and so on. Took the idea back to Ohio. And one day in the laboratory, he was trying to prepare a batch of sulfonated rubber. And it was a laboratory accident. He knocked over the vessel containing this sulfonated rubber, and it landed on a hot stove. Things were powered by fire. Landed on a hot stove, and then by heating it, he gave birth to the process of vulcanization. And hence was born the American rubber tire industry, by that accident, starting with the trip to Roxbury to learn about this. And you could have done it all with what you learned today. You're just about 150 years too late.

OK. I will see you on Friday.